THE KINETICS AND MECHANISM OF OXIDATION AND HALOGENATION REACTIONS IN THE GAS PHASE

by

JOHN H. KNOX

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ABSTRACT OF THESIS

Name of Candidate John Henderson Knox

Address [redacted]

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Title of Thesis The Kinetics and Mechanism of Oxidation and Halogenation Reactions in the Gas Phase.

THE WORK described in this thesis has been carried out over the last ten years at the Chemistry Department of the University of Edinburgh. The work is in the field of gas phase reaction kinetics. Two main aspects of the subject have been studied - gas phase halogenation and gas phase oxidation. These are connected experimentally by the extensive use of gas chromatography as the analytical tool. The author's early studies in both fields were amongst the first in which gas chromatography was applied to reaction kinetics.

The work on competitive halogenation reactions (that is the halogenation of mixtures) has resulted in the accurate determination for the first time of forty rate constants and Arrhenius parameters of reactions of the general type:

$$X + RH = XH + R \qquad (X = F, Cl, Br)$$

and an attempt has been made to give a theoretical interpretation of the A factors of these reactions using a simple model. The results should be of particular value as a check on any more sophisticated theoretical calculations which may be made in the future. They may also form the basis of a valuable method for the accurate determination of bond strengths in hydrocarbons.

The work on oxidation developed from a study of the cool flame oxidation of propane carried out for a Ph.D. degree. By the use of gas chromatography for the analysis of the products from the earliest stages of the oxidation of propane between 318 and 475°C and of ethane between 320 and 386°C it has been established that at least 80% of the alkane initially removed appears in the products as an olefin with the same number of carbon atoms. The most probable

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reactions are (with propane for example)

$$X + C_3H_8 = XH + C_3H_7$$

$$C_3H_7 + O_2 = C_3H_6 + HO_2$$

X may be HO_2 but there are thermochemical arguments against this view and the nature of X is still a matter for speculation. Below 400°C the minor products are apparently formed by decomposition of the RO_2 radical but above 400°C pyrolysis reactions of the alkyl radicals become important.

By oxidising mixtures of alkanes it has been established that the radical, or radical mixture, X has a reactivity between that of Cl and CH_3O and is therefore unlikely to be HO_2 which is expected to be much more selective than CH_3O or Cl.

Kinetic studies of the oxidation of propane and ethane at about 320°C have shown that surface reactions are kinetically important during the induction period and that the autocatalysis of the oxidations is assisted by the formation of olefins which probably yield branching intermediates more readily than the parent alkanes.

The overall mechanism of alkane and olefin oxidation, taking account of the above observations, is discussed in the most recent papers of the series on the oxidation of ethane and ethylene.

The thesis concludes with a brief section on the author's work on various aspects of gas chromatography.

PREFACE

The work described in this thesis was carried out between 1953 and 1963 in the department of Chemistry at the University of Edinburgh. I am deeply indebted to Professor Kendall, Professor Hirst and Professor Cottrell for the continual encouragement they have given me and for their generous provision of laboratory facilities. I am also indebted to my colleagues past and present who by their friendship, criticism and exhortations have always been a stimulating influence. Lastly I should like to thank those research students whose work has contributed so largely to the success of any of the projects undertaken. Without their help only about a third of the work could have been carried out. They have provided the greater part of the experimental data and have contributed in no small measure to its interpretation.

THE KINETICS AND MECHANISM OF OXIDATION AND HALOGENATION REACTIONS IN THE GAS PHASE

THE WORK presented in this thesis can be conveniently divided into two main parts: (1) the study of the kinetics and mechanism of the uncatalysed oxidation of simple hydrocarbons in the gas phase, and (2) the determination of the rate constants of the reactions of halogen atoms (mainly chlorine) with hydrocarbons and their derivatives. Gas chromatography, which was used as the main analytical and kinetic tool in both studies, has formed a link between them, and not unnaturally this has led to some work directed to its development rather than to its application.

The work has been carried out in the Department of Chemistry of the University of Edinburgh. The majority of papers presented describe work carried out either by the author personally or by research students directed by the author. The work on competitive oxidations [24-27] was directed jointly by the author and A. F. Trotman-Dickenson, and the work on competitive fluorination and bromination reactions [12,13] was directed by A. F. Trotman-Dickenson. The author's contribution to papers 12 and 13 was the calculation of the theoretical A factors.

Much of the work included in this thesis was initially stimulated by the author's research at Cambridge under the direction of Professor R. G. W. Norrish [1,2]. After completing a study of the cool flame oxidation of propane [1], which formed the material of a Ph.D. thesis, it became apparent that the detailed steps in gas phase oxidation processes could properly be understood only if much more sensitive and selective analytical techniques became available. A chance visit to an I.C.I. research laboratory suggested that gas chromatography might prove the ideal technique. Soon after this visit in 1953, J. H. Purnell and the author set up a simple gas chromatography apparatus and succeeded in separating a number of aliphatic hydrocarbons [3]. This work formed the basis of a paper which was unfortunately never published. The paper gives one of the earliest accounts of the analysis of C_4-C_6 hydrocarbons by gas chromatography; it is the first account of the effects of operating conditions on column performance; and it contains an early description of temperature rising gas chromatography not seriously investigated until 1957. The power of the method and its great potential when applied to reaction kinetics were obvious even at this early stage: very soon it became a major tool in the independent researches of the authors.

The technique was applied in Edinburgh to two problems; (a) the chlorination of propane and of methane + ethane mixtures [4]; and (b) the oxidation of propane between 435 and 475°C [5].

The chlorination systems were chosen because they seemed simple and because they used a characteristic feature of gas chromatography, its ability to determine on a micro-scale the relative amounts of similar compounds such as homologous or isomeric chlorides. By measuring the yields of the alkyl chlorides formed in the chlorinations the ratios of rate constants for the pairs of reactions (1a,1b) and (2a,2b) were determined.

$$\mathrm{Cl} + \mathrm{C_3H_8} = \mathrm{HCl} + n\text{-}\mathrm{C_3H_7} \qquad (1a)$$

$$\mathrm{Cl} + \mathrm{C_3H_8} = \mathrm{HCl} + \text{iso-}\mathrm{C_3H_7} \qquad (1b)$$

$$\mathrm{Cl} + \mathrm{CH_4} = \mathrm{HCl} + \mathrm{CH_3} \qquad (2a)$$

$$\mathrm{Cl} + \mathrm{C_2H_6} = \mathrm{HCl} + \mathrm{C_2H_5} \qquad (2b)$$

This work was the first application of gas chromatography to gas kinetics and clearly demonstrated the value of the technique for obtaining quantitative kinetic data: it led on to the study of competitive reactions in general using gas chromatographic analysis.

The study of the oxidation of propane (with J. W. Falconer) [5] was carried out between 1954 and 1957. It illustrated how the technique could be used effectively to follow the course of a complex reaction which yielded a large number of products. While at Cambridge the oxidation of propane had been studied in a flow system [1], the only type of apparatus which yielded sufficient quantities of products for analysis by the methods then available. Flow systems have the disadvantage that they cannot usually be used to derive kinetic parameters and rarely allow precise specification of the reaction conditions. By employing gas chromatography and a static system it is possible to avoid these difficulties and to obtain both analytical and kinetic data under the same conditions.

The work on propane [5] showed clearly that the initial distribution of products differed greatly from that obtained later in the reaction: water, propene and smaller quantities of ethylene were the main initial products, while oxides of carbon, some organic condensables and methane appeared only later: they were presumably formed by oxidation of the primary products. The work drew attention to the necessity of determining the yields of products in the early stages of the reaction if the true sequence of steps in the process was to be discovered; it also confirmed a conclusion hinted at earlier [1,2] that alkyl radicals generally react with oxygen at moderately high temperatures to give an olefin and an HO_2 radical. With propyl for example the reaction would be

$$C_3H_7 + O_2 = C_3H_6 + HO_2 \qquad (3)$$

These two papers [4,5], linked by the common use of gas chromatography, set the stage for much of the remainder of the work on oxidation and halogenation. The three main fields of interest - gas chromatography, gas phase halogenation and gas phase oxidation - have from time to time been reviewed by the author. An early review of gas chromatography was published in 1957 [6] and a Methuen Monograph in 1962 [7]. Halogen atom reactions have been reviewed by G. C. Fettis and the author [8] and recent work on gas phase oxidation has been covered in Annual Reports on the Progress of Chemistry [9].

Competitive Halogenation Reactions and the Absolute Rate Constants of Halogen Atom Reactions

Following the first competitive chlorination experiments [4] a comprehensive study was undertaken with R. L. Nelson [10] in which hydrogen, C_1-C_5 hydrocarbons, cyclopropane and cyclobutane were chlorinated in pairs. Since the rate constant for chlorine atom attack on hydrogen was known, absolute rate constants for all the reactions carried out in direct or indirect competition with hydrogen could be determined. The rate constants and Arrhenius parameters for some eleven chlorine atom reactions were thus derived with a high degree of precision, many of them for the first time. During the course of this work an attempt was made in collaboration with A. F. Trotman-Dickenson [11] to calculate A factors for a number of chlorine atom reactions by transition state theory. Later the competitive technique was applied with G. C. Fettis and A. F. Trotman-Dickenson to fluorination and bromination reactions [12,13], and more detailed transition state calculations were carried out for these and the chlorination reactions making allowance for both rotational and vibrational motions in the activated complexes: the author's contribution to papers 12 and 13 was the calculation of the theoretical A factors. The calculated values showed a remarkable degree of agreement with experiment considering the crude nature of the model employed for the transition state. A striking feature of the three sets of results was the common trend in the discrepancies between calculated and experimental A factors as the hydrocarbon was altered. The collected results of the four experimental papers were presented in 1960 at a Symposium on Fundamental Aspects of Atomic Reactions at McGill University, Montreal [14].

Recently competitive chlorinations have been carried out with methane, propane and the chloromethanes [15]. By using two independent competitors for each chloromethane it was shown that the derived rate constants and Arrhenius parameters were independent of the competitors; the assumed mechanisms for the reactions were thus confirmed. The results, apart from their intrinsic interest, enabled the absolute rate constant and Arrhenius parameters for the addition of Cl to C_2Cl_4 to be derived from the results of competitive experiments carried out by Goldfinger and co-workers.

In the review of the rate constants of halogen atom reactions [8] a critical examination of all reliable data on halogen atom reactions was attempted. This comprehensive treatment revealed (a) that the accepted values for the Arrhenius parameters of the reaction of bromine with hydrogen and deuterium were almost certainly in error, and (b) that an excellent linear relation existed between the activation energies and endothermicities of the reactions of halogen atoms with hydrogen isotopes. This suggested that the Evans-Polanyi relation may apply in the hydrocarbon bromination series and that the activation energies of bromination and the more endothermic iodination reactions may yet provide the most accurate values of bond strengths in hydrocarbons.

An obvious extension of the competitive halogenation experiments was to olefin + alkane mixtures. Such experiments might be expected to provide rate constants and

Arrhenius parameters for the addition of halogen atoms to olefins. A study (with A. K. E. Hagopian) of the competitive chlorination of propane against the olefins, ethylene, propene and isobutene [16] showed that the reactions are unfortunately more complicated than had been anticipated. The olefins readily chlorinate heterogeneously on nearly all surfaces and it is difficult to isolate the homogeneous free radical component. The ease of heterogeneous chlorination increases from ethylene to isobutene and with the last it is almost impossible to observe the homogeneous free radical reaction. Furthermore, with ethylene at least, the initially formed C_2H_4Cl radical contains sufficient energy to dissociate again into Cl and C_2H_4 before being deactivated by collision. Thus it is only at rather high pressures that reaction (4) leads inevitably to (5)

$$C_2H_4 + Cl = C_2H_4Cl \qquad (4)$$

$$C_2H_4Cl + Cl_2 = C_2H_4Cl_2 + Cl \qquad (5)$$

The results suggest that it will be difficult to isolate the rates of addition of Cl to simple olefins. Fortunately with chlorinated olefins the difficulties seem less serious since the heterogeneous reactions are slower and the activated radicals are probably longer lived.

The Kinetics and Mechanism of Hydrocarbon Oxidation

The study of the oxidation of propane between 435 and 475°C [5] showed that the major initial reaction products were propene and water and suggested strongly that the main free radical processes were

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2 \qquad (6)$$

$$C_3H_7 + O_2 = C_3H_6 + HO_2 \qquad (3)$$

Ethylene was a minor initial product whose yield relative to propene increased with temperature and decreased with oxygen pressure: thus the pyrolysis of the propyl radical by (7) evidently competed with its oxidation by (3)

$$C_3H_7 = C_2H_4 + CH_3 \qquad (7)$$

The temperature dependence of the yields of propene and ethylene indicating that $E_7 - E_3 = 25 \pm 5$ Kcal mole^{-1} agreed with this view.

At the time this work was carried out it was thought that the mechanism of hydrocarbon oxidation changed radically between 350 and 450°C in the region associated with cool flames and the negative temperature coefficient: it was generally accepted that while olefin forming reactions predominated above 400°C, reactions forming oxygenated products, particularly aldehydes and peroxides, predominated below 400°C. Thus Norrish supposed that the oxidation of the propyl radical, for example, gave propionaldehyde and hydroxyl while Walsh, Hinshelwood and others supposed that a stable propyl peroxy radical was formed which could abstract hydrogen from propane to give propyl hydroperoxides. In either case complete conversion of the alkyl radicals to oxygenated products was proposed. Although aldehydes and peroxides had indeed been isolated in the range 300-400°C their yields were always small and it was usually argued that this was because they were very reactive and did not survive. However an equally likely explanation is that they were not formed in quantity.

In order to examine this possibility and to determine whether there was any marked change in the importance of olefin forming reactions as the temperature fell, the gaseous products from the oxidation of propane at 318°C were examined [17]. By using gas chromatography it was possible to detect these products at a very early stage in the reaction when their oxidation was unlikely because of the vast excess of propane. The work showed conclusively that at least 75% of the propane consumed in the early stages appeared in the products as propene and a further 5% as ethylene. Since the initial proportions were independent of oxygen pressure over a tenfold range, ethylene was not formed by a pyrolysis reaction as at high temperatures but by reaction of the propyl radical with oxygen or by the decomposition of the propyl peroxy radical. The results finally disposed of the earlier theories of low temperature oxidation and clearly established that reaction (3) was the main remover of propyl radicals at all temperatures between 320 and 475°C.

They also explained why earlier workers with inadequate analytical techniques had not observed the high initial conversion to propene. The propene is itself readily attacked and oxidised, and its maximum concentration never exceeds about 10% that of the propane; thus it appears as a minor product in the intermediate stages of the oxidation. Furthermore the main oxidation products of propene, as shown by Neiman and co-workers, are acetaldehyde and formaldehyde. Thus any examination of the reaction products at a moderately advanced stage in the reaction (say beyond 10% conversion of the propane) would give substantial yields of aldehydes. Propene might well appear as an unimportant by-product along with methanol, acetone etc.

The study did not however establish whether aldehydes were minor initial products or entirely secondary products. Since the condensable products from propane were known to be complex [5] it was decided to undertake a comprehensive investigation of the low temperature oxidation of ethane which previous work [2] had shown to possess all the characteristics normally associated with the higher hydrocarbons. This work with C. H. J. Wells [18,19] has shown that the main features of the slow oxidation are similar to those of propane. Ethylene constitutes about 90% of the initial products above 360°C and about 60% at 320°C. Formaldehyde is the only other important initial product. At 320°C small quantities of acetaldehyde appear in the initial products (up to 4%). A concurrent study of the oxidation of ethylene showed that the main initial product is formaldehyde in 80-90% yield with ethylene oxide as the minor product. Very small initial yields of acetaldehyde were found at all temperatures. Since the ethylene and formaldehyde concentrations both passed through maxima in the oxidation of ethane, and since carbon monoxide is the main oxidation product of formaldehyde and is a secondary product from the oxidation of ethylene, the main course of the reaction above 320°C is probably

Ethane ⟶ Ethylene ⟶ Formaldehyde
(+ formaldehyde) (+ ethylene oxide)

⟶ Carbon Monoxide

where minor products are given in brackets. This sequence is different from any that has previously been proposed. The results clearly emphasise the danger of deducing reaction mechanisms without complete analytical data.

Concurrently with the analytical studies on the oxidation of single hydrocarbons two other methods of investigation were pursued, kinetic measurements based on pressure change, and competitive oxidations of hydrocarbons in mixtures. The latter work was carried out in collaboration with A. F. Trotman-Dickenson.

In the paper with J. W. Falconer [5] a general method for dealing with the acceleration and maximum rate of degenerately branched chain reactions was developed. This method was elaborated later and applied to the low temperature oxidations of ethane, propane and isobutane [20,21]. The kinetic studies showed that with ethane and propane at 318°C the time constant for the exponentially accelerating part of the reaction increased linearly with hydrocarbon pressure above a certain limiting pressure below which no acceleration occurred. According to the theory the lifetimes of the branching intermediates could be determined from these plots and were of the order of 1 minute.

Amongst other observations it was shown that the induction period of the oxidation of propane was greatly reduced by the addition of otherwise inert gases (carbon dioxide and nitrogen) while the acceleration constant and maximum rate of reaction were unaffected. This indicated that a diffusion controlled process was important during the early part of the reaction but not later, although the nature of the process was obscure. It was also noted that the acceleration during this period was not uniform but increased from zero to a maximum value which was held almost until the maximum reaction rate was achieved. A third unexplained observation was the marked catalysis effected by replacing a part of the propane by propene. The effect was termed "promotion" and has since been observed with ethane [18] but at the time its cause was not clear.

The work on the oxidation of ethylene [18,19] taken in conjunction with work done elsewhere on other olefins has shown that the predominant mode of oxidation is by the overall reaction (8)

$$O_2 + R_aR_bC{=}CR_cR_d = R_aR_bCO + R_cR_dCO \qquad (8)$$

For all but fully substituted ethylenes one or both of the carbonyl products will be an aldehyde which will strongly catalyse the reaction. Thus replacement of an alkane by the appropriate olefin immediately makes available a source of branching agent which would otherwise not be formed until sufficient olefin had accumulated. This explains three puzzling observations: (1) the slow initial acceleration of the oxidation [5,17], (2) the fact that in the high temperature oxidation at least the period of slow acceleration is removed by the replacement of propane by the maximum amount of propene found in the uncatalysed oxidation [5], and (3) the fact that the addition of larger amounts of propene greatly accelerate the development of the reaction and increase the maximum rate [5,17,18].

The derivation of the lifetime of the branching intermediate from the kinetic studies prompted the investigation with A. D. Kirk of the rates of homogeneous pyrolysis of alkyl hydroperoxides [22] which had often been proposed as the main branching agents in the low temperature oxidation. Ethyl, isopropyl and t-butyl hydroperoxides were studied. The homogeneous pyrolysis occurs according to reaction (9)

$$\mathrm{ROOH} = \mathrm{RO} + \mathrm{OH} \qquad (9)$$

followed in these three particular cases by the decomposition of the alkoxy radical into a carbonyl compound and methyl, for example

$$(\mathrm{CH_3})_2\mathrm{CHO} = \mathrm{CH_3} + \mathrm{CH_3CHO} \qquad (10)$$

In order to separate the homogeneous from the heterogeneous reaction and to prevent chain decomposition the Szwarc toluene carried technique was initially used but the uncertainty as to the fraction of methyl radicals which would react with the toluene led to its replacement by benzene which would react only with OH radicals. The final product of this reaction was diphenyl which was determined by weighing. The system yielded first order homogeneous rate constants which were independent of the surface/volume ratio of the reaction vessel. The Arrhenius parameters for the pyrolysis of the three peroxides were similar $A \approx 10^{14}$ sec^{-1}, $E \approx 38 \cdot 5$ kcal mole^{-1}, and the lifetimes of the peroxides at 320°C were between 2 and 4 sec. The shortness of these lifetimes [23] ruled out the possibility that they could be important branching agents in the oxidations of ethane, propane and isobutane above 320°C.

The competitive experiments were undertaken to measure the apparent selectivity of the radical or radical mixture attacking hydrocarbons undergoing oxidation. Since oxidation products, except in the earliest stages, are not characteristic of the parent hydrocarbons, the relative consumptions of the hydrocarbons could only be found from the change in their concentrations. This method is inevitably less accurate than the product method used in the halogenation work and demands at least 10% reaction, but it makes fewer assumptions about the reaction mechanism. The first study, with R. F. Smith [24,25] using ethane + propane mixtures showed that the relative rate of removal of the two hydrocarbons was unaffected by mixture composition and temperature between 270 and 495°C. Later work with W. E. Falconer [26] covering more hydrocarbons and wider concentration ranges confirmed the general features except that above 400°C there was a decrease in selectivity as the extent of reaction was increased by increasing the oxygen/hydrocarbon ratio. The effect was particularly noticeable with methane + ethane mixtures at 495°C where the reactivity of methane relative to ethane increased linearly from near zero as the oxygen content of the mixture increased.

Undoubtedly the most important conclusion from the work was that the rates of oxidation of hydrocarbons when mixed are very similar while their rates of oxidation singly depend strongly upon their structure. The results confirm that hydrocarbon oxidations are free radical chain reactions and show that the radical or radical mixture responsible for removing the hydrocarbons has a reactivity between that of Cl and CH_3O.

The thermal experiments were followed by a series of competitive oxidations induced by the photolysis of ketones at 145 and 230°C [27]. The relative rates of removal of the hydrocarbons were independent of the nature of the initiator and were close to those observed in the thermal experiments. Initially the results were interpreted as meaning that the reactivities of HO_2 and alkyl peroxy radicals were the same. However it was always realised that this view suffered from an objection. On the basis of thermochemistry the HO_2 radical should have a similar selectivity to the bromine atom. While HO_2 seemed to be the most likely chain propagating radical in the thermal oxidations [5,17-20] the low selectivity found in the competitive oxidations coupled with what is known from other experiments on the reactivity of HO_2 [9] makes it more likely that the attacking radical is OH. Recently further work by Trotman-Dickenson and co-workers has supported this view by showing that the alkyl peroxy radicals probably do not abstract hydrogen from alkanes but react mutually to give hydroperoxides which are themselves photolysed to provide OH radicals.

If it is accepted that OH is the radical attacking hydrocarbons during their oxidation and yet that alkyl radicals react with oxygen to give HO_2 it is necessary to introduce an additional reaction for the conversion of HO_2 to OH. This matter is fully discussed in papers 18 and 19. It is possible that the very early stages of oxidations may involve straight wall terminated chains with HO_2 as the propagating radical, thus explaining the sensitivity of the induction period to inert gases and the very slow initial acceleration. However as soon as the HO_2 concentration rises mutual reaction may occur which could give OH by reaction (11)

$$2HO_2 = 2\ OH + O_2 \qquad (11)$$

The chains are probably short and may be terminated either by (12) or by first order removal of OH

$$2\ HO_2 = H_2O_2 + OH \qquad (12)$$

During the main part of the reaction diffusion processes would be unimportant and inert gases would have no effect on the rate. Autocatalysis which occurs in this part of the reaction could result from the oxidation of the aldehydes formed by oxidation of the primary olefins.

These conclusions and hypotheses represent the author's current views on hydrocarbon oxidation, but much more work will be required before they are proved to be sound or otherwise. A promising line of investigation is the determination of the selectivity in competitive oxidations in their earliest stages. Since it is now clear that the majority of alkyl radicals react with oxygen to give olefins as the major products, it is possible to apply the product method to the very early stages up to about 1% conversion. Preliminary experiments with propane + isobutane mixtures have indeed indicated that the selectivity in the very early stages at 300°C is about twice that in the intermediate and later stages of the reaction.

In the foregoing it has generally been assumed that the establishment of a maximum concentration of olefin in the intermediate stages of the oxidation of an alkane results from the destruction of the olefin rather than from the cessation of the reactions forming it. Although the latter is most unlikely it is conceivable, for example, that some of the alkyl radicals formed later in the reaction could add to unsaturated compounds rather than react with oxygen. In order to test this, competitive oxidations on ethane + propene mixtures were undertaken with M. D. Carabine [28]. From these and earlier data [24] the relative rates of oxidation of propane and propene could be obtained and compared with values derived from the maximum fractional yield of propene in the oxidation of propane. The agreement between the two values was reasonably good and therefore substantiated the main assumption.

Gas Chromatography

Since gas chromatography has been used extensively throughout the work on gas kinetics it was inevitable that the author should have become interested in the theory and practice of the technique itself. Indeed reference has already been made to some early work in this direction [3].

In most of the kinetic work katharometers have been used as the gas chromatographic detectors but there was always the possibility that a more suitable and sensitive detector could be developed. One detector which showed initial promise was R. P. W. Scott's thermal hydrogen flame detector, in which the column effluent passes through a small hydrogen flame impinging on a thermocouple. When an eluted organic substance passes through the flame the temperature increases: the temperature change may be recorded to give a typical differential chromatogram. The quantitative aspects of this detector were investigated with J. I. Henderson [29] and the response was shown to be directly proportional to the heats of combustion of the compounds eluted. The ultimate limit of detection proved to be similar to that of a katharometer and for this reason it never became widely used. Nevertheless with further development it might form the basis of a sensitive micro-flame calorimeter.

More recently the author became interested in the problem of high speed gas chromatography and published a paper on the theoretical aspects of this problem [30]. Within the last year it has become clear that one of the main causes of the inefficiency of packed columns in gas chromatography when compared with open tubular columns is the poor geometry of the gas phase with the consequent slowness of mass transfer in the gas phase and the possibility of eddy diffusion. The actual magnitudes and interrelations of these two effects are only now becoming clear.

In a paper with Miss L. McLaren presented at a Symposium on Advances in Gas Chromatography at Houston, Texas [31] evidence was presented in general agreement with that of other workers in the field showing that mass transfer in the gas phase was indeed a significant effect whereas eddy diffusion was probably much less important.

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Low-temperature oxidation and cool flames of propane

By J. H. Knox and R. G. W. Norrish, F.R.S.
Department of Physical Chemistry, University of Cambridge

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A detailed analytical study of the cool-flame oxidation of propane has been carried out using a continuous-flow technique with a view to the further elucidation of the mechanism of the low-temperature oxidation of hydrocarbons. The formation of the three theoretically possible aldehydes has been demonstrated and the initially formed peroxide shown to be hydrogen peroxide. Measurements of the yields of the different products formed under varying conditions of temperature, composition and time of contact have been made and correlated with measurements of the luminous intensity and temperature of the flame.

The results confirm the earlier conclusions of Norrish (1948) that aldehydes are the important branching agents in the temperature range of 300 to 400° C, and a detailed scheme based on that proposed earlier has been developed to account for the observations. The scheme has further been shown to allow of a simple explanation of the origin of the periodic character of the cool flame in terms of the thermal instability of the normal slow reaction.

Early studies of the oxidation of hydrocarbons containing three or more carbon atoms showed that two distinct types of oxidation could take place (Pease 1929). Above 400° C cracking reactions predominated, while below that temperature the formation of intermediate compounds was more important. The two regions were separated by a zone in which the rate of the slow oxidation fell with increase of temperature and the lower of the two regions was characterized by the occurrence of cool flames (Townend 1937). In both regions the slow reactions are of the type known as degenerate branching chain reactions (Semenov 1935). Detailed kinetic schemes have been proposed for both types of reaction, but considerable doubt still remains as to the mechanisms actually in operation.

The work to be described was concerned with the reaction below 400° C for which the mechanisms fall into two main classes, namely, those in which organic peroxides are regarded as the important autocatalytic agents (see, for example, Ubbelohde 1935), and those in which aldehydes are regarded as the important intermediates (Norrish 1948). In the present work we have made a detailed examination of the products of the cool flame of propane in an attempt to obtain more definite evidence in support of one or other of the theories. Particular attention has accordingly been paid to the identification and determination of the peroxidic and aldehydic fractions of the reaction product. In addition to the elucidation of the low-temperature oxidation we were also interested in the processes leading to the formation of cool flames and to this end measurements of the temperature and the light emission of the flames were made.

The results of the work have provided further evidence that aldehydes rather than peroxides are the important intermediates in the low-temperature type of oxidation. The measurements of the temperature and the light emission lend further support to the view that the periodic phenomena associated with the cool flame arise out of the thermal instability of the normal slow reaction which is prevented from developing into a true ignition by the decrease in the rate of reaction as the temperature rises above 400° C.

EXPERIMENTAL

Apparatus and experimental methods

The gases used in the experiments were contained in cylinders under pressure, and the nitrogen and oxygen were used directly without purification. The propane which was given as 98 % pure was passed before use through bubblers containing concentrated sulphuric acid and strong caustic soda respectively, and was then dried by means of calcium chloride. The propionaldehyde used in some of the later experiments was obtained by distillation of B.D.H. propionaldehyde and had a boiling-point range of 47·5 to 47·9° C.

The apparatus was of the conventional flow type and, except in minor details, was identical to that used by Bailey & Norrish (1952). The gases were delivered at known rates by means of three calibrated capillary flow-meters and, after mixing in a vessel where the direction of flow was twice reversed, passed into the conical reaction vessel made of either Pyrex or quartz. This was housed horizontally in a furnace whose temperature could be maintained by means of a regulator to within 2° C of any temperature between 200 and 500° C.

The measurements of the light intensity were made by focusing the light on to a Mazda photomultiplier cell housed in a light-tight brass can mounted axially at the outlet end of the furnace. The cell was supplied with a potential of 700 V from a pile of high-tension batteries and the current measured by a sensitive galvanometer. The temperature measurements were made with a copper/constantan thermocouple enclosed in a very thin-walled glass capillary which was sealed across the reaction vessel. In measuring the flame temperature the flow rate was varied so that the flame passed over the thermocouple and the maximum temperature recorded taken as the flame temperature.

In the course of the early experiments it was found that reproducible results could be obtained only when a standard procedure was observed in carrying out each run. The reaction vessel was accordingly evacuated for 30 min. before and after each run, and the reaction was allowed to proceed for 30 min. before the collection of any product. It was also found advisable to maintain the furnace at a temperature of about 400° C between successive runs and to carry out any given series in the shortest possible time. By observing these precautions consistent results were obtained in each series. Agreement between similar runs in different series is less satisfactory, since the reaction vessel was often allowed to cool and in some cases removed between the successive series.

After reaction the liquid products were condensed along with some of the unburnt propane by passage through two traps cooled to -80°C. The gaseous products which remained were then sampled by means of a 100 ml. sampling bulb attached to the gas-analysis apparatus. After the completion of each run the traps were isolated from the rest of the system and connected with a calibrated expansion bulb of about 2 l. capacity. By warming the traps to -21°C in a mixture of salt and ice the propane was evaporated and the quantity present found from the pressure developed. The traps were then weighed to obtain the weight of the remaining liquid products, and the product finally transferred with water to a 50 ml. standard flask for further analysis. In all the runs described the product from precisely 100 millimoles of propane entering the furnace was collected and the yields of the different products are accordingly given in millimoles percent.

The analytical methods used for the liquid products were as follows:

Acids were determined by titration with N/50 alkali under nitrogen.

Aldehydes plus acids were determined by oxidation on a column of silver oxide as described by Bailey & Knox (1951). The separate acids and aldehydes were determined by the chromatographic method described in the same paper.

Methyl alcohol and its derivatives were determined by the standard Zeisel method for the determination of methoxyl groups.

Peroxides were determined by titration of the iodine which they liberated from a saturated solution of sodium iodide in glacial acetic acid under carbon dioxide.

Water could not be determined directly, but the amount formed could be estimated from the weight of the liquid product in the light of the identification of the methoxyl compounds and the peroxide as dimethyl formal and hydrogen peroxide respectively (see below).

The uncondensed gases were analyzed in a constant-volume gas-analysis apparatus. The different gases were successively removed and the resulting pressure decrease measured by means of a Pyrex spoon gauge. The methods of analysis and the order of removal were as follows:

Carbon dioxide—by reaction with slightly moist potassium hydroxide. The absorption tube was cooled to -80°C during the admission and removal of the gas as a precaution against the back-diffusion of water vapour.

Oxygen—by reaction with white phosphorus.

Hydrocarbons other than methane—by condensation at liquid-nitrogen temperatures. The condensate was retained for further analysis by combustion which enabled its empirical formula to be found.

Carbon monoxide and hydrogen—by oxidation on copper oxide heated in a small furnace to 305° C. The carbon dioxide and water were removed by drawing the gases through a U-tube cooled in liquid nitrogen. By subsequently warming the tube to −80° C the carbon dioxide was evaporated and the respective amounts of carbon monoxide and hydrogen found.

Methane—by combustion with excess oxygen.

Nitrogen. The only gas remaining after the removal of the above was nitrogen. Since the amount of nitrogen used in each experiment was known the amounts of the different gaseous products could readily be calculated from the composition of the gas samples.

These methods gave a complete analysis of all the major products of the reaction and enabled carbon, oxygen and hydrogen balances to be constructed for each run. These normally showed deficiencies of between 2 and 5 % on the amounts of the reactants entering the furnace. The reason for this is not clear, but the formation of polymers in the tubes leading from the reaction vessel to the traps may be the explanation.

Identification of the various liquid products

Only with the aldehydic and acidic products of the reaction was it possible to identify the compounds directly by the analytical methods employed. For the identification of the methoxyl and peroxidic compounds additional methods were required. The former was shown by infra-red analysis to consist mainly of dimethyl formal along with a little methyl formate. The identification of the latter, however, proved to be more troublesome, and several experiments were necessary before this was finally achieved.

Shtern & Pollyak (1939) showed that the polarograpn could be used to distinguish between hydroperoxides and hydrogen peroxide. Experiments were therefore carried out on the reaction product and on a number of peroxides prepared in the laboratory (figure 1). The waves due to the peroxidic compounds all lie between 0·0 and 1·4 V; the small waves at 1·7 V, seen in the polarograms of di-oxymethyl peroxide and the reaction product, result from the presence of free formaldehyde, and the larger waves at 1·8 to 2·0 V in the polarograms of di-oxyethyl peroxide, di-oxypropyl peroxide and the reaction product are due to higher aldehydes.

An examination of the polarograms shows that the wave due to the peroxide in the reaction product is similar to those of methyl hydroperoxide and of the di-oxyalkyl peroxides. Of the latter only di-oxymethyl peroxide need be considered in view of the much lower stability of the other two peroxides and the predominance of formaldehyde over the other aldehydes in the reaction product. The peroxide in the reaction product is thus probably one of two, either methyl hydroperoxide or di-oxymethyl peroxide.

A second attempt at identification was made by examining the effect of the addition of strong alkali to the reaction product. Previous workers have shown that a mixture of oxygen and hydrogen is usually evolved (see, for example, Harris & Egerton 1937). Under our conditions only hydrogen was evolved. With di-oxymethyl peroxide and methyl hydroperoxide in the presence of excess formaldehyde hydrogen was likewise the only gas liberated. The discrepancy between the earlier experiments and our own is probably due to the presence of excess of hydrogen peroxide in the former and an excess of formaldehyde in the latter. Although the results confirm the findings of the polarograph they do not add any further information.

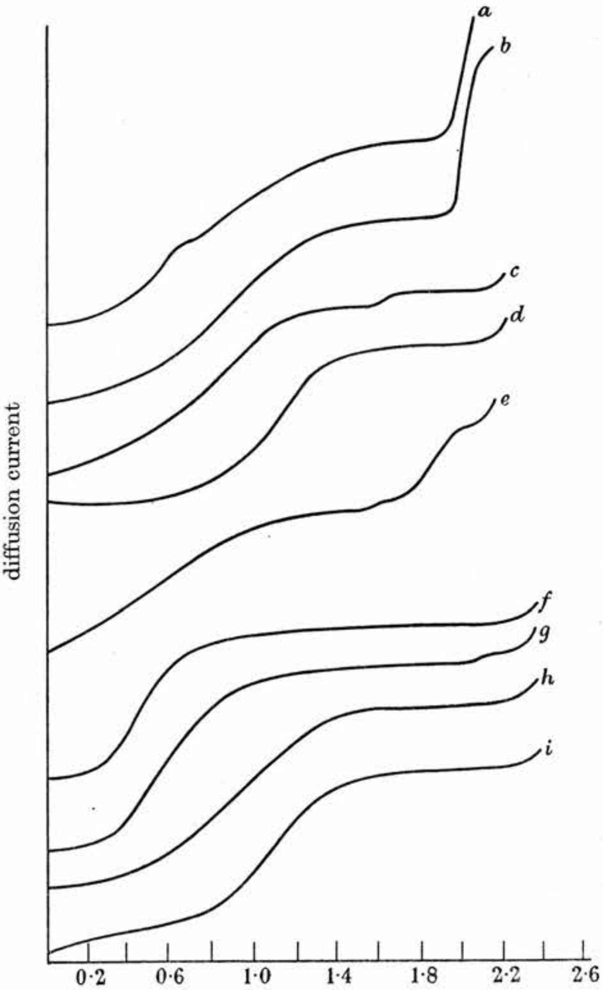


FIGURE 1. Polarograms of the reaction product and of various peroxides: *a*, $\{C_2H_5.CHOH.O\}_2$, *b*, $\{CH_3.CHOH.O\}_2$; *c*, $CH_2OH.OO.CH_2OH$; *d*, H_2O_2; *e*, reaction product of propane cool flame (370°C); *f*, $(CH_3)_3COOH$; *g*, C_2H_5OOH; *h*, CH_3OOH; *i*, H_2O_2.

The final attempt at identification was prompted by the observations of Kooijman & Ghijsen (1947) on the retarding effect of formaldehyde on the reaction between hydrogen peroxide and an acid solution of potassium iodide. Experiments were therefore carried out in which the rates of reaction of different peroxides with acid potassium iodide were measured. In the presence of excess of iodide the reactions would, *a priori*, be expected to be first order. $\log_{10} a/(a-x)$ has accordingly been plotted against time (figure 2), where a is the initial amount of peroxide present and x the amount reacted at any given time.

It will be seen that, while the reactions of hydrogen peroxide, di-oxyethyl peroxide, methyl hydroperoxide and methyl oxymethyl peroxide are all first order, those of di-oxymethyl peroxide and of the reaction product begin as higher order reactions and become first order only after some 60 % of reaction has taken place. There can therefore be little doubt that the peroxide obtained from the experiments on propane is di-oxymethyl peroxide, not methyl hydroperoxide. Since this peroxide is readily formed in solution by condensation of formaldehyde and hydrogen peroxide (Fenton 1914) and is unstable above 190° C (Egerton, Harris & Young 1948), it is highly probable that the peroxide initially formed in the cool flame is hydrogen peroxide and that the di-oxymethyl peroxide is formed subsequently as the products of the reaction cool.

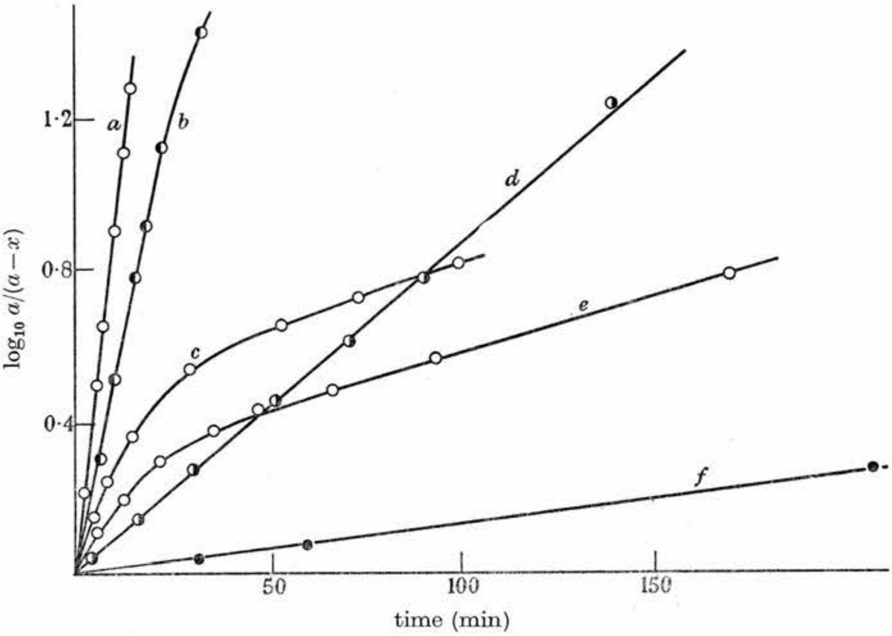


FIGURE 2. Rates of reaction of different peroxides with acid potassium iodide. a = initial amount of peroxide; x = amount reacted at any given time. a, H_2O_2; b, $\{CH_3CHOH.O\}_2$; c, reaction product (320° C); d, CH_3OOH; e, $CH_2OH.OO.CH_2OH$; f, $CH_3OO.CH_2OH$.

Static experiments and measurements of flame temperature

Before beginning the continuous-flow experiments it was necessary to determine the conditions under which cool flames could be obtained in our reaction system. For this purpose the apparatus was used as a static system. The reaction mixture, which for these experiments was equimolecular in propane and oxygen, was admitted to the reaction vessel at the highest convenient rate of flow. When the vessel was thoroughly flushed out it was isolated from the rest of the apparatus and the pressure changes followed on a manometer. The slow reaction outside the cool-flame region was accompanied by a regular pressure increase, the pressure-time curves being of the usual sigmoid shape. Cool flames were accompanied by a pressure pulse of up to 5 cm Hg. The final pressure after the passage of the flame was somewhat greater than that to be expected if the slow reaction had proceeded normally for the same time.

Cool flames could be obtained at any temperature between 320 and 400° C (figure 3), and in the region of 330° C as many as five successive flames could be seen to pass through the reaction vessel (see Newitt & Thornes 1937). A well-defined low-pressure ignition peninsula was also observed at about 320° C.

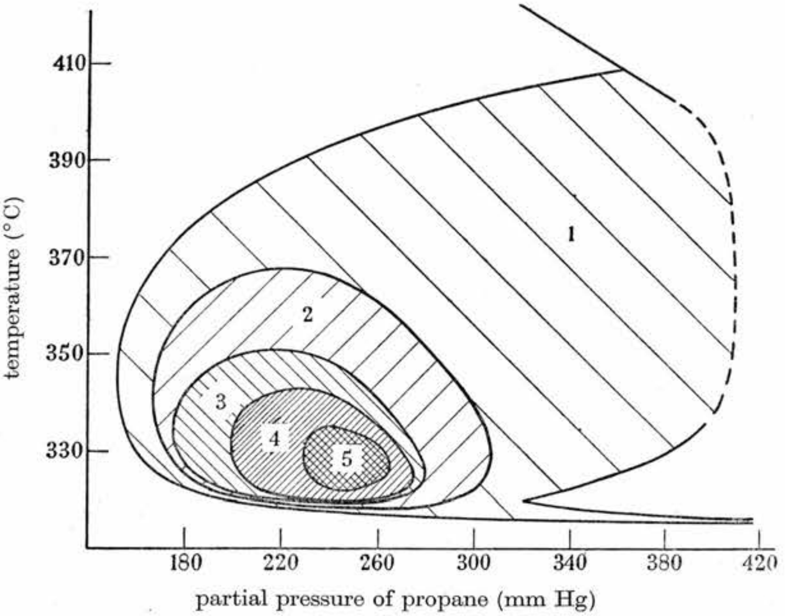


FIGURE 3. Regions for 1 to 5 cool flames in equimolecular propane/oxygen mixtures diluted with nitrogen.

The lower cool-flame limit at 320° C was found to be very sharp and below it no reaction appeared to take place. The upper limit at about 400° C, on the other hand, was indistinct, and cool flames became increasingly difficult to observe as the temperature rose above 370° C. At this temperature the slow reaction before and after the flame became more pronounced and the flame appeared to be gradually swamped as the temperature rose towards 400° C. This continuity between the cool-flame reaction and the slow reaction is well illustrated by the curves for the temperature of the cool flame (figure 4). With an equimolecular mixture of propane, oxygen and nitrogen (lower curve) the temperature of the flame rose slowly from 420 to 450° C as the furnace was heated from 320 to 420° C, and there is clearly no evidence of a discontinuity at the upper cool-flame limit.

The points for furnace temperatures below 320° C were obtained by allowing the furnace to cool slowly while still maintaining a cool flame in the reaction vessel. Below this temperature, that of the lower limit in a static system, the flame temperature falls very rapidly, and it is apparently a necessary condition for the formation of a cool flame *ab initio* that the slow reaction should be capable of attaining a minimal degree of thermal instability. This point will be referred to later in the discussion.

The upper curve in figure 4 was obtained with a richer mixture, and it will be noted that ignitions always occurred when the temperature of the reacting gas rose above 455° C. It is of interest to note that the temperature at which the gas ignited was independent of the furnace temperature over a range of some 30° C. This provided a useful confirmation that the temperature measurements were in fact reliable, and also gives support to the view generally held that the ignition of hydrocarbons is governed essentially by thermal considerations.

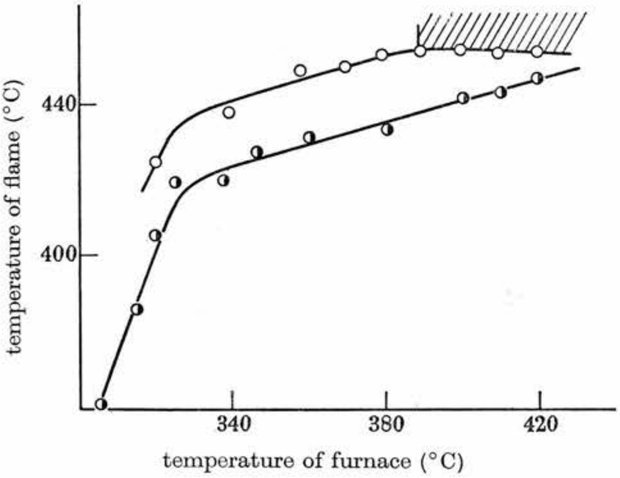


FIGURE 4. Cool flame temperatures at different furnace temperatures. ○, $O_2+C_3H_8+0{\cdot}40N_2$; ///, ignitions; ◑, $O_2+C_3H_8+N_2$.

The variation of the products of the cool flame with conditions of reaction

The changes in the yields of the different products of the cool flame as temperature, flow rate and composition are varied are shown in figures 5 to 17. In addition to the analytical data the results of the flame intensity measurements have also been given for each series. The values actually plotted have been scaled from the observed readings so as to be proportional to the amount of light emitted per mole of propane entering the furnace. They are therefore directly comparable with the results of analysis. The units of measurement of the light intensity are arbitrary. Curves have been given for all the products mentioned in the section on analysis with the exception of propionaldehyde. This substance was always present in very small yield, and within the experimental error, which here was proportionately large, the yield was always close to 0·1 mmole %.

The effect of change of furnace temperature on the cool-flame products is shown in figures 5 to 9. The mixture used had a composition of $10C_3H_8+10O_2+4N_2$, and a total flow rate of 2·40 ml./s was used throughout. This corresponded to a time of residence in the reaction vessel of about 20 s at 350° C. The products show remarkably little variation over a range of furnace temperatures of nearly 100° C, and no general trend is discernible. This result is not altogether unexpected when it is remembered that the actual flame temperature rises by only some 20° C in the region considered (figure 4). Interesting changes are, however, to be noted in the region of 360 to 390° C. At 380° C there is a definite minimum in the yields of nearly all the products. This decrease in reactivity was found to be associated with marked fluctuations in the intensity of the flame which visual observation showed to be flickering. The origin of the phenomenon is not clear, but a possible explanation may be found in terms of minor changes in reaction mechanism such as have been suggested by Chamberlain & Walsh (1948) to account for the 'lobes' observed in the cool-flame boundary of diethyl ether. Above 400° C the reactivity once more begins to fall and the yields of all major products except ethylene decrease. The increase in the yield of the latter is in agreement with earlier evidence (see, for example, Pease 1929) that cracking reactions become more important as the temperature rises.

Figures 10 to 13 illustrate the effect of change of flow rate on the cool-flame products. The mixture used throughout the series had a composition of $10C_3H_8 + 10O_2 + 8N_2$ and the temperature was 350° C. Cool flames, once initiated, could be maintained in the reaction vessel with flow rate as high as 7·00 ml./s (time of residence 7 s), although the normal induction period in the static system was 22 s. If a flame was not allowed to establish itself a flow rate as low as 4·2 ml./s could be maintained without a flame striking back. Visual observation showed that, with a flow rate of 7·00 ml./s, the cool flame established itself close to the outlet end of the reaction vessel, and products taken in this run are to be compared with those taken immediately after a cool flame in a static system. With decrease of flow rate the flame moved towards the inlet end of the vessel, and the changes which occur in the products as the flow rate is lowered are thus the result of the slow reaction occurring after the passage of the flame. It is clear from the figures that the yields of the aldehydes and peroxides are already at a relatively high value immediately after the flame, while the yields of the end-products, methyl alcohol, carbon monoxide, water, etc., and the light output of the reaction are low and increase only slowly as the subsequent reaction proceeds. The cool flame appears therefore to be characterized by the rapid formation of intermediate products, while the end-products of the reaction are formed more slowly after the flame.

The unusual changes which occur in the yields of aldehydes, acids and peroxides at a flow rate of about 2·8 ml./s are most easily accounted for in terms of the decomposition of di-oxymethyl peroxide according to the reaction

$$CH_2OH.OO.CH_2OH = 2HCOOH + H_2.$$

In a separate experiment with this peroxide it was found that, by the methods of analysis described above, it appeared to contain one molecule of formaldehyde and one molecule of formic acid. The decomposition represented above would therefore appear to be accompanied by the formation of one mole each of formic acid and hydrogen and the disappearance of one mole of formaldehyde, the total acid plus aldehyde remaining constant as is in fact observed. Similar changes have previously been observed by Newitt & Thornes (1937) and by Bardwell & Hinshelwood (1951) and have been regarded as evidence for the identification of the autocatalytic agent in the oxidations. In our own experiments it is, however, clear that the destruction of the aldehyde and peroxide are interconnected, and that both are subsequent to the passage of the flame rather than coincident with it.

In addition to the runs with cool flames a run was carried out in which product was collected from the induction period using a flow rate of 4·2 ml./s. The yields of the different products were about one-tenth of those obtained from the cool flame. The results are given in table 1 along with those for two runs with cool flames. The figures in parentheses give the yields relative to the total aldehyde = 10. The results are of particular interest in showing that the products of the induction period are identical to those of the cool flame, and that they are present in roughly the same proportions although peroxide and methoxyl compounds are slightly less abundant in the former. A polarogram of the product from the induction period was identical to those of the cool flame product, and there was no evidence for the presence of any hydroperoxide.

The results of the variation of composition are shown in figures 14 to 17. The runs were carried out at a temperature of 370° C, and flow rates of 0·50 ml./s of

FIGURES 5 TO 9. Variation of the cool flame products of propane with temperature of furnace.

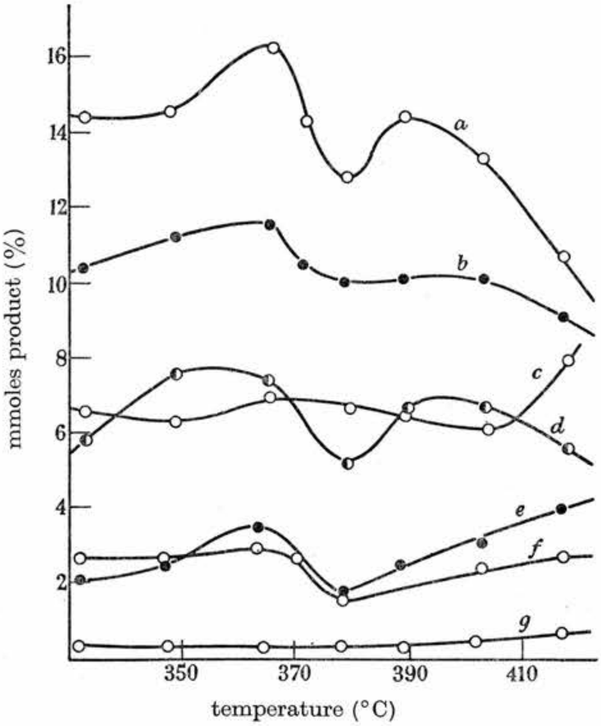


FIGURE 5. *a*, methoxyl; *b*, aldehyde + acid; *c*, ethane + ethylene; *d*, carbon dioxide; *e*, acid; *f*, acetic aldehyde + acid; *g*, peroxide.

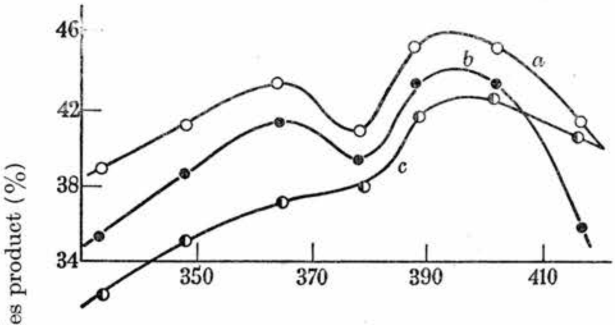


FIGURE 6.
a, oxygen used × ½
b, carbon monoxide
c, water × ½

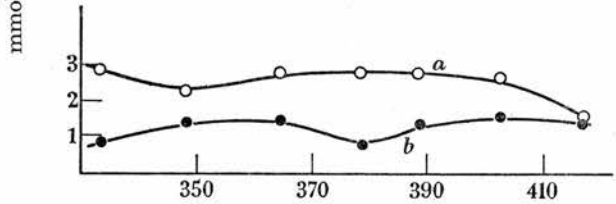


FIGURE 7.
a, hydrogen
b, methane

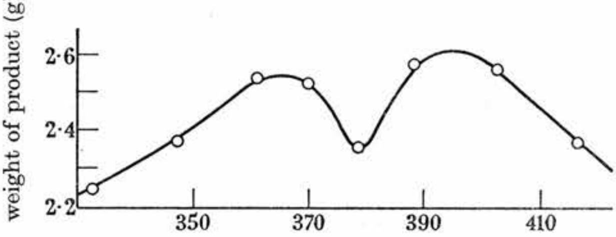


FIGURE 8.
Weight of product

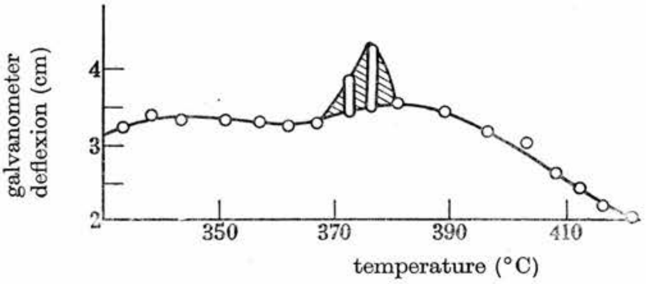


FIGURE 9.
Light intensity
▨, fluctuating flame

TABLE 1. COMPARISON OF PRODUCTS FROM THE INDUCTION PERIOD AND FROM THE COOL FLAME

	induction period	cool flames	
flow rate (ml./s, n.t.p.)	4·2	7·0	4·2
acid + aldehyde	0·46 (14)	6·6 (12)	10·2 (14)
acid	0·13 (4)	1·2 (2·2)	2·8 (3·8)
aldehyde	0·33 (10)	5·4 (10)	7·4 (10)
propionic acid + aldehyde	0·009 (0·3)	0·1 (0·2)	0·1 (0·1)
acetic acid + aldehyde	0·052 (1·6)	0·8 (1·5)	1·5 (2·0)
peroxide	0·053 (1·6)	2·1 (3·7)	3·5 (4·8)
methoxyl compounds	0·066 (2·0)	4·1 (7·5)	10·6 (14·5)

nitrogen and 2·00 ml./s of oxygen plus propane were used throughout. The yields of the products increase with increase of oxygen content up to an equimolecular ratio. Further addition of oxygen at the expense of propane results in a slight

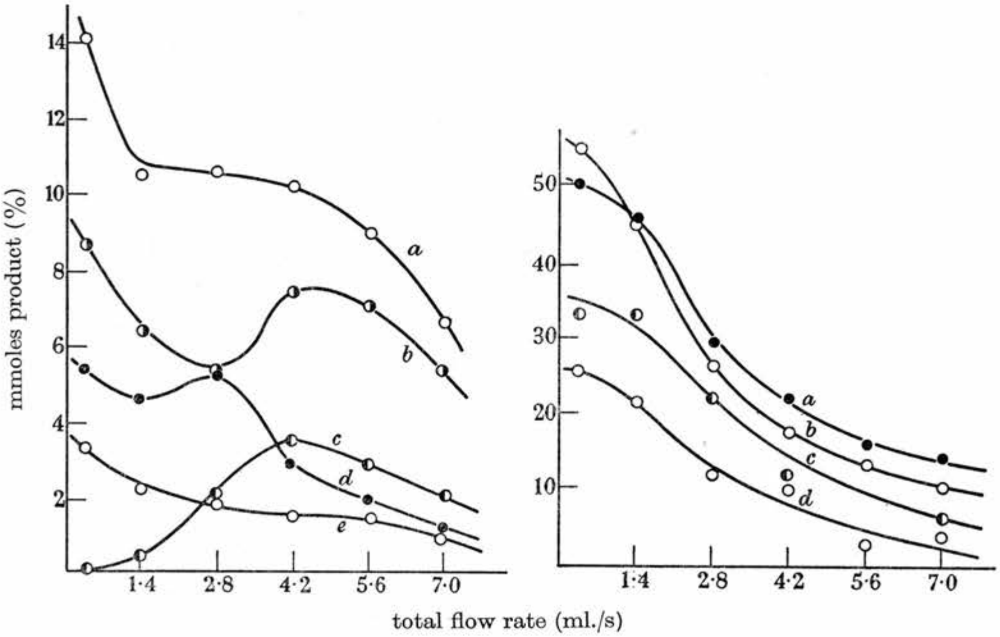


Figure 10. a, aldehyde + acid; b, aldehyde; c, peroxide; d, acid; e, acetic aldehyde + acid.

Figure 11. a, oxygen used × $\frac{1}{2}$; b, carbon monoxide; c, water × $\frac{1}{2}$; d, methoxyl.

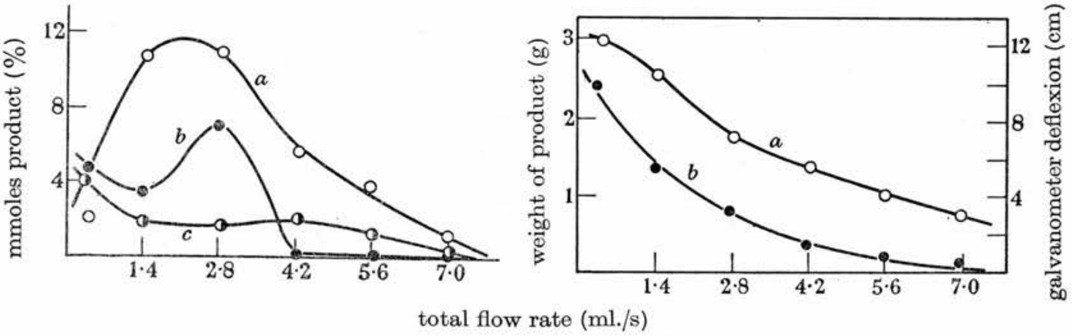
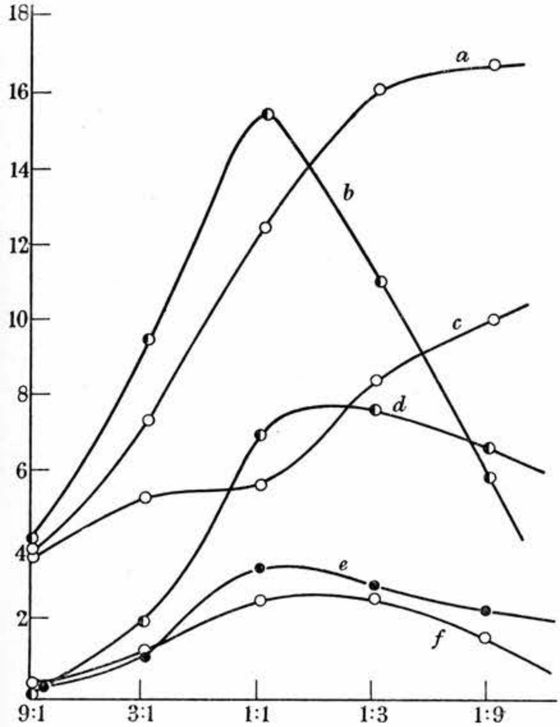


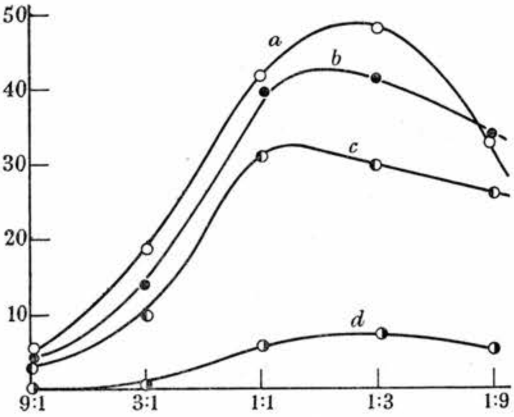
Figure 12. a, ethane + ethylene; b, hydrogen; c, methane.

Figure 13. a, weight of product, b, light intensity. Temp. 350 °C.

Figures 10 to 13. Variation of the cool flame products of propane with flow rate.

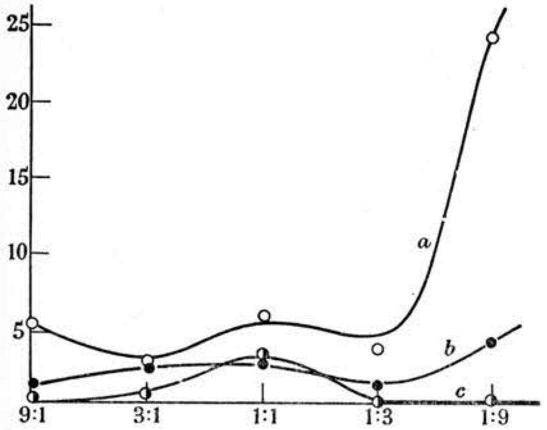
decrease in the amount of propane reacted. If the results are plotted in such a way that the yields are proportional to rates of formation of the different products (for example, by multiplying them by the flow rate of propane in each case), it is found that the equimolecular mixture is by far the most reactive.





URE 14. *a*, aldehyde + acid; *b*, methoxyl; *c*, aldehyde; *d*, acid; *e*, peroxide; *f*, acetic aldehyde + acid.

FIGURE 15. *a*, oxygen used × ½; *b*, carbon monoxide; *c*, water × ½; *d*, carbon dioxide.



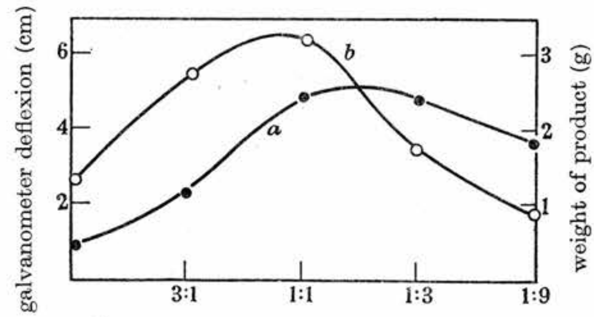


FIGURE 16. *a*, ethane + ethylene; *b*, methane; *c*, hydrogen.

FIGURE 17. *a*, Light intensity, *b*, weight of product. Temp. 370 °C.

FIGURES 14 TO 17. Variation of the cool flame products of propane with mixture composition.

Experiments with propionaldehyde

In order to test the hypothesis that higher aldehydes are important in the oxidation of propane a number of experiments were undertaken on the cool flame of propionaldehyde. Table 2 gives some of the results obtained. The products of the cool flame of propionaldehyde at 270 and 350° C are compared with those of propane at 350° C. Although the products of the cool flame of propionaldehyde are the same as those of propane, it is clear that the aldehyde is very much more reactive than the hydrocarbon. From the theoretical point of view the most important observations are (1) that ethylene is the only hydrocarbon formed in the cool flame of propionaldehyde, and (2) that methoxyl compounds are formed in quantity in the cool flame of the aldehyde. The first of these results indicates that the C_2 hydrocarbon cannot be formed entirely by disproportionation of ethyl radicals, and the second leads to interesting conclusions as to the source of the methoxyl compounds. It may also be noted that increase of temperature favours the formation of products derivable from the cracking of the aldehyde in agreement with the results obtained with propane.

TABLE 2. COMPARISON OF THE COOL FLAME PRODUCTS OF PROPANE AND PROPIONALDEHYDE (QUANTITIES IN MILLIMOLES)

temperature (°C)	270	350	350
nitrogen passed (mmoles)	500	500	133
oxygen passed (mmoles)	100	100	110
aldehyde passed (mmoles)	115	115	—
propane passed (mmoles)	—	—	100
time of contact (sec)	14	12	9
total acid + aldehyde	72·8	53·6	9·3
total acid	9·5	11·8	2·8
formic acid + aldehyde	33·6	32·2	8·4
acetic acid + aldehyde	8·2	4·6	0·9
propionic acid + aldehyde	33·0	16·8	0·2
peroxide	2·7	0·7	1·1
methoxyl compounds	27·4	37·0	5·9
water	43·0	32·2	22·6
weight of liquid (g)	5·60	4·52	1·06
carbon dioxide	12·8	6·0	0·0
carbon monoxide	80·6	116·2	10·7
hydrogen	0·0	12·0	0·0
methane	9·0	1·6	1·1
formula of condensed hydrocarbon	$C_{2\cdot0}H_{4\cdot0}$	$C_{2\cdot0}H_{4\cdot0}$	$C_{2\cdot75}H_{6\cdot8}$
ethane + ethylene	16·6	23·2	12·3

DISCUSSION

It is convenient at this point to summarize the important points which have emerged from our investigations on the cool flames of propane and propionaldehyde.

(1) Cool flames could be obtained with propane between 320 and 400° C. Multiple cool flames were noted in the region of 330° C and a low-pressure ignition peninsula was found at 320° C. The lower cool-flame limit was well defined in the

static system, but cool flames could be maintained at lower temperatures in a flow system if they have previously been initiated above that temperature. The upper cool-flame limit was indistinct at about 400° C. The temperature of the flame lay between 420 and 450° C.

(2) All three theoretically possible aldehydes were found in the cool-flame product of propane. The relative amounts were in the ratio of approximately 1 part propionaldehyde to 20 parts of acetaldehyde to 60 parts of formaldehyde. The only peroxide detectable in the reaction was hydrogen peroxide.

(3) The products of the flame vary only slightly with temperature, although there are two regions of reactivity within the cool-flame region separated by a zone of lower reactivity at about 380° C.

(4) Intermediate products such as aldehydes and peroxides are formed rapidly during the cool flame, while end-products are formed slowly after it.

(5) The equimolecular mixture of propane and oxygen is the most reactive.

(6) The cool-flame products of propionaldehyde are the same as those of propane, although the former is the more reactive. Importance is attached to the facts that the only hydrocarbon formed in the flame of propionaldehyde is ethylene and that methoxyl compounds are formed in quantity.

The mechanism of the slow reaction

That the products of the cool flame are essentially those of the normal slow reaction. This is confirmed by comparison of the products of the cool flame with those of the induction period (see table 1). Evidence for the belief in the importance of aldehydes as the intermediate compounds responsible for degenerate branching in hydrocarbon oxidations has already been found in the photochemical work of Norrish & Patnaik (1949), and evidence of their strong catalytic effect on the oxidations has been obtained recently by Norrish & Galvin (not yet published), who showed that the addition of 1 % of acetaldehyde reduced the induction period of the cool flame of propane at 290° C from several hours to zero (see Norrish 1951). It is clear, therefore, that if acetaldehyde is present in sufficient quantity in the reacting mixture it will result in the initiation of reaction chains, and if it is formed in the reaction it will act as a branching intermediate. In our own experiments the presence of acetaldehyde to the extent of approximately 1 % in the reacting mixture has been clearly demonstrated, and the question at issue is not so much whether acetaldehyde acts as a branching agent but rather whether or not any other substance (in particular a hydroperoxide) is present in sufficient quantity to compete effectively with the aldehyde known to be present.

Although the actual branching reaction cannot easily be investigated directly, useful information can be obtained from photochemical experiments. In the work of Norrish & Patnaik (1949) a strong catalytic effect of light on the oxidation of methane and ethylene was demonstrated which is well explained in terms of an aldehyde as intermediate responsible for degenerate branching.

Evidence for an alternative reaction derived from peroxide is, however, lacking, and an assumed reaction of the type

$$R\mathrm{OOH} = R\mathrm{O} + \mathrm{OH}$$

does not account for the above-mentioned results. The experiments of Blat, Gerber & Neuman (1939) indicated that approximately 1 % of a hydroperoxide would be required to initiate a cool flame at 320° C, but there is no conclusive evidence that hydroperoxides are formed in quantities of this order. In fact, in our own experiments with propane, hydrogen peroxide was apparently the only peroxide formed in measurable yield in the oxidation. The results of Bardwell & Hinshelwood (1951), who showed that the occurrence of cool flames could be correlated with the rapid destruction of peroxide, are not necessarily good evidence for a peroxide theory, since the yield of any thermally unstable product of the reaction, such as hydrogen peroxide, would be expected to behave in this way as a consequence of the self-heating in the flame.

We conclude therefore that the concept of aldehyde branching is the more acceptable of the two alternatives, and the more detailed reaction scheme which follows is accordingly based upon that originally proposed by Norrish (1948).

It has been noted that a marked increase in the yield of ethane plus ethylene occurs as the upper cool-flame limit is crossed. It has also been shown that ethylene is the only hydrocarbon formed in the cool flame of propionaldehyde. These results can be readily explained if it is supposed that an olefine-forming chain reaction involving alkyl radicals begins to operate effectively above 400° C:

$$\begin{aligned} CH_3CH_2CH_2 + O_2 &= CH_2{=}CH.CH_3 + HO_2, \\ CH_3CH_2 + O_2 &= CH_2{=}CH_2 + HO_2, \\ HO_2 + RH &= H_2O_2 + R—. \end{aligned}$$

This scheme, similar to one recently proposed by Appleby, Avery, Meerbolt & Sartor (1953) for the high-temperature oxidation of butane, not only explains the formation of ethylene in the absence of ethane but also the profuse formation of hydrogen peroxide. It furthermore leads to an explanation of the remarkable decrease in the rate of oxidation of hydrocarbons when the temperature approaches 400° C. When the olefine-forming chain reaction begins to operate the normal aldehyde-forming reactions are to some extent replaced by an olefine-forming reaction. That is,

$$CH_3CH_2CH_2 + O_2 = CH_3CH_2CHO + OH$$

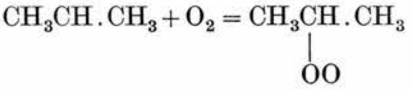
is replaced by

$$CH_3CH_2CH_2 + O_2 = CH_3CH{=}CH_2 + HO_2,$$

and branching due to the molecular oxidation of the aldehyde is thereby reduced. The reaction rate may therefore fall as the temperature rises and will rise again only when some other branching reaction, possibly involving formaldehyde, becomes important.

The formation of methyl alcohol and of its derivatives as a major reaction product has been regarded by Bailey & Norrish (1952) as being the outcome of radical attack at secondary carbon atoms thus:

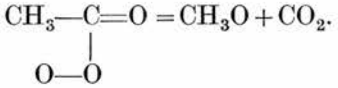
$$CH_3CH_2CH_3 + OH = CH_3CH.CH_3 + H_2O$$



$$CH_3CH.CH_3 + O_2 = CH_3\underset{\substack{|\\ OO}}{C}H.CH_3$$

$$\begin{aligned} &= CH_3CHO + CH_3O \\ CH_3O + C_3H_8 &= CH_3OH + C_3H_7—. \end{aligned}$$

It appears, however, that this is not the only possible reaction which may produce methyl alcohol. Newitt & Baxt (1939) found that methyl alcohol was a major product of the slow and cool-flame oxidation of acetaldehyde. Our own results with propionaldehyde have been similar. Since it is probable that the initial hydrogen abstraction will occur at the aldehydic group, decomposition of the type envisaged by Bailey & Norrish would lead to the formation of at least as much carbon dioxide as alcohol:



$$\underset{\text{O—O}}{\text{CH}_3\text{—C=O}} = CH_3O + CO_2.$$

In Newitt & Baxt's experiments the amount of carbon dioxide formed is normally less than half the yield of methyl alcohol; in our experiments with propionaldehyde the ratio is even smaller. It appears probable that while a portion of the methyl alcohol, especially in the oxidation of hydrocarbons, is formed by reactions of the type proposed by Bailey & Norrish, some at least may be formed by a reaction of the type

$$R.CH_3 + OH = R\text{—} + CH_3OH,$$

where $R.CH_3$ may be either a hydrocarbon or an aldehyde.

We believe that the above-mentioned reactions coupled with the original scheme of Norrish (1948) give a complete explanation of the formation of the main products of the oxidation of propane. The final reaction scheme is as follows. The heat data for radicals have been taken from Swarc (1950) and from Evans, Hush & Uri (1952):

Initiation and branching

$$R.CH_2CHO + O_2 = [R.CH_2COOOH] = R.CH_2COOH + O \quad \Delta H = -9\ \text{kcal.} \quad (1)$$

Propagation (low temperature)

$$C_3H_8 + OH = CH_3CH_2CH_2 + H_2O \quad \Delta H = -26\ \text{kcal}, \quad (2)$$

$$= CH_3CH.CH_3 + H_2O \quad \Delta H = -32\ \text{kcal}, \quad (3)$$

$$= CH_3CH_2 + CH_3OH \quad \Delta H = -8\ \text{kcal}, \quad (4)$$

$$CH_3CH_2CH_2 + O_2 = CH_3CH_2CHO + OH \quad \Delta H = -59\ \text{kcal}, \quad (5)$$

$$CH_3CH.CH_3 + O_2 = CH_3CHO + CH_3O \quad \Delta H = -56\ \text{kcal}, \quad (6)$$

$$CH_3O + RH = CH_3OH + R. \quad (7)$$

Degradation

$$CH_3CH_2CHO + OH = CH_3CH_2 + CO + H_2O \quad \Delta H = -22\ \text{kcal}, \quad (8)$$

$$CH_3CH_2 + O_2 = CH_3CHO + OH \quad (9)$$

$$CH_3CHO + OH = CH_3 + CO + H_2O \quad \Delta H = -20\ \text{kcal.} \quad (10)$$

Propagation (high temperature)

$$CH_3CH_2CH_2 + O_2 = CH_3CH{=}CH_2 + HO_2 \quad \Delta H = +3\ \text{kcal}, \quad (11)$$

$$CH_3.CH_2 + O_2 = CH_2{=}CH_2 + HO_2 \quad \Delta H = +3\ \text{kcal}, \quad (12)$$

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2 \quad \Delta H = -13\ \text{kcal.} \quad (13)$$

Termination OH wall deactivation, (14)

HO_2 wall deactivation. (15)

Light emission of cool flames

The chemiluminescence of hydrocarbons and other substances undergoing oxidation is due to the fluorescence of excited formaldehyde. The measurements of the light emission of the cool flames of propane were carried out with a view to obtaining further evidence relating to the reaction producing this excited formaldehyde. The results were not, however, as useful as it had been hoped. In the series of runs where the flow rate was varied it is clear that the light emission is to be correlated with the formation of end-products rather than with the formation of intermediate products. In the series where the composition of the reaction mixture was varied the best correlation exists between the light output and the yield of methyl alcohol. These results are most simply explained by supposing that the light-producing reaction is one involving the reaction of a methoxyl radical. The simplest reaction which has the necessary exothermicity is

$$CH_3O + OH = CH_2O + H_2O \quad \Delta H = -98 \text{ kcal.}$$

Several other simple radical/radical reactions are, however, sufficiently exothermic, and it is not possible at this stage to decide finally in favour of any one of them.

The origin of the cool flame

Cool flames are characterized by the emission of a pale blue light due to the fluorescence of excited formaldehyde and are normally associated with a mild pressure pulse as they travel through the reaction vessel. That the light emission is due to a secondary reaction associated with the slow combustion is proved by the work of Topps & Townend (1946), who showed that but one quantum of radiation is emitted for every 10^6 molecules of fuel oxidized. It is nevertheless to be regarded as a normal characteristic of the slow reaction, and the intensity of the light emission can accordingly be regarded as a measure of the rate of the main oxidation. This is supported by our observation that there is no discontinuity in the light emission as the upper cool-flame limit is crossed into the region of falling reaction rate, and by the results of the runs in which the flow-rate was varied.

The pressure pulse which accompanies the burst of light emission appears, in the main, to be the result of a rapid self-heating which, if not quenched, would pass to thermal ignition, but which, due to the 'negative temperature coefficient' of the reaction, is but short-lived and reversed as the reaction rate falls to a low value with rise of temperature.

The slow reaction is a degenerately branching chain reaction in which, as we have postulated, a higher aldehyde is the essential intermediate for temperatures below 400° C. Above this temperature the reaction velocity is found to decrease with increase of temperature until a second oxidation mechanism based on formaldehyde as the essential intermediate becomes important and the reaction velocity increases again. The existence of this so-called negative temperature coefficient is an indication that the low temperature mechanism cannot operate effectively above 400° C. This, in our opinion, results from two main factors, first from the increased rate of destruction of the higher aldehyde above 400° C by reactions which do not give rise to branching (reactions 8 and 10), and secondly from the appearance of competing reactions (reactions 11 and 12) which above this temperature progressively replace the low-temperature reactions normally producing the higher aldehyde.

It is not difficult to show that in a system of this type thermal instability of the normal slow reaction can lead to the periodic processes which are observed under conditions associated with single and multiple cool flames. Self-heating of a charge undergoing slow reaction will normally occur when the rate of heat production begins to outstrip the rate of heat removal by the surroundings. With hydrocarbons the self-heating may be rapidly quenched by the operation of the 'negative temperature coefficient' when the temperature of the charge reaches about 400° C. At this temperature the aldehyde formed originally in the early stages of the self-heating is rapidly destroyed and, because of the competing reactions, is not replenished. The rate of reaction and the temperature thus fall rapidly to relatively low values; thermal stability is re-established, and the reaction can once more accelerate in the normal way. Self-heating may again occur and the whole cycle of self-heating, quenching and cooling may be repeated. This periodic process will then continue until the consumption of the reactants prevents the recurrence of the required thermal instability. The periodic waxing and waning of the reaction, which is observed in static systems exhibiting cool flames, can thus find a simple explanation in terms of the interaction of thermal and chain processes.

Other properties of cool flames can also be explained on a thermal basis. The sharpness of the lower cool-flame limit results from the fact that self-heating of the slow reaction will occur only when the maximum rate of reaction under approximately isothermal conditions exceeds a certain critical value. The boundary for this condition is sharp and the boundary between the thermally stable and thermally unstable reactions will likewise be sharp. The diffuseness of the upper limit, which was noted in the measurements of flame temperature and the light intensity, and in the magnitude of the pressure pulse, can also be simply explained. The maximum temperature reached in the flame, being governed by the 'negative temperature coefficient', is relatively independent of the temperature of the surroundings, and consequently the degree of self-heating in the flame decreases with rise of temperature. As a result both the pressure pulses and the light emission of the flame become increasingly difficult to detect as the temperature rises.

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COOL FLAME PHENOMENA IN THE OXIDATION OF ETHANE

COOL FLAME PHENOMENA IN THE OXIDATION OF ETHANE

By J. H. Knox and R. G. W. Norrish
Dept. of Physical Chemistry, Cambridge

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The development of a thermal theory for the periodic nature of the cool flame phenomena as a result of work on the oxidation of higher hydrocarbons has led to a reinvestigation of the oxidation of ethane. Experiment has shown that there exists a well-defined " negative temperature coefficient " in the rate of the slow oxidation of ethane between 350 and 410° C. In addition, it is shown that cool flames can be obtained in sufficiently large reaction vessels between 300 and 380° C at pressures of 600 mm Hg upwards with ethane + oxygen compositions ranging from 32/1 to 3/2.

It is well established that hydrocarbons containing three or more carbon atoms can be oxidized by two different degenerate branching chain mechanisms dependent upon the temperature. The " high " temperature reaction (above 400° C) is characterized by the formation of products normally obtained from cracking reactions together with formaldehyde as an intermediate, while the " low " temperature reaction (between 250 and 400° C) is characterized by the formation of oxygenated compounds such as alcohols, aldehydes, acids and peroxides. The transition between the two regions is generally associated with certain closely related features which may conveniently be summarized under the headings of low pressure ignition peninsulae in the pressure-temperature ignition limits, " negative temperature coefficients " in the velocities of the slow reactions in the transition region, and cool flame phenomena. The fact that the low temperature reaction fails at temperatures in the region of 400° C is taken to indicate that it depends for its success upon the autocatalytic effect of some intermediate product of the reaction which cannot survive in sufficient quantity above 400° C to be effective.

In recent papers by Norrish and co-workers [1-4] evidence has been put forward that the low temperature oxidation system can best be explained in terms of a higher aldehyde as the important intermediate. Elaboration of this view gives an explanation of the negative temperature coefficient and some aspects of the cool flame phenomena. The periodicity of cool flames, with which the present communication is particularly concerned, is believed by the authors to arise out of the thermal instability of the normal slow reaction. This will generally arise in the course of a reaction when the rate of heat production begins to outstrip the capacity of the surroundings to remove heat. For any given reaction the point at which this occurs will depend largely upon the dimensions of the containing vessel and in general the larger the vessel the greater the tendency to self-heating. Thermal instability of this type would normally lead to ignition, but with the higher hydrocarbons the degree of self-heating may be limited by the operation of the negative temperature coefficient which prevents any further self-heating when the temperature of the charge has reached a value near to 400° C. When the reacting hydrocarbon mixture self-heats rapidly, the higher aldehyde which accumulates in the early stages and which is believed by the authors to be the agent responsible for the autocatalysis of the reaction, is very rapidly degraded in the later stages of the self-heating—probably to formaldehyde, which is only active as a degenerate branching agent at much higher temperatures, as in the methane oxidation. Owing furthermore to a progressive replacement of the low temperature mechanism by a high temperature mechanism, the higher aldehyde is not replaced. There then results a rapid fall in the concentration of the aldehyde and a corresponding fall in the rate of reaction and the temperature. Once the temperature has fallen to a sufficiently low value the whole process can be repeated often a number of times until there is no longer a sufficient quantity of the reactants to promote the necessary thermal instability. In this way it is possible, within the framework of a scheme originally proposed for the slow reaction, to envisage the occurrence of periodic processes which bear a close resemblance to those occurring in single and multiple cool flames.

THE OXIDATION OF ETHANE

Townend in 1937 [5] showed that ethane possessed at least a rudimentary low temperature oxidation system, and although he was not able to obtain evidence for the existence of cool flames or of a low pressure ignition peninsula, there was reason to suppose that they might be obtainable under suitable experimental conditions. The question of whether or not the ethane oxidation system possessed a negative temperature coefficient was partially answered by Chirkov and Entelis [6] who showed that the maximum rate of oxidation, as measured by the rate of pressure rise, rose steadily in the regions 270-340° C and 400-480° C but remained almost constant between 340 and 400° C. According to the thermal theory advanced above, however, a definite decrease in the reaction velocity with rise of temperature is necessary for the formation of cool flames.

Our first experiments were therefore designed to determine whether or not the slow oxidation of ethane exhibited a definite negative temperature coefficient in the region of 350-400° C. The experiments were carried out with equimolecular ethane + oxygen mixtures at atmospheric pressure in a 5 cm diam. cylindrical Pyrex reaction vessel. The reaction vessel was mounted horizontally in a furnace. The premixed gases were admitted rapidly to the reaction vessel and the reaction followed by means of a mercury manometer. Two methods were used to measure the rate of reaction. In the first the rate of pressure rise was taken as the measure of the reaction rate but owing to a considerable measure of self-heating, the rate of pressure rise gave a rather unreliable measure of the actual rate of reaction and tended to exaggerate any changes in the reaction rate. In the second method, the actual temperature rise of the reacting mixture was used to measure the reaction rate. In doing this the assumption was made that the heat of reaction is approximately constant in the temperature range considered and that the self-heating of the charge undergoing reaction could accordingly be taken as a reasonable approximation to the rate of reaction itself. The temperature of the reacting gas was measured in these experiments by a fine copper/constantan thermocouple enclosed in a thin-walled glass sheath mounted with the thermojunction in the centre of the reaction vessel. The results of the two sets of experiments, illustrated in fig. 1, show clearly that there exists a pronounced negative temperature coefficient in the rate of the slow reaction. The rate rises to a maximum at about 350° C and falls thereafter to a minimum at about 410° C, finally rising again. The results are in good agreement with those of the Russian workers although the effect observed by us is very much more marked. Analysis of the products of the reaction showed that there was a characteristic change from predominantly oxygenated products—methyl alcohol, aldehydes, etc., below 360° C to predominantly cracking products—methane, hydrogen and ethylene—above 400° C. In these two respects, therefore, ethane behaves similarly to the higher hydrocarbons.

Having established the existence of a definite negative temperature coefficient in the rate of the slow reaction we then investigated the possibility of obtaining cool flames in a larger reaction vessel which would encourage self-heating. The reaction vessel, a 1000 ml spherical Pyrex bulb, was mounted in a well-lagged 15 cm diam. furnace. The gases were premixed in a large aspirator over water and the pressures throughout the reaction were measured by a wide-bore mercury manometer. When equimolecular mixtures of ethane and oxygen were used no cool flames or pressure pulses were recorded but positive results were obtained with 4/1 ethane + oxygen mixtures between 300 and 380° C at pressures of over 600 mm Hg. Under suitable conditions of temperature and pressure as many as three successive pressure pulses were observed at intervals of 10 to 20 sec. A number of typical pressure time traces obtained with 4/1 mixtures at atmospheric pressure are shown in fig. 2. It will be noted that there is no sharp boundary

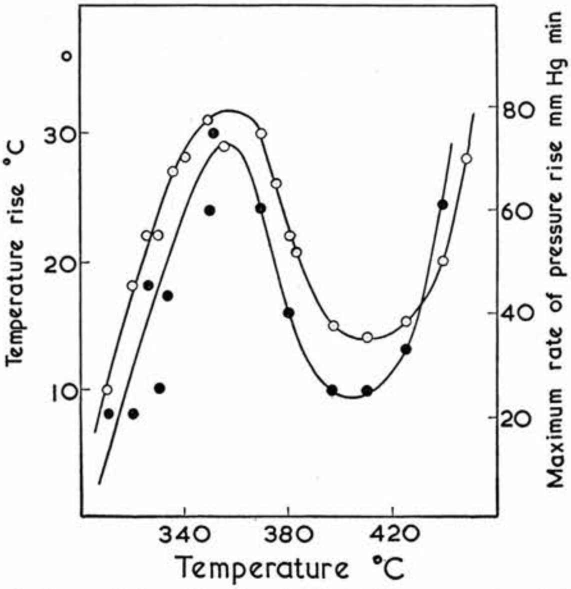

FIG. 1.—Rate of slow oxidation of equimolecular ethane + oxygen mixtures at different temperatures in a 5 cm diam. Pyrex reaction vessel.

⊙ temperature rise; ● maximum rate of pressure rise.

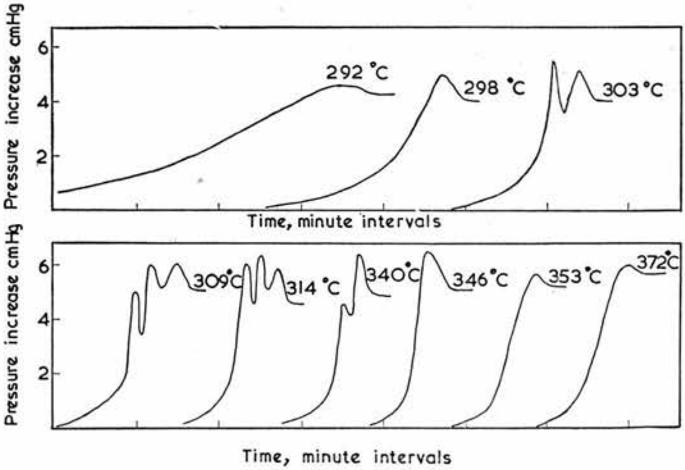

FIG. 2.—Pressure against time curves for the oxidation of 4/1 ethane + oxygen mixtures at 760 mm Hg pressure. The induction periods, which are not given in the figure, decrease with increase of reaction temperature.

between the curves for slow reaction and for multiple pulses nor is the boundary between the regions of, say, two and three pulses well defined. We have accordingly arbitrarily defined a cool flame reaction as one in which the maximum rate of pressure rise exceeds 100 mm Hg/min. The cool flame region so defined and the regions for two and three pressure pulses in the 1000 ml reaction vessel are shown in the topmost diagram in fig. 3.

Concurrent visual and manometric observations made in a darkened room showed that the slow reaction was accompanied by the emission of a very pale diffuse blue light. On the appearance of a pressure pulse the light intensity greatly increased and the outlines of the reaction vessel became clearly visible. When multiple pressure pulses were noted a similarly fluctuating light emission was recorded, each pressure pulse being accompanied by a light pulse. The most intense light emission appeared to coincide with the most rapid pressure rise. This light emission appeared to be very similar to that associated with the cool flame of propane and there seems little reason to doubt that the emitters in both cases are the same, namely, excited formaldehyde. It should perhaps be emphasized that in all cases whether it be slow reaction or cool flame reaction, the light emission is extremely feeble and can be seen only in a completely darkened room when the eyes have become fully accustomed to the darkness.

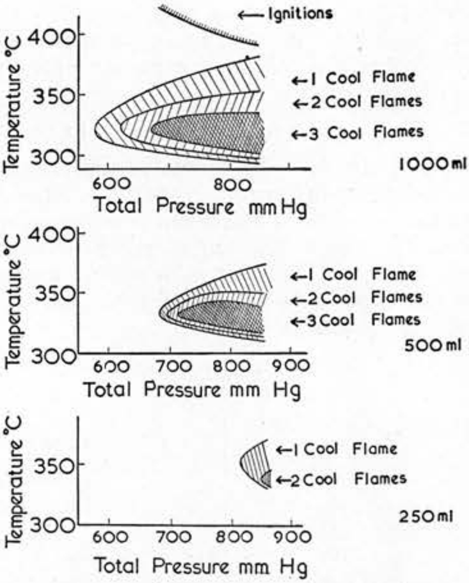

FIG. 3.—Cool flame regions for 4/1 ethane + oxygen mixtures in 1000 ml, 500 ml and 250 ml spherical Pyrex reaction vessels.

The marked effect of vessel diameter on the cool flame region, predicted by a thermal theory, is illustrated by the three diagrams in fig. 3 which show the cool flame limits for 1000 ml, 500 ml and 250 ml spherical reaction vessels (12·3 cm, 9·8 cm and 7·8 cm diam.). With the smallest reaction vessel, cool flames could be obtained only with pressures greater than 800 mm Hg, while with the largest vessel the lower cool flame limit was at a pressure of 600 mm Hg. It is of interest to note that the lower cool flame limit is very much more sensitive to the size of the reaction vessel than the upper limit. This is not altogether unexpected since the degree of self-heating limited by the fall in reaction rate at 400 °C increases as the temperature is lowered and the cooling effect of the walls will have a correspondingly greater effect at lower temperatures. This striking effect of the size of the reaction vessel on the cool flame limits while confirming a thermal theory of the cool flame may also in part explain the inability of previous workers, who used smaller vessels, to obtain cool flames with ethane + oxygen mixtures.

Our own inability to obtain cool flames with equimolecular mixtures was of interest in view of the conclusions of Hsieh and Townend [7] that equimolecular mixtures were the most reactive in the low temperature region and the most conducive to cool flame formation. The results of the determination of the pressure/composition cool flame limits at 330° C obtained with ethane + oxygen mixtures in the 1000 ml reaction vessel are presented in fig. 4. Once more the boundaries are not absolutely clear-cut and they have again been drawn through points where the maximum rate of pressure rise was 100 mm Hg/min. From our results it is clear that, in contrast to the results of Hsieh and Townend, an approximately 6/1 ethane + oxygen mixture is the most reactive. Well-defined pressure pulses could be obtained even with 32/1 ethane + oxygen mixtures. This unexpected result was confirmed by some rough measurements of the maximum rates of slow oxidation of mixtures at 290° C, a temperature at which self-heating was negligible. It was found using mixtures with compositions ranging from 8/1 to 1/3 that the following expression for the maximum rate was obeyed to a first approximation:

$$\text{maximum rate} \propto [\text{hydrocarbon}]^3\,[\text{oxygen}]^{\frac{1}{2}},$$

where square brackets denote partial pressures of the reactants. For a mixture obeying such an expression the 6/1 mixture of hydrocarbon + oxygen would be the most reactive in agreement with the experiments conducted at the higher temperature. While this expression differs from those obtained by previous workers (e.g. Bone and Hill [8]) it is in general agreement with them in emphasizing the greater importance of the concentration of combustible than of oxygen in the rate expression.

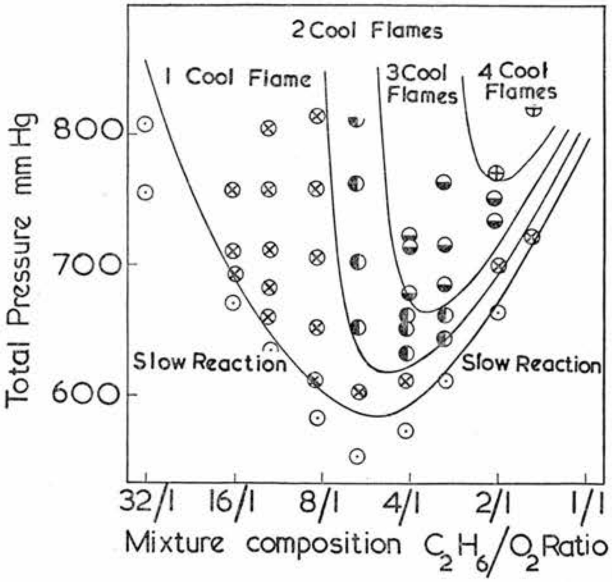

FIG. 4.—Pressure/composition limits for single and multiple cool flames in ethane + oxygen mixtures at 330° C.

⊙ slow reaction ⊗ 1 cool flame ◐ 2 cool flames ◒ 3 cool flames ⊕ 4 cool flames.

It is of interest to note that the number of cool flames obtainable with a given mixture is more or less independent of the pressure above a certain minimum value. This might be expected in view of the minor role of oxygen in the rate expression provided that it is supposed that the proportion of the reactants as a whole consumed in any cool flame does not depend upon the pressure. The reaction will continue without great change in velocity until the larger part of oxygen is consumed, thereafter it will fall rapidly to zero. In the first cool flame a given amount of oxygen will be consumed, in the second another similar amount. The factor which governs the occurrence of further cool flames will simply be the amount of oxygen left. Consequently the total number of cool flames obtainable from any mixture will depend only upon its composition.

CONCLUSIONS

The experiments which have been described were in the main prompted by conclusions reached as a result of the study of the cool flame oxidation of hexane and propane.[3, 4] These experiments led to the further development of a theory of hydrocarbon combustion based upon the autocatalytic effect of higher aldehydes and suggested to us that periodic cool flame phenomena could be regarded as the outcome of the thermal instability of the slow oxidation reaction. This view is contrasted with that of Neumann[9] who supposed that cool flames arise out of the explosion of peroxide which accumulates during the induction period of the cool flame. The results obtained with ethane, however, have confirmed the thermal theory and have further shown that ethane can be regarded as exhibiting all the properties of the low temperature oxidation system previously recorded for the hydrocarbons containing three or more carbon atoms.

It will be noted that no hypothesis as to the origin of the cool flame has been advanced, but the view is here recorded that they represent a side reaction indicative of the presence of higher aldehydes or their peroxide derivatives. It is significant that the only aldehyde which will not produce a cool flame is formaldehyde, and we believe that formaldehyde can persist and accumulate at temperatures above the cool flame region, and may eventually be responsible for the high temperature ignition mechanism.

The phenomena reported by Gray[10] take place at temperatures widely outside those characteristic of cool flames and are probably not of the same type. The apparent periodicity of the reaction observed in a flow system could well be the result of a balance between flow rate, induction period and maximum reaction velocity. Provided that the induction period is shorter than the time of residence in the reaction vessel and that the reaction can propagate itself through the reaction vessel with sufficient speed to overcome the flow rate, it is possible for a reaction starting at the outlet end of the reaction vessel to move quickly through the whole vessel and leave it filled with reacted gas. Reaction cannot then commence again until this reacted gas has been swept out of the vessel. A periodic process can thus occur which depends not upon the existence of a negative temperature coefficient but upon a subtle balance between factors which are peculiar to a flow system, the periodicity being equal to the time required for the gas reacted in the previous pulse to be replaced by fresh reactants.

The authors wish to record their thanks to the Shell Petroleum Company for a research grant to one of us (J. H. K.) throughout the period of the research.

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[3]

GAS PHASE CHROMATOGRAPHY OF ALIPHATIC HYDROCARBONS

By J. H. Purnell and J. H. Knox.

Physical Chemistry Department, University of Cambridge.

The method of gas-liquid partition chromatography has been shown to be eminently suitable for the separation, identification and quantitative estimation of the components of complex mixtures of paraffin and olefin hydrocarbons. The influence of various factors on the efficiency of separation has been investigated and a simple apparatus, incorporating a thermal conductivity cell for detection of the various components is described.

ALTHOUGH Martin and Synge[1] suggested the possibility of separating gases and vapours by gas-liquid chromatography as early as 1941, it was not until 1952 that an account of such a separation was given (Martin, James et al.[2-5]). An account was given[2] of the separation of a mixture of fourteen fatty acids using silicone oil as the immobile solvent supported by a column of Kieselguhr and also of the analysis of several amine mixtures using liquid paraffin as the stationary phase. The gas used to elute these mixtures was in each case nitrogen. James and Martin[3] also report that Dr. N. H. Ray of Imperial Chemical Industries has applied the technique to the separation of a wide variety of organic mixtures including some aromatic hydrocarbons.

The successful application of this method to the analysis of such diverse types of compounds led us to investigate the possibility of its use in the separation of complicated aliphatic hydrocarbon mixtures such as are met with in the products of hydrocarbon cracking reactions. Using dibutyl phthalate supported by silica gel and a simple apparatus, a large number of paraffins and olefins have been successfully separated, and we consider that the method offers great advantages over existing methods of hydrocarbon analysis.

APPARATUS

The apparatus used is shown in Figure 1 and was similar to that described by James and Martin.[2,3] It consisted in essence of a jacketed U-tube which contained silica gel and dibutyl phthalate in equal proportions by weight as the supporting material and stationary phase respectively. Samples of between 0·1 and 1·0 millimoles were introduced either as gases or liquids by means of a syringe inserted through a self-sealing rubber gasket situated at the inlet end of the column. The samples were eluted either by nitrogen or carbon dioxide. Detection and quantitative determination of the different components as they emerged from the column was effected by a thermal conductivity cell of the type illustrated in Figure 2. It was decided to adopt this method since it appeared to offer several advantages over other possible methods. According to Phillips[6] the method is sensitive to about 1 part in 5000 of each component in the eluted gas; furthermore the data are obtained in the form of a differential curve, each component producing a peak the area beneath which is proportional to the amount of the component present since the change in thermal conductivity is proportional to concentration. Other important considerations were the ease of construction of the cells and the simplicity of the electrical circuit involved.

The eluting gas was conveniently obtained from either liquid nitrogen or solid carbon dioxide contained in a Dewar flask when the required pressure did not exceed 50 cm.Hg. Higher pressures, however, necessitated the use of a cylinder of gas, the supply being controlled by a sensitive needle valve. In each case a constant head of pressure was maintained across the column by a simple bubbler device which proved adequate for the purpose since any small pressure fluctuations which occurred were smoothed out during passage of the gas through the column and there was therefore no necessity for complicated pressure stabilisers.

Various columns were used in the experiments in order to determine the best conditions for separation of the mixtures. Their lengths and diameters varied from 100 to 200 cm and from 0.5 to 1.5 cm respectively; their operation at any desired temperature above room temperature was achieved by placing the column in a glass jacket wound with an electrical heating element. Insulation was achieved by inserting the whole apparatus inside another wider glass jacket which was lagged with asbestos tape. By means of this arrangement the column temperature could readily be controlled to within 0·5°C for long periods.

The conductivity cell (figure 2) consisted of a 25 ohm coiled tungsten filament, from an electric light bulb, spot welded to two heavy tungsten electrodes which were directly sealed into a thick walled Pyrex tube about 6 cm in length and 0·3 cm diameter. The cell formed one arm of a Wheatstone bridge whose other three were standard manganin resistances. A potential of 6 volts was applied across the bridge. The bridge was normally adjusted to give null deflection when the carrier gas alone was passing through the cell. The off balance potential, measured on a sensitive mirror galvanometer, then gave a measure of the difference in conductivity between the pure carried gas and the eluted mixture. The cell was immersed in a well-thermostatted bath since it was found necessary to maintain the walls of the cell at a constant temperature in order to avoid wide fluctuations in the null point.

RESULTS

The cell response to any component depends only upon the difference between its thermal conductivity and that of the carrier gas, and the linear relation between thermal conductivity and concentration suggests that the area under each curve should depend upon the amount of component present. Figure 3 shows that this is in fact the case.* The peak height, however, is not linearly related to the concentration due to peak tailing which is especially noticeable with olefins. This tailing is probably due to change in the partition coefficient with concentration.

The thermal conductivity of hydrocarbons decreases on ascending the series and the similarity between the values for the C_4 hydrocarbons and nitrogen made their detection difficult. In consequence we were led to use carbon dioxide as the carrier for the gaseous hydrocarbons, and

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* The original of figure 3 has unfortunately been lost.

nitrogen for the separation of the liquid members of the series. In general it was found that carbon dioxide gave slightly sharper separations than nitrogen: this is presumably due to the greater difficulty of diffusion in the former.

Investigation into the effect of flow rate at constant temperature showed that separation increased steadily with decreasing flow rate down to a certain limiting value. Below this value there was little or no improvement. This is illustrated in figure 4 for the separation of n-butane and 1-butene at 20° on a 100 cm column 1·0 cm in diameter. It seems likely that above the limiting flow rate equilibrium is not fully established between the liquid and gaseous phases and that the critical flow rate marks the attainment of equilibrium and the limiting efficiency of the column.

Increasing the length of the column increased the degree of separation considerably but decreasing the diameter had relatively little effect, probably, as suggested by James and Martin,[23] because of the small ratio of diameter to length. The small maximum permissible loading with the narrower columns led us to adopt 1.0 cm as the diameter for later experiments.

Change of column temperature has a profound effect on the separation obtained as would be expected in view of the change in vapour pressure and solubility, and the corresponding change in retention volumes of the various components. Figure 5 shows the effect of temperature on the separation of n- and iso-pentane. At 75°C there is little separation, at 50°C two peaks are clearly seen, and at 20°C separation is complete. Similar results were obtained for other isomeric mixtures. Although a lower temperature gives a better separation this factor has to be balanced against the longer retention times in selecting the final working temperature. The retention time increases as the temperature decreases and the appearance of each component may become unduly delayed so that the time for complete analysis may become prohibitive when substances of high boiling point are present. Furthermore with gaseous hydrocarbons, the temperatures desired may be so low that the viscosity of the stationary phase becomes very great and equilibrium is not established at reasonable flow rates. Experiments at -80°C, for example, designed to separate C_2 and C_3 hydrocarbons were a failure for this reason and further experiments were carried out above 0°C.

Diminution of particle size of the support was found to have such a marked effect that while a column with 40 mesh silica gel failed to separate a mixture of C_4 hydrocarbons, a column of identical dimensions packed with 120 mesh silica gel gave complete separation above room temperature.

As a consequence of the above findings it was finally decided to separate the gaseous hydrocarbons by elution with carbon dioxide from a 120 mesh silica gel + dinonyl phthalate column at 20°C. The separation of a 5 cm^3 sample of such a mixture is shown in figure 6 where six gaseous hydrocarbons are resolved. It has not yet proved possible to separate ethane and ethylene since they are only very slightly soluble in dibutyl phthalate. A solution to this difficulty may be found in the use of a more polar solvent in which there is a considerable difference in solubility.

The method adopted for the analysis of liquid mixtures was similar to that for gases except that nitrogen was used as carrier, and higher temperatures and flow rates were required because of the higher retention volumes of the higher homologues. A separation of seven liquid hydrocarbons is shown in figure 7. In general it was found that good separations consistent with reasonable times of appearance of the various components could be effected if the column temperature was close to the boiling point of the components to be analysed. Thus a mixture of pentanes, hexanes and heptanes could be separated by commencing the analysis at 35°C and subsequently, when all the pentanes had passed through the column, raising the temperature to 65°C. When the hexanes had been removed the temperature could be further raised to 100°C for the elution of the heptanes. By raising the temperature stepwise a much quicker and more efficient separation could be achieved than by the alternative method in which the column temperature was kept constant at some intermediate value and a higher flow rate used.

CONCLUSIONS

The series of experiments described have shown that the technique of gas phase chromatography is eminently suited to the analysis of mixtures of aliphatic hydrocarbons. The power of the method is illustrated by the separations achieved and by the accuracy of quantitative determination which is about one percent. A further valuable attribute of the method lies in the possibility for qualitative analysis and identification since with any given column at a definite temperature and flow rate each component is characterised by unique break through and peak maximum times which are quite independent of any other components present in the mixture. The accuracy and scale of quantitative determination of any component is limited only by the methods of detection used and with the simple apparatus employed in the present work determinations could be carried out with an accuracy of about 1 percent. Within reasonable limits the accuracy does not depend upon the amounts of the individual components present since the sensitivity of the galvanometer can readily be altered by the inclusion of a series resistance.

The nature of the solvent evidently has a considerable effect on the relative retention times of different types of compound. Figure 6, for example, shows that 1-butene (b.p. -5°C) appears after isobutane (b.p. -10°C) and n-butane (b.p. 0°C) although as a general rule components appear in the order of their boiling points. While the rule holds in any homologous series it is clear that it is not true for compounds in different series. The greater hold up of olefins is evidence of their greater solubility and is probably due to the polar nature of dibutyl phthalate. It seems likely that by using a more polar solvent the separation could be further increased while the use of a completely non-polar solvent such as liquid paraffin would produce the reverse effect. With complicated mixtures of paraffins and olefins where serious overlapping of bands is likely to occur it may be possible by using two columns with different solvents to carry out an otherwise impossible analysis. Many possibilities exist in the use of mixed solvents and in the inclusion of blending agents such as soaps or higher fatty acids in the stationary phase, and it is in this direction that the method may find application to a much wider range of compounds.

The authors would like to thank Professor R. G. W. Norrish for his encouragement and assistance throughout the work and also the Shell Oil Company for a grant to one of them (J.H.K.).

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Cambridge 1953.

Note on figures

The original manuscript of this paper has been kindly lent to me by Dr. J. H. Purnell. Figures 1-3 have unfortunately been lost. Figures 1 and 2 have been redrawn and figures 4-7 copied from the originals.

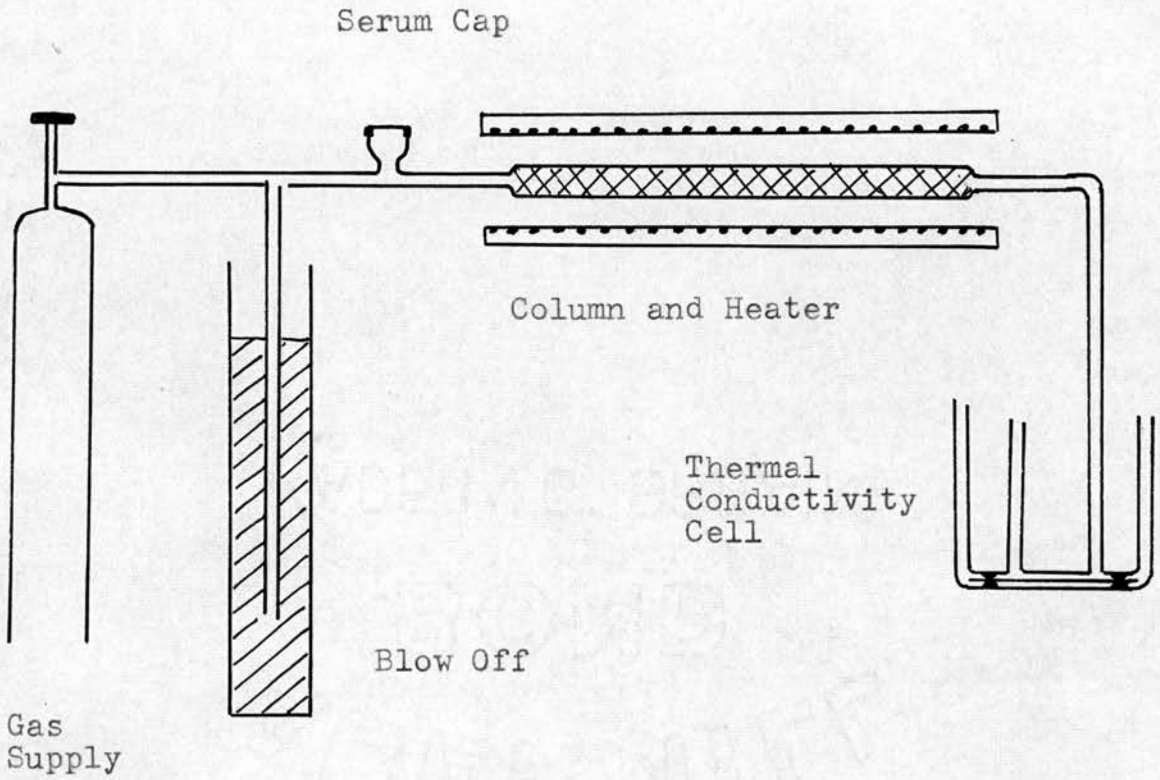

FIGURE 1 Apparatus

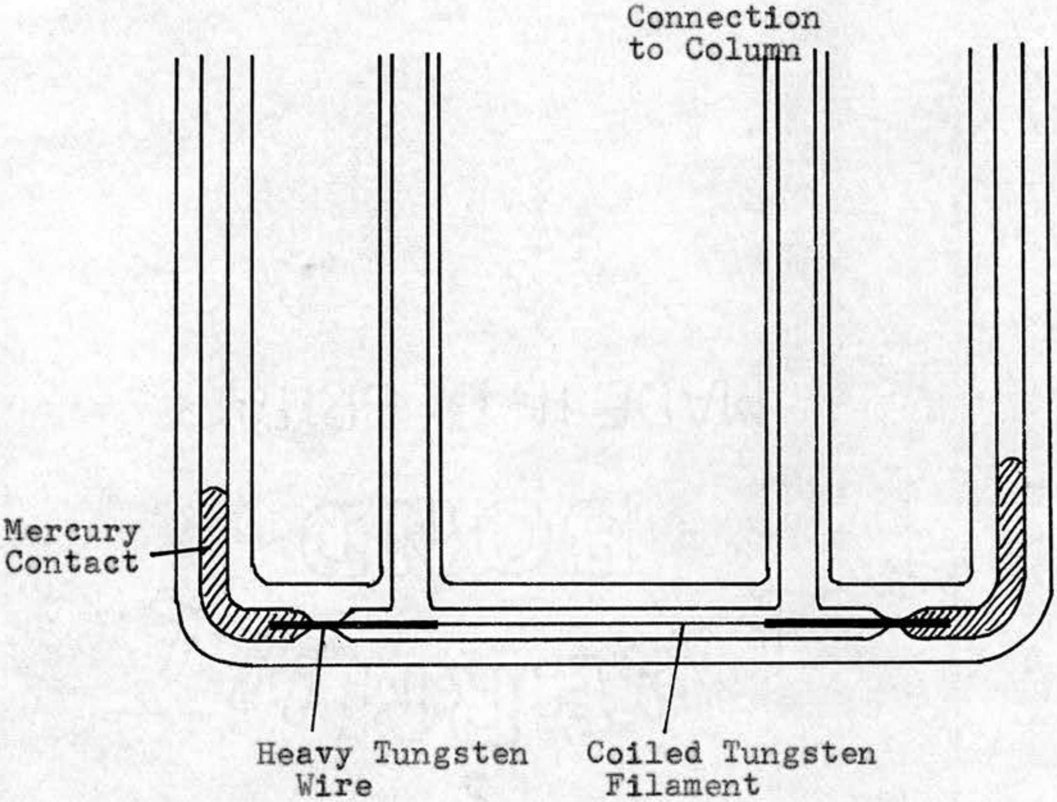

FIGURE 2 Thermal Conductivity Cell

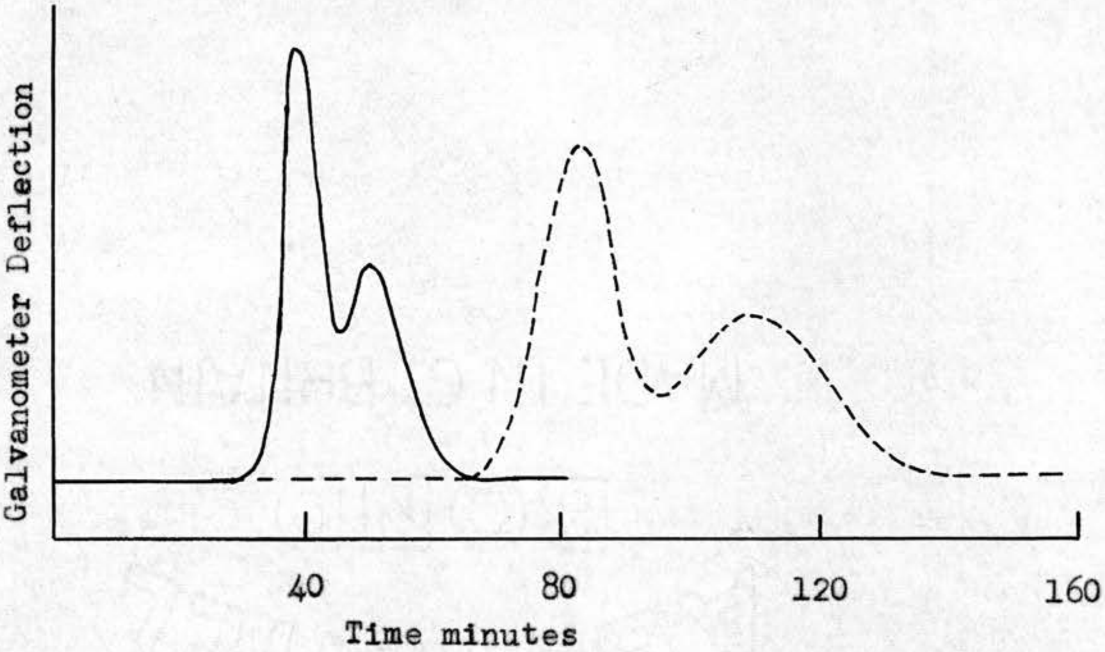

FIGURE 4 Effect of flow rate on Resolution

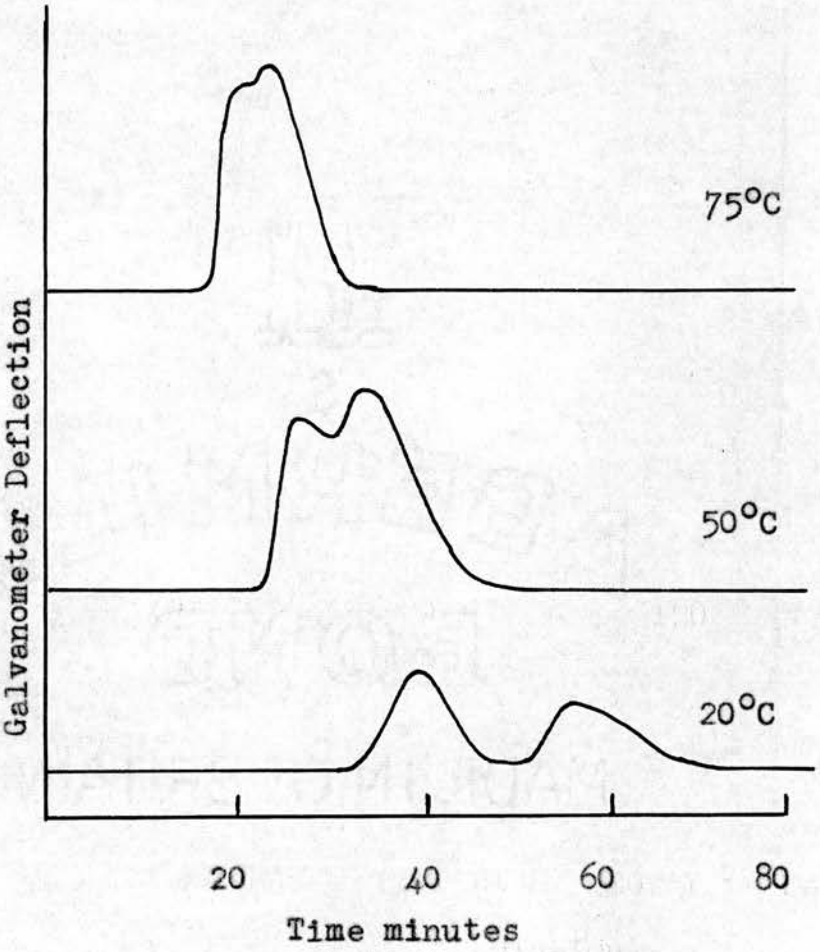

FIGURE 5 The Effect of Temperature on Resolution

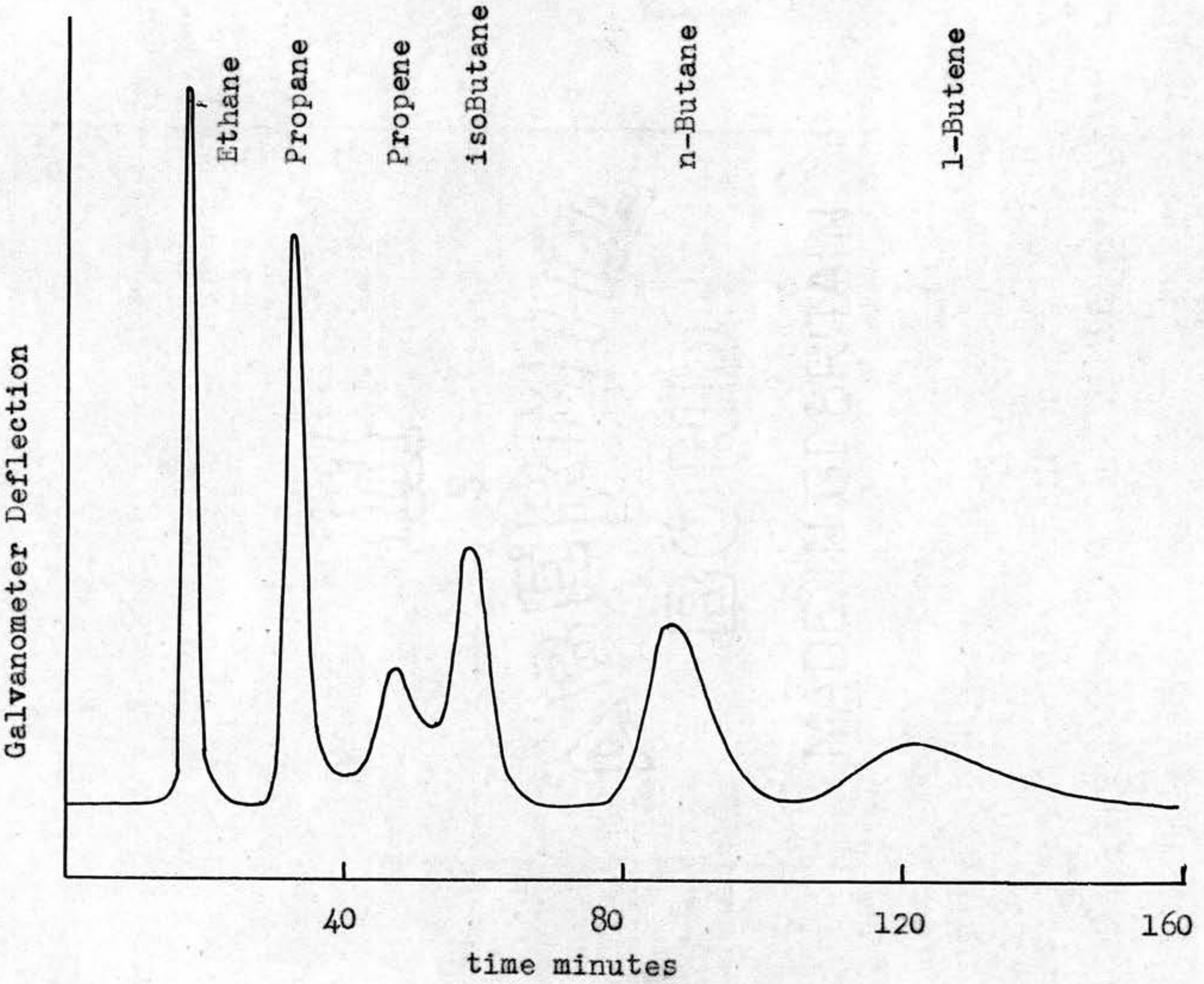

FIGURE 6 Chromatogram of a Six Component Gas Mixture.

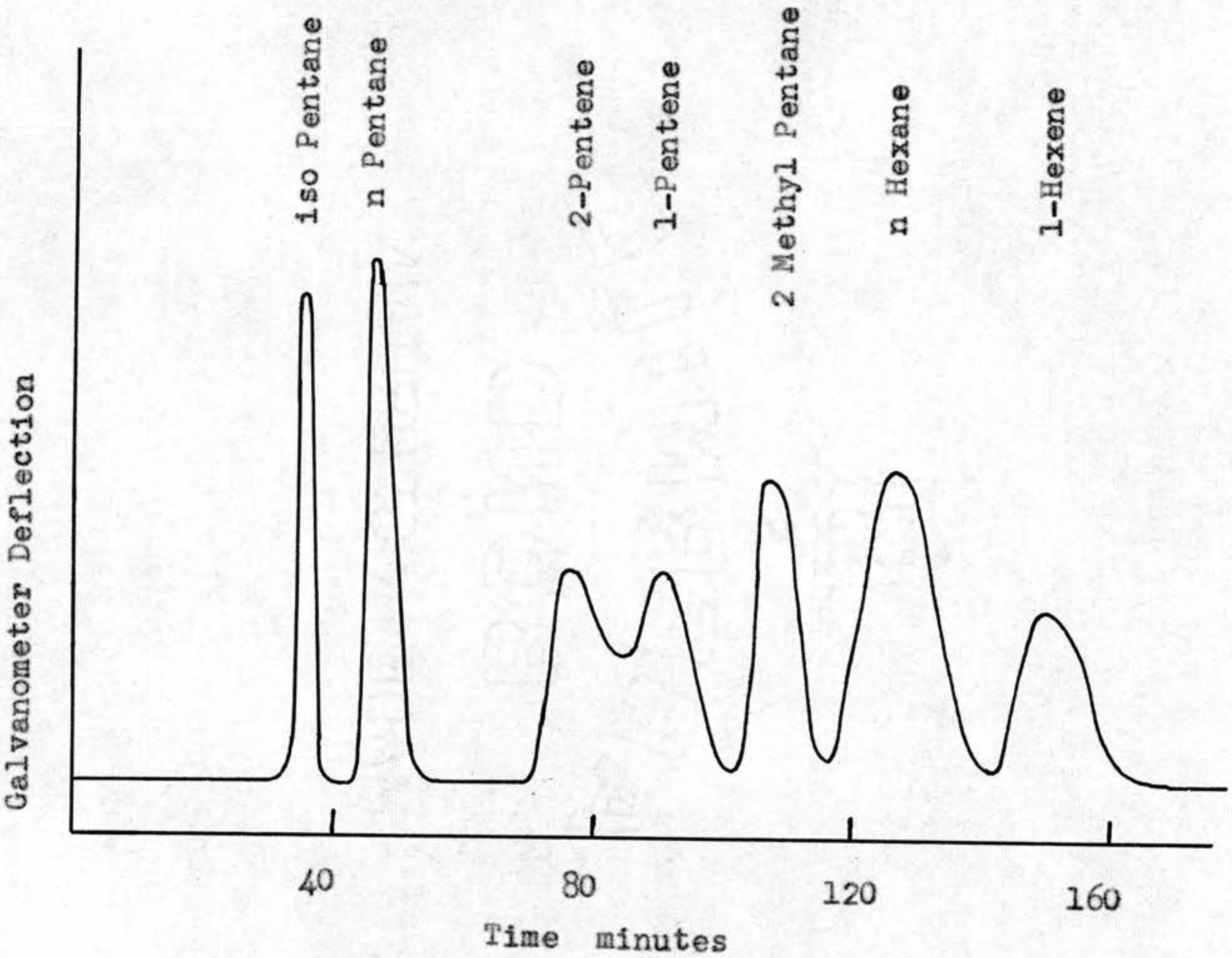

FIGURE 7 Chromatogram of a Seven Component Mixture

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[4]

APPLICATION OF GAS PHASE PARTITION CHROMATOGRAPHY TO COMPETITIVE CHLORINATION REACTIONS

By John H. Knox

Department of Chemistry, University of Edinburgh

Although the direct study of the rates of individual chlorination reactions is difficult a large amount of useful data can be obtained relatively easily by employing the competitive reaction technique. Chlorine atoms are produced in the presence of two substances and the relative rates of reaction with these substances determined by measurement of the amounts of typical products formed from each. With ethane and methane, for example, the following chain steps occur:

$$(a)\quad \mathrm{Cl} + \mathrm{C_2H_6} = \mathrm{C_2H_5} + \mathrm{HCl}$$
$$\mathrm{C_2H_5} + \mathrm{Cl_2} = \mathrm{C_2H_5Cl} + \mathrm{Cl}$$
$$(b)\quad \mathrm{Cl} + \mathrm{CH_4} = \mathrm{CH_3} + \mathrm{HCl}$$
$$\mathrm{CH_3} + \mathrm{Cl_2} = \mathrm{CH_3Cl} + \mathrm{Cl}$$

The relative rate constants of the two chlorine atom reactions are then given to a good approximation by

$$\mathrm{k_{C_2H_6}/k_{CH_4}} = \frac{[\mathrm{CH_4}]_{\mathrm{mean}} \cdot [\mathrm{C_2H_5Cl}]}{[\mathrm{C_2H_6}]_{\mathrm{mean}} \cdot [\mathrm{CH_3Cl}]}$$

provided that the initial [hydrocarbon]/[chlorine] ratios are not too low. $[\mathrm{CH_4}]_{\mathrm{mean}}$ and $[\mathrm{C_2H_6}]_{\mathrm{mean}}$ are the mean concentrations of methane and ethane during the reaction; $[\mathrm{CH_3Cl}]$ and $[\mathrm{C_2H_5Cl}]$ are the final concentrations of the two chlorides.

The technique can also be applied to a single substance, and with propane, for example, the rate constants of chlorine atom attack at primary and secondary positions are given by

$$\mathrm{k}_{iso}/\mathrm{k}_n = [iso\text{-}\mathrm{C_3H_7Cl}]/[n\text{-}\mathrm{C_3H_7Cl}]$$

From the rate constant ratios over a range of temperature activation energy differences and "A factor" ratios may be obtained. Absolute values can then be obtained for a whole series if the activation energy and "A Factor" for one of the series is known.

Hass, McBee and Weber[1] used a large-scale flow method combined with distillation of the products to examine the relative rates of formation of isomers from the chlorination of propane and *iso*butane. Their high temperature results (300–600°C.) led to a value of 1·45 Kcal./mole for the difference in activation energy of primary and secondary attack on propane.[2] A value close to 0·5 Kcal./mole can, however, be derived from their low temperature results and the actual value is therefore still in doubt. Pritchard, Pyke and Trotman-Dickenson[3] have more recently applied the competitive method with considerable success to the chlorination of a wide range of hydrocarbon and hydrocarbon/alkylchloride mixtures using changes in concentration of the parent compound as the means for determining the relative reaction rates. This method is satisfactory when both substances react at roughly the same rate, but it is inaccurate when there are large differences in reactivity and, furthermore, cannot be applied to reaction at different points in the same molecule.

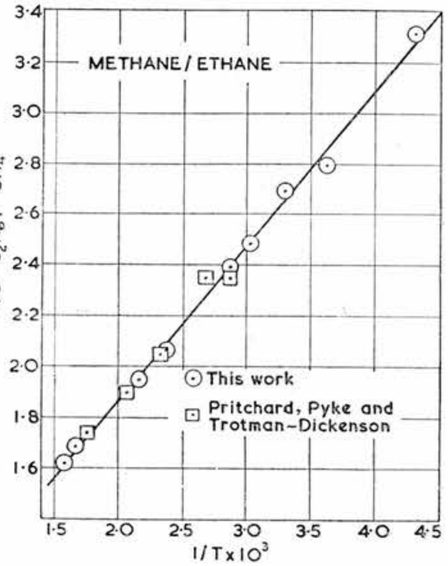

FIG. 1

With the development of gas phase partition chromatography during the last few years[4, 5] an ideal technique has become available for the analysis of very small amounts of similar compounds such as are obtained from static kinetic experiments. With the apparatus used in the present work amounts of the order of 10^{-6} moles could be analysed with an accuracy of about 2 per cent. The alkyl chlorides were separated on a Celite/silicone oil column 150 cm. in length at column temperatures of 110° C. for the propyl chlorides and 55° C. for the methyl and ethyl chlorides. Nitrogen was used as the carrier gas and two balanced thermal conductivity gauges as the detector unit.

The reaction was carried out in a 50 c.c. Pyrex reaction vessel which could be heated in a vapour bath or cooled in a freezing mixture as desired. During the reaction the mixture was illuminated for approximately 30 minutes with a 250-watt projector lamp fitted with a copper sulphate filter to remove excess heat. The propane-chlorine mixtures normally contained 10 mm. of propane and 1 mm. of chlorine, and were made up to a total pressure of 600 mm. with nitrogen. In the methane-ethane experiments 5 mm. of ethane, 1 mm. of chlorine and from 100 to 500 mm. of methane were used. With this low chlorine pressure all possibility of self heating was eliminated, and in the methane-ethane experiments a sufficiently high methane-ethane concentration ratio was obtained to accommodate the great differences in reactivity.

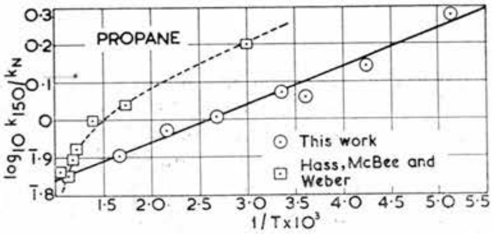

FIG. 2.

The experimental results are presented in Figs. 1 and 2 along with those of previous workers. A least-squares analysis of the complete experimental data leads to the following values of the relative rate constants:

$$\text{Methane/ethane}\quad k_{C_2H_6}/k_{CH_4} = 3\cdot65 \times \exp.\ (2800 \pm 30\ \text{cal./RT})$$

$$\text{Propane}\quad k_{iso}/k_n = 0\cdot55 \times \exp.\ (445 \pm 30\ \text{cal./RT})$$

The methane-ethane results agree excellently with those of Pritchard, Pyke and Trotman-Dickenson. The value of E for propane is in rough agreement with the low temperature value of Hass, McBee and Weber, but their actual rate constant ratios are too high; only their high temperature points lie on the above line, but here their activation energy is high. There seems no obvious explanation of this discrepancy although decomposition of the chlorides above 300° C. would lead to curvature of the activation energy plot. In the present work with propane it was in fact observed that above 320° C. reliable results could be obtained only when the time of residence in the reaction vessel was kept as short as possible. With long periods of heating the ratio of *iso*- to *n*-propyl chlorides was found always to be low leading, under conditions of constant residence time, to a downward curvature of the plot as exhibited by the results of Hass, McBee and Weber.

It is considered that the preliminary results now reported demonstrate that the technique of gas phase partition chromatography is a powerful and accurate tool for the quantitative analysis of small quantities of reaction products such as are obtained in kinetic experiments, and have provided values for the relative activation energies of chlorination of methane, ethane and propane which are very much more accurate than those previously reported. It is intended to extend the chlorination experiments to a wider range of compounds.

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[5]

The high-temperature oxidation of propane

By J. W. Falconer and J. H. Knox
Department of Chemistry, University of Edinburgh

(*Communicated by R. G. W. Norrish, F.R.S.—Received* 27 *September* 1958)

Above 400 °C propane is oxidized by a two-stage degenerately branching chain reaction. The first 20 % of reaction proceeds by an HO_2/C_3H_7 radical chain where the main immediate products are propylene and hydrogen peroxide. Pyrolysis of a small fraction of the propyl radicals gives rise to methyl radicals and finally formaldehyde. The further oxidation of formaldehyde by molecular oxygen probably accounts for the observed chain branching although at temperatures above 475 °C homogeneous decomposition of hydrogen peroxide may lead to the initiation of new chains. In the second stage of the reaction the secondary oxidation of propylene becomes important. While propane still in the main reacts to form propylene the subsequent oxidation of the propylene alters both the kinetics and the oxidation products so that the reaction appears overall to proceed by a mechanism similar to that operative at temperatures below 400 °C where the important branching agents are probably higher aldehydes.

The oxidation of aliphatic saturated hydrocarbons containing two or more carbon atoms can proceed by two distinct mechanisms, depending upon the temperature. One operates between approximately 250 and 380 °C and the other above 400 °C. In the intervening region the low-temperature mechanism begins to fail before the high-temperature mechanism has established itself. This may be observed in the well-known negative temperature coefficient of the slow oxidation rate (Pease 1938; Mulcahy 1947; Knox & Norrish 1954*b*) and in the phenomenon of cool flames (Townend 1937; Prettre 1948; Neuman 1938; Bailey & Norrish 1952; Knox & Norrish 1954*a*, *b*; Malherbe & Walsh 1950). Kinetic experiments have shown that at all temperatures above 250 °C the oxidation proceeds by a degenerately branching chain reaction (Semenov 1935) whose overall order is usually about four, the rate being much more sensitive to hydrocarbon pressure than to oxygen pressure (Norrish 1948; Bardwell & Hinshelwood 1950; McEwan & Tipper 1953).

The products of the oxidation of hydrocarbons and related substances in the low-temperature region have been widely investigated and of those propane has been particularly extensively studied (Newitt & Thorness 1937; Pease 1938; Harris & Egerton 1937; Knox & Norrish 1954*a*). However, little detailed work has been carried out on the high-temperature oxidation of the higher hydrocarbons with a view to elucidating the mechanism of the reaction. Most of the information available has been obtained using flow systems (Satterfield & Wilson 1954; Kooyman 1947) in which kinetic measurements cannot be made with precision. Their results show that the most likely high temperature chain is

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2, \tag{1}$$

$$C_3H_7 + O_2 = C_3H_6 + HO_2. \tag{2}$$

This scheme has been established chiefly through the observations that propylene is the major product of the oxidation (Satterfield & Wilson 1954) and that under suitable conditions large yields of hydrogen peroxide may be obtained (Kooyman 1947). The scheme has also been suggested independently by Knox & Norrish (1954*a*) to explain the decrease in the rate of oxidation of propane above 370 °C. In further support of mechanisms involving the HO_2 radical, the work of Bell & Tipper (1956) and of Cullis & Newitt (1956) on the oxidations of methanol and ethanol may be cited.

The purpose of the present investigation was to ascertain how far a basic chain of the above type could explain the main features of both the kinetics and products of the high-temperature oxidation of propane, and whether further major reactions would be required for their complete explanation. The difficulties met with in the past in carrying out both kinetic and analytical experiments under the same conditions have now been largely solved by the development of gas chromatography which has been used almost exclusively for the analytical work. The technique is ideal for the analysis of quantities of the order of 0·1 to 1·0 mmole obtainable from kinetic experiments. It is furthermore relatively rapid, a complete analytical run requiring about 3 h only.

The work has substantially confirmed the validity of the basic scheme given above. Chain branching appears to result from the pyrolysis of the propyl radical followed by oxidation of the methyl radical formed giving formaldehyde. The subsequent oxidation of the formaldehyde by molecular oxygen then leads to the initiation of new chains. The simple scheme is, however, complicated by the accumulation of propylene. As the partial pressure of propylene grows it exerts an ever increasing influence over the course of the reaction. After some 30 % of reaction an equilibrium pressure is reached and a little before this point the kinetics of the reaction alter markedly from those typical of the high-temperature mechanism to those of the low-temperature type of oxidation.

EXPERIMENTAL

Materials

The gaseous reactants, which were stored in 5 l. Pyrex bulbs, were obtained as follows:

Propane. The propane used in the analytical experiments was a sample kindly given by the British Petroleum Company which contained 0·2 % of *iso*butane as the only impurity. The propane used in the kinetic experiments was obtained by purification of commercial propane which contained a considerable percentage of propylene. This was removed by passage through the following reagents: (1) concentrated sulphuric acid containing 0·6 % wt./wt. of silver sulphate; (2) 30 % sodium hydroxide solution; (3) same as (1), (4) a charcoal column saturated with bromine; and (5) phosphorus pentoxide. The purified propane was fractionated and the middle fraction retained. It contained 0·2 % propylene as the only detectable impurity.

Oxygen was taken directly from cylinders after passage through a spiral cooled in liquid air to remove any condensables. It contained 0·5 % argon.

Propylene was prepared by dehydration of *iso*propanol using phosphorus pentoxide and scrubbed with 10 % sodium hydroxide. It was then fractionated and the middle fraction retained.

Carbon dioxide was obtained from commercial Cardice by repeated sublimation and condensation, the middle fraction being retained in each case.

APPARATUS AND EXPERIMENTAL METHODS

The static reaction system was of standard design. Mixtures were prepared in a 500 ml. mixing vessel and after standing for a few minutes were equilibrated with the reaction vessel. The 522 ml. Pyrex glass reaction vessel was cylindrical and had an internal diameter of 5·5 cm. It was housed in a furnace whose temperature was controlled to within 1 °C and was uniform along the length of the reaction vessel to within 1 °C. Pressures in the mixing vessel and in the reaction vessel were measured by mercury manometers; pressure changes during the reaction were measured by a glass spoon gauge fitted with an all-glass link system operating a mirror. The rotation of the mirror was observed by means of an optical lever arrangement which gave a final gauge sensitivity 7·93 times that of a mercury manometer.

When product analysis was required the gauge was isolated from the reaction vessel and the latter connected to a sampling vessel of about half its volume. By placing liquid air in the central finger of this vessel between 75 and 90 % of the contents could be removed from the reaction vessel. The sample so obtained was then analyzed by gas chromatography and in certain instances also by volumetric methods. For complete analysis by gas chromatography the sample was divided into three fractions:

(1) gases uncondensable at −196 °C: H_2, O_2, CO, CH_4;

(2) gases uncondensable at −78 °C: CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8;

(3) substances involatile at −78 °C: water, hydrogen peroxide, alcohols, aldehydes, acids and other oxygenated products.

TABLE 1

Carrier gas, nitrogen throughout; packings, 52 to 72 B.S.S. mesh.

column packing	length (cm)	temperature (°C)	gases separated
carbon	85	20	H_2, O_2, CO, CH_4
silica gel	190	35	C_2H_4, CO_2, C_2H_6
silica gel	90	89	C_3H_6, C_3H_8
20 % dinonyl phthalate on firebrick	500	100	condensables

The amounts of fractions (1) and (2) were measured in the standardized volume of a Töpler pump and the amount of fraction (3) by difference from the known decrease of pressure in the reaction vessel. Fractions (1) and (2) were stored in small bulbs while fraction (3) was distilled straightway into the sampling U-tube of the chromatography apparatus. Complete analysis of these fractions required four separate chromatography columns, details of which are given in table 1.

The gas chromatography apparatus was of conventional design. Samples for analysis were transferred to a by-pass U-tube and were then entrained by the carrier gas stream. They were thereby driven through the appropriate column which was selected by means of a double channel tap. Detection of the components of the mixture as they emerged from the column was by a brass-block thermal conductivity gauge maintained at room temperature. The apparatus was calibrated for each of the gases to be determined by measurement of peak heights under standard conditions of injection. This, along with standardization of bridge e.m.f., careful control of column temperature and flow rate enabled an accuracy of 2 % to be obtained on the amount of each component.

Identification of the simple gaseous products presented no difficulties owing to the small number of possibilities and the wide differences in their retention times. The identification of the components in fraction (3) was not however generally possible. A typical chromatogram of this fraction is shown in figure 1. Of the six components present only the first two were definitely identified. By comparison of their infra-red spectra and retention times with those of standard samples the first peak was identified as propane dissolved in the fraction and the second as acetaldehyde. The later components could not be identified with certainty, although infra-red analysis indicated the presence of carbonyl and hydroxyl groups. Chromatograms of pure substances showed that the later peaks might be due to esters, alcohols, acetals or aldehydes containing two or three carbon atoms. The quantities of these substances were, however, all small and accounted for only 10 % of the total condensables. The remainder was assumed to be water. Since considerable interest, however, attaches to the yields of aldehydes, peroxides and alcohols in oxidation reactions these substances were in a number of cases determined separately by volumetric methods. Formaldehyde was determined by the chromotropic acid method (Bricker & Johnston 1945); hydrogen peroxide by the thiocyanate method (Egerton *et al.* 1954), and methoxyl by a modified Zeisel method (Scott 1939).

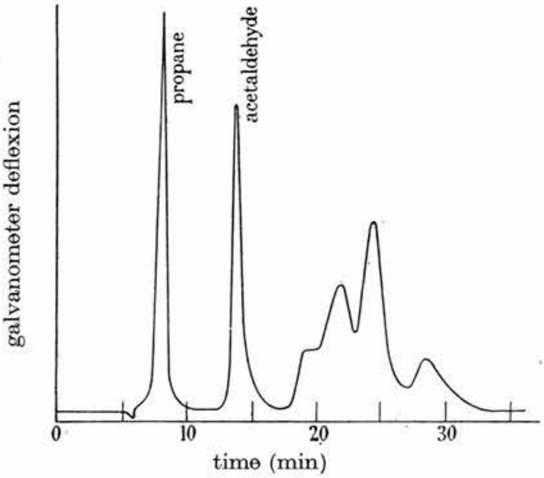


FIGURE 1. Gas chromatogram of condensable products at 435 °C.

Experimental results

The oxidation of propane between 400 and 470 °C shows the broad characteristics of a degenerately branching chain reaction. The chief of these is a slow exponential development of the reaction with time. This is illustrated in figure 2, where the rate of pressure rise, $d\Delta p/dt$, for a typical reaction mixture is plotted against the pressure rise, Δp. The linear relationship up to a considerable percentage reaction implies that

$$d\Delta p/dt = \phi \Delta p$$

or

$$\Delta p = A\,e^{\phi t},$$

where ϕ is the acceleration constant or net branching factor of the reaction. The value of ϕ at any stage in the reaction is most simply obtained from a plot of reaction rate against pressure rise. In any interpretation of the variation of the rate of reaction or acceleration constant with reaction conditions it is, however, essential that the pressure rise should be shown to give a true measure of the extent of reaction.

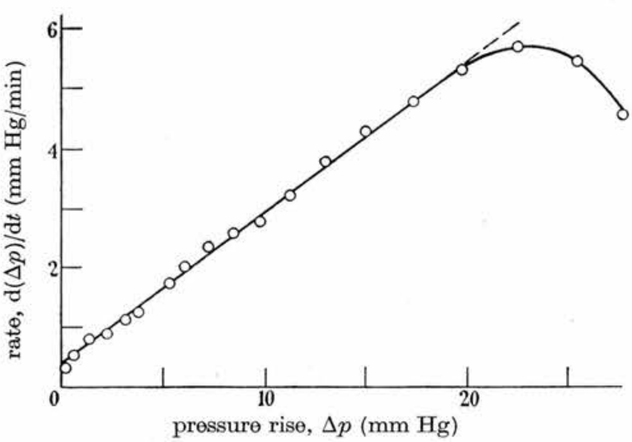


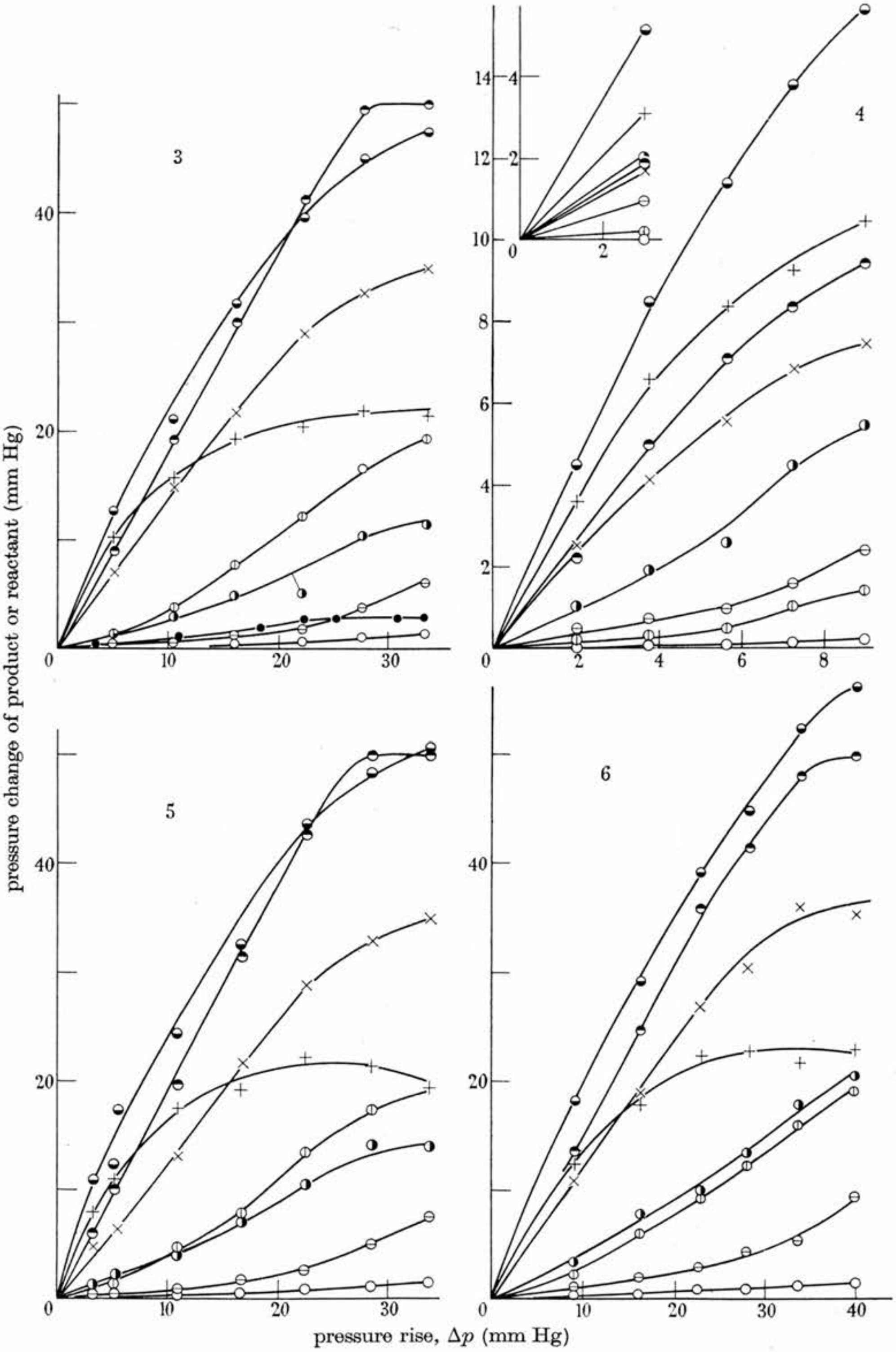
FIGURE 2. Development curve for reaction at 460 °C. $P_{C_3H_8} = 80$ mm; $P_{O_2} = 40$ mm. Acceleration constant, $\phi = 0{\cdot}250$ min^{-1}.

That this is the case is shown in figures 3 to 6 by the approximate linearity of the curves for disappearance of propane and oxygen against pressure rise. The removal of 1 cm pressure of propane is seen to be accompanied by a pressure rise of approximately 0·6 cm with oxygen concentrations from 2 to 50 mm and over a temperature range of 400 to 475 °C.

The effect of oxygen concentration on the development of the reaction is shown in figures 3 and 4. The main qualitative features are clear. In the initial stages of the reaction the only products formed in any quantity are propylene, condensables (mainly water), ethylene and carbon monoxide. To a first approximation the amounts of each formed or removed follow the relations

$$-\Delta[C_3H_8] = \Delta[C_3H_6] + \Delta[C_2H_4] \approx \Delta[\text{condensables}],$$
$$\Delta[C_3H_6] > -\Delta[O_2] > \tfrac{1}{2}\Delta[\text{condensables}],$$

where $\Delta[X]$ is the increase in the concentration of any component X. As the oxygen pressure is reduced the yield of ethylene relative to propylene increases and the yield of carbon monoxide relative to propylene decreases. The initial yield of methane rises as the oxygen pressure is reduced; it also rises sharply at the end of the reaction when the oxygen is almost completely exhausted.



FIGURES 3 TO 6. (For legends see opposite page.)

These relations suggest that the main chain reaction produces either a molecule of propylene or a molecule of ethylene for every molecule of propane disappearing. Since the amount of oxygen disappearing is slightly less than the propylene formed, and since the yield of ethylene relative to propylene increases as the oxygen pressure decreases, it is likely that propylene is formed by an oxidation reaction while ethylene is formed without the intervention of oxygen. The yield of methane initially follows that of ethylene but increases rapidly when the oxygen is exhausted. Methane is thus almost certainly formed by a hydrogen abstraction reaction of methyl radicals the majority of which are normally oxidized. The observations are most readily explained by the following reaction scheme:

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2 \qquad (\Delta H = +9\,\mathrm{kcal}), \tag{1}$$

$$C_3H_7 + O_2 = C_3H_6 + HO_2 \qquad (\Delta H = -12\,\mathrm{kcal}), \tag{2}$$

$$C_3H_7 = C_2H_4 + CH_3 \qquad (\Delta H = +21\,\mathrm{kcal}), \tag{3}$$

$$CH_3 + O_2 + M = CH_2O + OH + M \quad (\Delta H = -51\,\mathrm{kcal}), \tag{4}$$

$$CH_3 + RH = CH_4 + R, \tag{5}$$

$$H_2O_2 + \text{walls} = H_2O + \tfrac{1}{2}O_2, \tag{6}$$

$$CH_2O \text{ oxidation} = CO, \text{ etc.} \tag{7}$$

The heat of formation of HO_2 has been taken from Foner & Hudson (1955) and heats of formation of other radicals from Trotman-Dickenson (1955).

A notable feature of the results so far not mentioned is the falling off in the rate of production of propylene as the reaction proceeds. After some 10 mm pressure rise has occurred the yield of propylene reaches a maximum and remains almost constant while the oxidation of propane continues. Thus in the later stages of the reaction a significant change in mechanism occurs and propylene is either no longer formed or else, if it is formed, it is destroyed equally rapidly. This possibility is not envisaged in the above scheme and the explanation of the role of propylene in the oxidation adds considerably to the complexity of the reaction mechanism.

The effect of increase of temperature on the development of the reaction products is shown in figures 3, 5 and 6 which give the development curves for 435, 445 and 475 °C. There is little change in the relative yields of propylene, carbon monoxide, hydrogen, carbon dioxide or condensables, but a marked increase in the yields of ethylene and methane with rise of temperature and a compensatory increase in the

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FIGURE 3. Development of reaction products at 435 °C. $P_{C_3H_8} = 100$ mm; $P_{O_2} = 50$ mm.

FIGURE 4. Development of reaction products at 435 °C. $P_{C_3H_8} = 100$ mm; $P_{O_2} = 9{\cdot}5$ mm. Inset, $P_{O_2} = 1{\cdot}9$ mm.

FIGURE 5. Development of reaction products at 445 °C. $P_{C_3H_8} = 100$ mm; $P_{O_2} = 50$ mm.

FIGURE 6. Development of reaction products at 475 °C. $P_{C_3H_8} = 100$ mm; $P_{O_2} = 50$ mm.

Key to figures 3 to 6. ◓, oxygen used; ◒, propane used; ×, condensables $\times \frac{1}{2}$; +, propylene; Φ, carbon monoxide; ◑, ethylene; ●, methanol; ⊖, methane; ○, carbon dioxide and hydrogen (each).

amount of propane consumed relative to oxygen. This increase in the yields of methane and ethylene is in agreement with the proposed scheme, since reaction (3) probably has an activation energy of about 25 kcal/mole (Kerr & Trotman-Dickenson, unpublished results). Temperature change evidently has little effect on the maximum partial pressure of propylene.

In order to ascertain whether the observed maximum in the yield of propylene resulted from a balance between formation and destruction or simply from a cessation of the reaction producing it, experiments were carried out in which a percentage of the propane was replaced by propylene. The replacement slightly decreased the overall pressure rise in the reaction (see table 4 for actual values), but the linearity of pressure rise against oxygen consumption was still maintained. Complete analyses of the products at various stages in the reactions where 0, 10, 20 and 40 % of propane was replaced by propylene showed that the yields of ethylene, methane and carbon dioxide were not affected by the substitution but that the yields of condensables fell slightly with progressive substitution. The condensables, however, contained more organic material the larger the initial pressure of propylene. The most interesting feature of the results is shown in figure 7, which gives the development curves for propylene and carbon monoxide. For the purpose of the figure the pressure rise for each reaction has been scaled to a total pressure rise of 34 mm. It is clear that irrespective of the initial pressure of propylene the final pressure tends towards an equilibrium value close to 25 mm, and that the substitution of propane by propylene

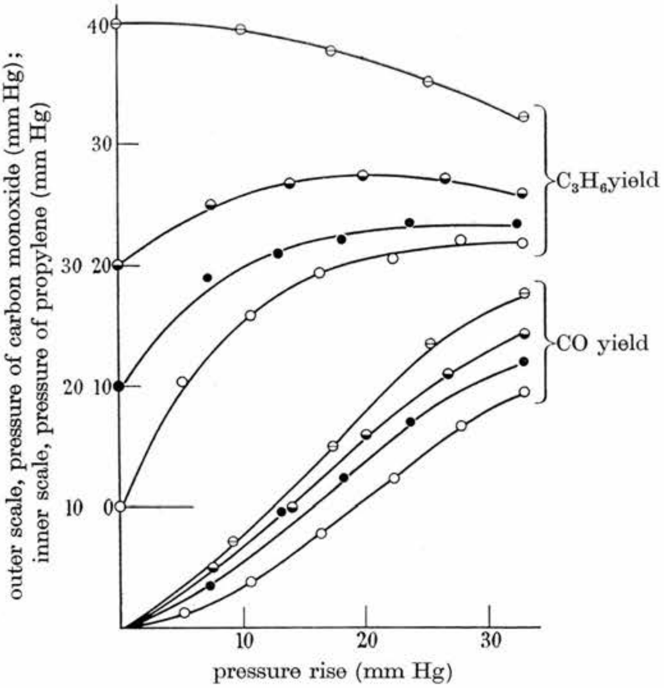

FIGURE 7. Development of carbon monoxide and propylene in mixtures with different amounts of propylene. $P_{C_3H_8}+P_{C_3H_6} = 100$ mm; $P_{O_2} = 50$ mm. ○, ●, ◒, ⊖ refer to experiments with 0, 10, 20 and 40 mm pressure of propylene, respectively.

leads to a more profuse production of carbon monoxide, particularly in the initial stages of the reaction. These results suggest that the maximum in the concentration of propylene results from an equilibrium between production and removal rather than from a cessation of the production reaction. The exact nature of the reaction removing propylene is not clear but two reactions seem possible

$$C_3H_6 + HO_2 = C_3H_7OO = C_2H_5CHO + OH \quad (\Delta H = -50\,\text{kcal}), \tag{8a}$$

$$C_3H_6 + HO_2 = C_3H_5 + H_2O_2. \tag{8b}$$

The occurrence of these reactions will lead to the production of products typical of the low-temperature oxidation, in particular carbon monoxide and organic condensable products.

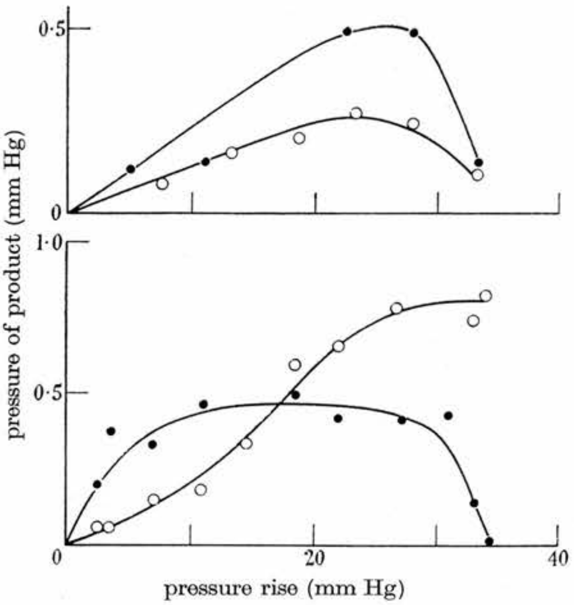

FIGURE 8. Development of condensables. $P_{C_3H_8} = 100$ mm; $P_{O_2} = 50$ mm. Upper graph: ●, acetaldehyde at 435 °C; ○, acetaldehyde at 475 °C. Lower graph: ●, hydrogen peroxide at 435 °C; ○, formaldehyde at 435 °C.

The analysis of the condensables by gas chromatography showed that apart from acetaldehyde all the components of fraction 3 increased regularly throughout the reaction. The yield of acetaldehyde could be estimated roughly from the gas chromatograms and there was no doubt that its yield passed through a maximum near the point of maximum reaction rate. The results for 435 and 475 °C are given in figure 8. The development of methoxyl, formaldehyde and hydrogen peroxide were obtained separately by volumetric methods. The development curve for methoxyl is given in figure 3 and its yield is seen to increase regularly throughout the reaction. The yield of formaldehyde behaved likewise (figure 8). The analysis for hydrogen peroxide gave very irreproducible results, but indicated that the yield rose to a flat maximum early in the reaction (figure 8), roughly following the propylene yield. At the end of the reaction it finally fell to a very low value.

Kinetic measurements of the maximum reaction rate and of the acceleration constant were made at 400 and 460 °C. The effects of the addition of propylene and of various aldehydes to the reaction mixture were examined at 435 °C.

Reasonably reproducible values for rates and acceleration constants were obtained only when the oxygen/propane ratio was below 1:2. However, at both temperatures it appeared that the order with respect to oxygen fell when the oxygen/propane ratio exceeded 1:2. This is in general agreement with the results of other workers who have reported zero orders with respect to oxygen (McEwan & Tipper 1953) and sometimes even negative orders (Bardwell & Hinshelwood 1950). With mixtures containing up to 33 % oxygen the orders with respect to total pressure, propane pressure and oxygen pressure at 400 °C were as follows:

	order of maximum rate	order of acceleration constant
total pressure	$3{\cdot}9 \pm 0{\cdot}1$	$3{\cdot}5 \pm 0{\cdot}4$
propane pressure	$2{\cdot}6 \pm 0{\cdot}2$	$2{\cdot}4 \pm 0{\cdot}4$
oxygen pressure	$1{\cdot}6 \pm 0{\cdot}2$	$1{\cdot}6 \pm 0{\cdot}2$

The occurrence of fractional orders in hydrocarbon oxidation rate expressions often indicates that a total pressure factor should be included in the true rate expression. This usually implies that chain termination is a diffusion-controlled wall reaction. A truer expression for the maximum rate of reaction may therefore be of the form

$$\text{maximum rate} = k[Hy]^2\,[\mathrm{O_2}]\,[P],$$

where $[Hy]$ is the hydrocarbon pressure and $[P]$ is a total pressure factor of the form

$$[P] = a[\mathrm{O_2}] + b[\mathrm{C_3H_8}] + \Sigma x[X],$$

where a, b and x are constants.

At 460 °C the kinetics were considerably more complicated than at 400 °C. An unexpected two-stage development was noted. This is illustrated in figure 9, where reaction rates are plotted against pressure rise for various concentrations of oxygen in 120 mm propane. The reaction starts with a low acceleration and after some 10 mm pressure rise begins to accelerate at a much faster rate. The kinetics of both initial and final acceleration constants as well as those of the maximum rate were determined. The values were as follows:

	order of max. rate	order of initial acceleration constant	order of final acceleration constant
total pressure	$3{\cdot}9 \pm 0{\cdot}1$	$1{\cdot}9 \pm 0{\cdot}2$	$2{\cdot}4 \pm 0{\cdot}2$
propane pressure	$2{\cdot}0 \pm 0{\cdot}2$	$1{\cdot}9 \pm 0{\cdot}2$	$1{\cdot}7 \pm 0{\cdot}2$
oxygen pressure	$1{\cdot}8 \pm 0{\cdot}2$	$0{\cdot}2 \pm 0{\cdot}2$	$1{\cdot}1 \pm 0{\cdot}2$

The most remarkable feature of the high-temperature results is the change from an acceleration independent of oxygen pressure in the early stages to one proportional to oxygen pressure in the later stages. Kinetic experiments on mixtures where a percentage of the propane was replaced by propylene have shown that this change appears to be associated with the accumulation of propylene in the reacting gas. Results for mixtures containing 100 mm of combustible and 50 mm of oxygen at 435 °C are shown in figure 10. Initial replacements of up to 10 mm of the propane progressively removed the initial slow acceleration of the reaction but had no effect on the later acceleration. Replacement of larger amounts of the propane by propylene not only eliminated the initial slow acceleration but increased the later acceleration roughly in proportion to the amount of propylene added. Reference to figure 3 shows that the concentration of propylene required just to remove the initial slow acceleration is close to the amount which has accumulated in the normal reaction when the break in the acceleration curve occurs. Experiments with mixtures containing different amounts of oxygen showed that the amount of propylene

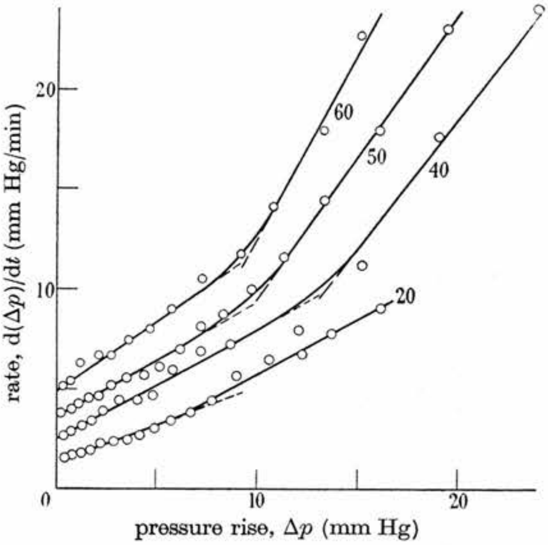

FIGURE 9. Curves of reaction rate against pressure rise for 460 °C. $P_{C_3H_8} = 120$ mm. Oxygen pressures given on individual lines.

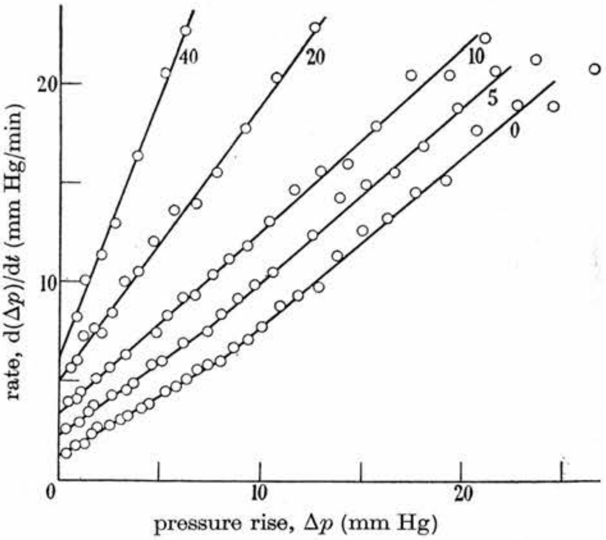

FIGURE 10. Effect of replacement of propane by propylene at 435 °C. $P_{C_3H_8} + P_{C_3H_6} = 100$ mm; $P_{O_2} = 50$ mm.

required to remove the initial slow acceleration was proportional to the concentration of oxygen. Both analytical and kinetic experiments thus show that the change in the nature of the reaction after some 20 % of reaction has occurred is closely associated with the reactions of the propylene formed in the early stages.

The effect of added carbon dioxide was studied at 460 °C. Figure 11 shows that carbon dioxide had a strong accelerating effect upon the reaction; both the maximum rate and the acceleration constant are increased linearly with pressure of added carbon dioxide. The inclusion of a total pressure factor in the rate expression is therefore further supported. Carbon dioxide evidently has an inert-gas effect comparable with that of oxygen and propane.

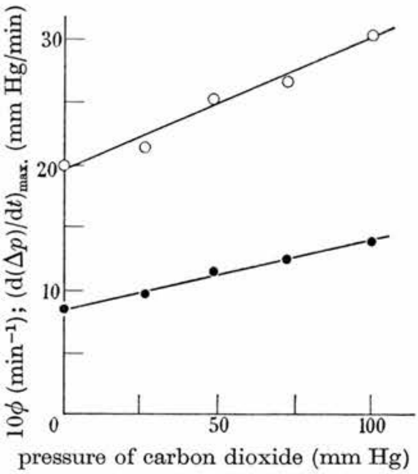

FIGURE 11. Variation of maximum rate (○) and acceleration constant (●) with pressure of carbon dioxide $P_{C_3H_8} = 100$ mm; $P_{O_2} = 50$ mm.

The effect of the addition of chain-initiating substances to the reaction mixture at 435 °C was studied in order to determine whether or not the maximum rate of reaction resulted simply from the consumption of the reactants or from the removal of branching intermediate by radical attack. In the latter case the maximum rate of reaction may be evaluated by the stationary state method, making the rough assumption that the concentration of the reactants does not alter during the reaction. If the amount of branching intermediate normally present at maximum rate is added initially to the reaction mixture, the reaction is expected to commence at its normal maximum rate. It will proceed at this rate without acceleration until the consumption of the reactants inevitably causes a fall in the rate. If a greater amount of intermediate is added than is normally present at maximum rate the reaction will start at an enhanced rate and quickly slow down to its previous maximum rate. This effect has been demonstrated in the oxidation of ethylene by Harding & Norrish (1952) and may be called the 'negative induction period effect'. When the consumption of reactants is the only factor limiting the maximum rate of reaction, it should be possible always to observe an initial exponential acceleration of the reaction however much branching intermediate is initially added.

It was found that the addition of up to 10 mm of acetaldehyde to a mixture of 80 mm propane and 40 mm oxygen was insufficient to cause the reaction to start at maximum rate. If, however, an amount of propylene was present equal to that normally present at maximum rate the reaction could be made to start at maximum rate by the addition of 4 mm of acetaldehyde and a 'negative induction period' could be produced by the addition of more than this quantity (see figure 12). Nevertheless, the addition of acetaldehyde considerably increased the maximum rate of reaction and it is therefore probable that the maximum rate is limited both by consumption of the reactants and by radical removal of the branching intermediate. The pressures of different aldehydes required just to remove the initial acceleration of the reaction in a mixture of 20 mm propylene, 60 mm propane and 40 mm oxygen were: formaldehyde, 8 mm, acetaldehyde, 4 mm and propionaldehyde, 4 mm. The maximum quantities of free formaldehyde and acetaldehyde present in the liquid products corresponded to pressures in the reaction vessel of 1·0 and 0·5 mm, respectively (see figure 8). However, the actual pressures present in the reaction at maximum rate were probably considerably greater than this owing to the great readiness with which aldehydes form condensation products in the liquid phase. Some, if not all, of the branching must therefore result from the reactions of aldehydes, although other branching agents cannot be ruled out.

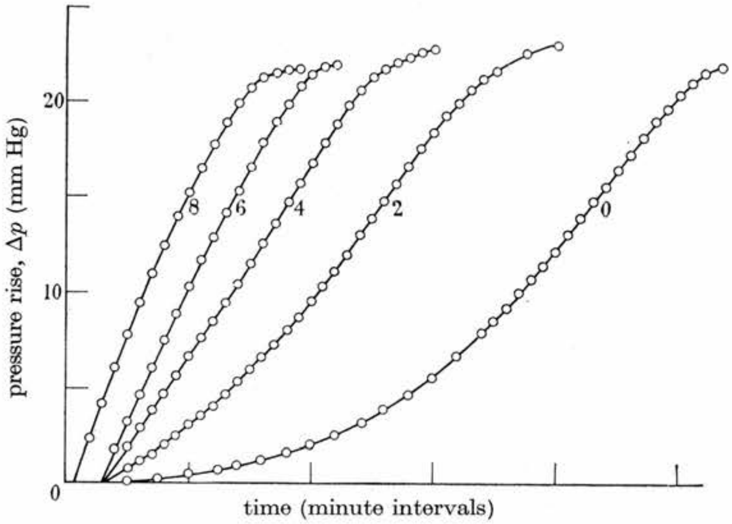

FIGURE 12. Effect of the addition of acetaldehyde at 435 °C. $P_{C_3H_8} = 60$ mm; $P_{C_3H_6} = 20$ mm; $P_{O_2} = 40$ mm. Pressures of acetaldehyde given on individual lines. All curves slightly displaced to right for clarity.

DISCUSSION

The reaction scheme proposed as a result of the analytical experiments gives a qualitative account of the variation of the yields of the various products with variation of the oxygen/propane ratio and temperature. A more detailed quantitative examination of the mechanism shows, however, that the actual reaction scheme must be somewhat more complex than that so far suggested.

The profound effect of propylene on the nature of the reaction results in the high-temperature mechanism operating in its pure form only in the initial stages of the reaction. In order to compare the experimental results with those predicted by the mechanism one should therefore examine the initial rates of formation of the products rather than their final yields. In tables 2 and 3 the initial rates of formation of the products relative to oxygen consumption have been calculated by dividing the initial gradients of the lines in figures 3 to 6 by the initial gradient for oxygen consumption.

TABLE 2. VARIATION OF INITIAL RATES OF FORMATION OF PRODUCTS WITH OXYGEN PRESSURE AT 435 °C

(Propane pressure, 100 mm Hg.)

oxygen pressure (mm Hg)	50	9·5	1·9
oxygen used	1·00	1·00	1·00
propane used	1·45	1·75	2·75
propylene	1·20	1·38	1·66
ethylene	0·12 (0·25)	0·39 (0·45)	1·08
methane	0·03 (0·17)	0·14 (0·30)	0·50
hydrogen carbon dioxide } each	0·01	0·01	0·02
carbon monoxide	0·12	0·07	0·10
condensables (90 % water)	1·56	1·82	1·84
methanol	0·05		
formaldehyde	0·02		
acetaldehyde	0·03		
$R_{C_3H_6}/R_{C_2H_4}$	10·0	3·5	1·55
$(R_{C_2H_4}/R_{CH_4})-1$	3·0	1·8	1·15

TABLE 3. VARIATION OF INITIAL RATES OF FORMATION OF PRODUCTS WITH TEMPERATURE

(Propane pressure, 100 mm Hg; oxygen pressure, 50 mm Hg.)

temperature (°C)	435	445	475
oxygen used	1·00	1·00	1·00
propane used	1·45	1·56	1·52
propylene	1·20	1·25	1·06
ethylene	0·12 (0·25)	0·17 (0·26)	0·26 (0·33)
methane	0·03 (0·17)	0·05 (0·16)	0·08 (0·22)
hydrogen carbon dioxide } each	0·01	0·01	0·015
carbon monoxide	0·12	0·13	0·14
condensables (90 % water)	1·56	1·32	1·56
acetaldehyde	0·03		0·015
$R_{C_3H_6}/R_{C_2H_4}$	10·0	7·3	4·1
$(R_{C_2H_4}/R_{CH_4})-1$	3·0	2·4	2·2

According to the proposed scheme propylene and ethylene are formed as a result of two competing reactions of the propyl radical, reactions (2) and (3). The relative rates of their formation should therefore follow

$$\frac{R_{C_3H_6}}{R_{C_2H_4}} = k_2[O_2]/k_3. \tag{A}$$

Methane is formed as a result of hydrogen abstraction by methyl radicals (reaction (5)), which is in competition with the oxidation of methyl radicals (reaction (4)). Since the total amount of methyl radical formed is the same as the total amount of ethylene according to the scheme, the relative yields of methane and ethylene should obey the equation

$$\frac{R_{C_2H_4}}{R_{CH_4}} - 1 = \frac{k_4[O_2][M]}{k_5[RH]}. \tag{B}$$

Examination of table 2 shows that the left-hand side of equation (A) increases only 7 times instead of 26 times when the oxygen concentration increases from 1·9 to 50 mm, and that the left-hand side of equation (B) increases only about 3 times instead of 26 times.

It is therefore necessary to suppose that both ethylene and methane can be formed by reactions which require the intervention of oxygen. Ethyl radicals which can form ethylene by a reaction analogous to (2) could result from a certain amount of low-temperature oxidation by way of reactions (9) and (10):

$$C_3H_7 + O_2 = C_2H_5CHO + OH \qquad (\Delta H = -14\,\text{kcal}), \tag{9}$$

$$C_2H_5CHO + HO_2 = C_2H_5 + CO + H_2O_2 \quad (\Delta H = +6\,\text{kcal}). \tag{10}$$

A reaction similar to (10) has already been proposed by Norrish (1948) for the radical destruction and degradation of aldehydes in the low-temperature oxidation of the higher hydrocarbons. The additional reaction eventually forming ethylene would then be more dependent upon oxygen concentration than that forming propylene. Methyl radicals could likewise be formed from the degradation of acetaldehyde. Further evidence that ethylene can be formed by a reaction other than the pyrolysis of the propyl radical is to be found in figures 3 to 6, where it may be seen that even when the oxygen is almost completely exhausted the rate of formation of methane never becomes equal to that of ethylene. The actual values are given in parentheses in tables 2 and 3. It would also be expected that the yield curves of methane and ethylene would be more curved than they are due to the depletion of oxygen as the reaction proceeds, if there were no other reactions forming them.

The variation of the yields of ethylene and methane with temperature, in contrast, agree well with the proposed scheme. The values of the left-hand sides of equations (A) and (B) at 435, 445 and 475 °C are given in table 3 and yield the following activation energy differences:

$$E_3 - E_2 = 25 \pm 5\,\text{kcal/mole},$$
$$E_5 - E_4 = 7 \pm 5\,\text{kcal/mole}.$$

E_3 is probably about 25 kcal/mole and E_2 close to zero; E_5, the activation energy of hydrogen abstraction by methyl radicals, is about 9 kcal/mole (Trotman-Dickenson 1955) while E_4 is probably either zero or slightly negative. The agreement between the predicted and experimental values is thus within the experimental error.

It is interesting to note that our results on the formation of methane support the conclusion of Hoare & Walsh (1957) that the oxidation of methyl radicals by oxygen requires a third body. They find that the reaction is third-order up to a pressure of at least 200 mm of acetone and at 200 °C the relative rate constants of reactions (4′) and (5′), that is of

$$CH_3 + O_2 + M = \text{products} \tag{4′}$$

and

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3, \tag{5′}$$

are

$$k_{4'}/k_{5'} = 0{\cdot}8 \times 10^{-16}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}.$$

With an oxygen pressure of 50 mm, and taking $E_{5'} - E_{4'} = 10$ kcal/mole, the relative rates of reaction at 450 °C will be

$$R_{4'}/R_{5'} = k_{4'}[O_2]/k_{5'} = 56.$$

Oxidation is therefore expected to be about 56 times as fast as abstraction from acetone. This value is some ten times that found in our experiments with propane. Two assumptions would, however, have to be made in applying the above value to our results; first, it would be necessary to assume that propane had the same efficiency as a third body as acetone, and secondly, that the activation energy of reaction (4′) is close to zero. Since third-order reactions very often have slightly negative activation energies and propane may be a less efficient third body than acetone it is quite possible that in the propane + oxygen + methyl radical system oxidation at 450 °C proceeds as little as five times as fast as abstraction. If, however, reaction (4′) were bimolecular it would be expected to be faster than hydrogen abstraction by a factor of about 10^4 at 450 °C. The oxidation of ethyl radicals is almost certainly bimolecular and accordingly the quantities of ethane found in oxidation products of propane are extremely small.

TABLE 4. RATE OF FORMATION OF CARBON MONOXIDE RELATIVE TO OXYGEN CONSUMPTION FOR MIXTURES CONTAINING PROPYLENE

(Propane + propylene pressure, 100 mm Hg; oxygen pressure, 50 mm Hg.)

propylene pressure (mm Hg)	0	10	20	40
initial rate of CO formation	0·12	0·23	0·31	0·37
max. rate of CO formation	0·35	0·41	0·45	0·54
propylene pressure at max. rate of CO formation	20	22	26	36
$\left(\dfrac{100\text{ max. rate CO formation}}{\text{propylene pressure}}\right)$	1·70	1·85	1·75	1·50
total pressure rise (mm Hg)	34	32	30	26

The reactions forming carbon monoxide and organic condensables are relatively little affected by oxygen concentration and temperature, but are markedly affected by the replacement of propane by propylene. From table 4 and figure 7 it is seen that the maximum rate of formation of carbon monoxide is roughly proportional to the pressure of propylene present at maximum rate, and that in the mixture without added propylene the maximum rate of formation of carbon monoxide is close to the initial rate of formation in a mixture containing 20 mm of propylene, the equilibrium pressure of propylene present in the unsubstituted oxidation. In addition the rate of formation of carbon monoxide increases throughout the normal oxidation to a much greater extent than when propane is initially replaced by propylene. These observations all strongly suggest that carbon monoxide is derived mainly from the oxidation of propylene and not directly from the oxidation of propane or any of its other immediate products.

For the purpose of evaluation of the expected kinetics of a reaction following the high-temperature scheme it may be written in the simplified form comprising only reactions (1), (2), (3) and (4) along with necessary chain termination and chain-branching reactions. Chain termination is probably a diffusion-controlled wall reaction and may be written as

$$HO_2 + \text{wall} = \text{radical destruction}. \tag{11}$$

Two possible reactions are possible for chain branching,

$$CH_2O + O_2 = 2 \text{ free radicals}, \tag{12}$$

$$H_2O_2 = 2OH. \tag{13}$$

The acceleration constant for such a scheme may readily be evaluated on the assumption that the duration of the chain is short in comparison to the lifetime of the branching intermediate. The acceleration constant is simply the net number of new chains produced per unit time by any one chain. It may thus be given as

$$\phi = (1/\theta)(n\alpha\nu - 1),$$

where θ = average lifetime of the intermediate I,

n = number of radicals produced by the reaction of one molecule of intermediate (usually 2),

α = proportion of chain steps producing the intermediate I,

ν = chain length of primary reaction chains.

With formaldehyde branching only,

$$1/\theta = k_{12}[O_2], \qquad \alpha = k_3/(k_3 + k_2[O_2]),$$

$$\nu = k_1[Hy][P]/k_{11}, \quad n = 2;$$

thus

$$\phi = k_{12}[O_2]\left\{2\frac{k_3}{k_3 + k_2[O_2]}\frac{k_1[Hy][P]}{k_{11}} - 1\right\}.$$

From the yields of ethylene and propylene recorded above it is clear that with not too small oxygen/propane ratios reaction (2) is much faster than reaction (3). If the reaction chains are not very short the second term in the bracket is small in comparison with the first. To a first approximation therefore the acceleration constant is given by

$$\phi = \frac{2k_1k_3k_{12}}{k_2k_{11}}[Hy][P] = A[Hy][P].$$

This expression is in agreement with that obtained experimentally. If branching results from reaction (14) rather than from reaction (13) the kinetic expression is not however significantly different. Here

$$1/\theta = (k_{13} + k_6),$$

$$\nu = k_1[Hy][P]/k_{11},$$

$$\alpha = k_{13}/(k_{13} + k_6),$$

where reaction (6) is the destruction of hydrogen peroxide at the walls of the reaction vessel. We then obtain

$$\phi = (k_{13}+k_6)\left\{2\frac{k_1 k_{13}[Hy][P]}{k_{11}(k_{13}+k_6)}-1\right\}$$
$$= k_{13}\{2k_1[Hy][P]/k_{11}-1\}-k_6.$$

If wall destruction of the peroxide is unimportant and if the chains are not very short this equation reduces to

$$\phi = \frac{2k_1 k_{13}}{k_{11}}[Hy][P] = B[Hy][P].$$

It would be difficult to distinguish between the two types of branching by purely kinetic experiments but it can be convincingly argued that hydrogen peroxide branching cannot become important below about 475 °C. At 435 °C the concentration of hydrogen peroxide found in the reaction vessel was 0·5 mm. If it is formed at the same rate as propylene its maximum rate of formation is about 10 mm/min. The average lifetime of a peroxide molecule in the reaction system is therefore about 3 s. This is slightly greater than the average time required for a molecule to diffuse to the walls of a cylindrical reaction vessel 55 mm in diameter when the total pressure of gas is about 150 mm, but only about 1/30th of the average lifetime of a hydrogen peroxide molecule undergoing homogeneous decomposition at 435 °C (Giguere & Liu 1957). By far the greater part of the peroxide must therefore be decomposing as a result of diffusion to the walls and not homogeneously to give free radicals. However at 475 °C the average lifetime of a hydrogen peroxide molecule undergoing homogeneous decomposition is only about 10 s and at this temperature homogeneous decomposition of the peroxide must produce an appreciable amount of chain initiation. There should therefore be a change in the high-temperature branching reaction at about 475 °C from one dependent predominantly on the oxidation of formaldehyde to one dependent upon the decomposition of hydrogen peroxide, the latter having the higher activation energy.

The oxidation at 400 °C and the later stages of the oxidation at 435 and 460 °C show similarities to the low-temperature oxidation. The reaction is one of rather high order. Termination of reaction chains occurs at the walls (inert-gas effect); branching probably involves oxygen (strong dependence of rate upon oxygen pressure), and the branching intermediate is removed by radical attack, this process largely governing the achievement of a maximum rate of reaction (negative induction period effect). These observations rule out any mechanism in which hydroperoxides act as branching agents. However, since aldehydes have been shown to be present in quantities comparable with those required to start the reaction *ab initio* at maximum rate they appear to be the most likely branching agents for this mode of oxidation. Aldehydes are known to react with molecular oxygen by a reaction of relatively low activation energy (Macdowell & Thomas 1950; Combe, Niclause & Letort 1955) and it is likely that they will be attacked by radicals rather more rapidly than the parent hydrocarbon. The maximum rate may thus be limited effectively by the removal of the branching intermediate as in reaction (16) below.

The simplest mechanism involving aldehydes is that proposed by Norrish (1948). For the purpose of kinetic analysis this may be written in a simplified form omitting the reactions for the progressive degradation of the aldehydes.

$$C_3H_8 + OH = C_3H_7 + H_2O \qquad (\Delta H = -20\,\text{kcal}), \tag{15}$$

$$C_3H_7 + O_2 = C_2H_5CHO + OH \qquad (\Delta H = -62\,\text{kcal}), \tag{9}$$

$$\text{or} = CH_3CHO + CH_3O \qquad (\Delta H = -67\,\text{kcal}), \tag{9a}$$

$$C_2H_5CHO + O_2 = C_2H_5 + OH + CO_2 \qquad (\Delta H = -13\,\text{kcal}), \tag{14}$$

$$C_2H_5CHO + OH = C_2H_5 + H_2O + CO \qquad (\Delta H = -19\,\text{kcal}), \tag{16}$$

$$OH + \text{wall} = \text{radical destruction}. \tag{17}$$

The acceleration constant may be evaluated using the equation given above and the maximum rate ($R_{\text{max.}}$) obtained by the stationary state method assuming that $d[C_2H_5CHO]/dt = 0$ and that the consumption of reactants is negligible. The two parameters are simply related by the equation

$$\begin{aligned} R_{\text{max.}} &= (k_{15}/k_{16})\,\phi[Hy] \\ &= \frac{k_{15}k_{14}[Hy][O_2]}{k_{16}}\left\{2\frac{k_{15}[Hy][P]}{k_{17}} - 1\right\}. \end{aligned}$$

When the chains are not very short, this effectively reduces to

$$R_{\text{max.}} = C\phi[Hy] = D[Hy]^2[O_2][P],$$

an expression agreeing with the results for 400 °C, and somewhat less exactly with the results for 460 °C.

The importance of propylene in the oxidation of propane above 400 °C has been fully demonstrated by the experimental results. It evidently acts as a catalyst and at the same time considerably modifies the reaction mechanism. The oxidation of propylene alone at temperatures up to 400 °C has recently been investigated by Mullen & Skirrow (1958). While their results are not directly comparable with ours since the temperature range is lower, their conclusion that the reaction is degenerately branching and that the active intermediate is acetaldehyde is in agreement with our results, which indicate that in the presence of propylene the oxidation of propane proceeds by a mechanism of the low-temperature type, dependent upon higher aldehydes as branching agents. Since propylene is well known as an inhibitor of simple chain reactions, its accelerating effect on the oxidation of propane is at first sight something of a surprise. The action of propylene as an inhibitor is usually ascribed to the formation of the relatively stable allyl radical and it has recently been shown by Bell, Vaughan & Rust (1957) that hydroxyl radicals formed by the pyrolysis of hydrogen peroxide react with propylene in this way according to

$$OH + C_3H_6 = H_2O + C_3H_5. \tag{18}$$

However, while considerable quantities of diallyl were isolated in their experiments there are no reports of its identification in the oxidation products of propane or propylene. Any allyl radicals formed are therefore oxidized before they can dimerize.

The role of propylene is therefore to be understood in terms of its removal of radicals such as OH and HO_2 and their replacement by the less reactive allyl or alkylperoxy radicals. If termination of the reaction chains normally occurs by the reaction of OH or HO_2 at the walls of the reaction vessel their replacement by radicals which are not so removed will lengthen the reaction chains and so increase the acceleration constant and maximum rate of the reaction. Its property of inhibiting simple chain reactions is thus in accord with its accelerating influence on degenerate chain-branching hydrocarbon oxidations.

In conclusion it therefore appears that the series of events which occurs in the oxidation of propane is as follows. In the initial stages of the reaction an HO_2 chain operates which forms propylene as its major product. This chain is carried also by propyl radicals and a certain proportion of them, dependent upon temperature and oxygen concentration, decomposes to give rise eventually to formaldehyde whose oxidation brings about chain branching. As the propylene accumulates, however, its reaction produces an increasing amount of alkyl or allyl peroxy radicals and higher aldehydes. These higher aldehydes being more reactive than formaldehyde soon take over the function of branching agents and so cause the reaction to accelerate at a faster rate than was possible in their absence.

The high-temperature oxidation of propane is thus a complex reaction in which at least two mechanisms can operate, depending upon the temperature and degree of advancement of the reaction. At higher temperatures than were used in the present investigation it is probable that a third mechanism based upon hydrogen peroxide branching comes into operation.

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GAS CHROMATOGRAPHY

By JOHN H. KNOX, B.Sc., Ph.D.
Lecturer in Physical Chemistry, University of Edinburgh

The technique of chromatography as a means of separating chemical compounds had been known for many years before its tremendous possibilities were recognised by Martin and Synge [1] in their famous paper of 1941. Until recently however chromatography was confined to the separation of substances in the liquid phase either by column or paper chromatography. The possibility of the chromatography of vapours using a gas as " solvent " was in fact originally suggested by Martin and Synge, but the idea was not developed until quite recently [2–4] owing to the difficulty of detecting minute amounts of impurities in the carrier gas stream as it emerged from the column. Since these original papers were published much progress has been made and recently the number published has approximately doubled each year. This very rapid expansion has been due to the realisation that gas chromatography is an analytical tool of very remarkable characteristics. A recent paper [5] shows that it is now possible to analyse samples of as little as one hundredth of a microgram for several components with an accuracy of 1% or 2%. More often however a sample of 1–10 milligrams is required and can readily be analysed for ten of twenty components with an accuracy of about 1% within an hour. The apparatus is relatively cheap compared with other comparable analytical equipment such as mass spectrometers and infra-red spectrographs, and although a commercial unit may cost between £500 and £700 a perfectly satisfactory laboratory unit can be constructed for less than one-tenth of this cost. The apparatus can be operated by an unskilled worker and the interpretation of the results is straightforward. Gas chromatography has furthermore the unusual features that analyses can be carried out quantitatively for substances whose identity is not even known and that the various components of a mixture may if necessary be collected after analysis in a state of extreme purity and identified subsequently by other methods. The range of application is wide and most substances boiling under 300° C. can be dealt with readily.

The principle behind all chromatography is essentially simple. The mixture of substances to be separated is placed at one end of a column of adsorbent where the various components in the mixture partition themselves between the mobile and fixed phases, each according to its own partition coefficient. On addition of further quantities of pure eluting solvent the various components begin to move down the column, the more strongly adsorbed components moving the more slowly. Given a column of sufficient length they eventually separate into distinct bands.

In gas chromatography, where the mobile phase or " solvent " is a gas, hydrogen, helium, nitrogen and carbon dioxide are widely used for elution. The solid packing may be either a solid adsorbent such as activated charcoal, silica gel or alumina, or an inactive support such as kieselguhr, impregnated with 20–50% by weight of a suitable involatile liquid. Phthalate esters, silicone oils and greases, Apieson oils and greases, liquid paraffin and tricresyl phosphate are some of the liquids more commonly used.

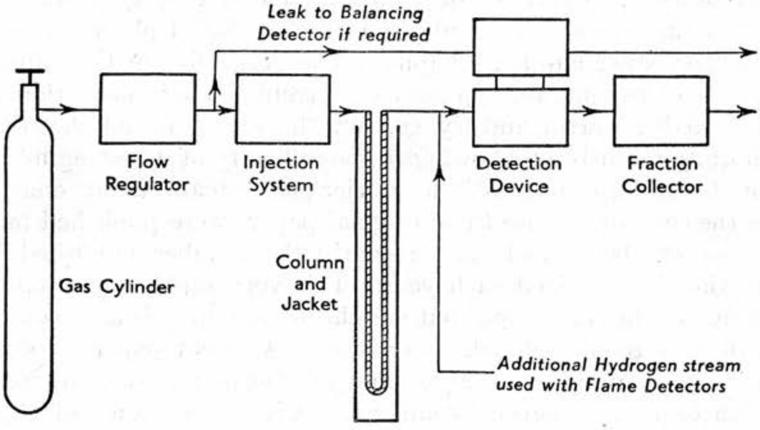

FIG. 1.—General gas chromatographic apparatus.

The experimental arrangement of a gas chromatography apparatus is shown in Fig. 1. The carrier gas is supplied from high-pressure cylinders via a number of reducing valves and flow stabilisers. The latter are necessary since most detectors used in gas chromatography are sensitive to fluctuations in flow rate and a regular flow free from both short- and long-term variations is required. A convenient form of stabiliser consists of a series of narrow bore capillary tubes each leading into a volume of about 50 c.c. When high-grade reducing valves are not available an even pressure across the column, and hence a steady flow rate, is most easily achieved by means of a mercury or water bubbler which allows excess gas to escape to the atmosphere. Samples are normally injected at the top of the column from a hypodermic syringe through a self-sealing rubber serum cap, but an alternative method employs a by-pass U-tube into which small quantities of mixture may be distilled from a vacuum system. This latter method is particularly useful in conjunction with gas kinetic experiments where only minute quantities of product are available. The column itself may be of various dimensions, but a convenient size for general use is 2–4 metres in length and 4–8 mm. in diameter. Columns are usually made of glass or copper tubing bent into the shape of a U or W and are thermostated at any desired temperature by means of an electrically heated jacket, a vapour jacket or liquid bath. A wide range of operating conditions is thus available and separations may be carried out at temperatures ranging from − 193° C. to 300° C. and with columns up to 20 metres in length.

The most important and most discussed part of the gas chromatography apparatus is the detector unit. Before describing the various types in detail, it is of some interest to consider briefly the problem involved in the detection of the various bands as they emerge from the column. The quantity normally used for analysis is a few milligrams and each component may be present in quantities of the order of 0·5 mg. If the components of the mixture have molecular weights in the region of 100 their volumes at NTP are about 0·1 ml. each. Normal flow rates in gas chromatography are about 30 ml. per minute and a typical band might emerge from the column over a period of say 3 minutes. The problem is therefore to detect and measure 0·1 ml. of gaseous impurity in 100 ml. of carrier gas. If an accuracy of 1% on each band is desired the noise level of the detector must be equivalent to not more than 1 mole of impurity in 100,000 of carrier gas. This requirement demands a very high stability in the detecting device and explains why, when using flow sensitive detectors, it is vitally important to have a highly stabilised flow rate.

Detectors may in general be divided into two classes :

(1) Those which measure a property of the impurity alone and give no response to the carrier gas itself. Measurement of gas volume after removal of carrier gas, titration of the eluant gas, measurement of the infra-red absorption of the emergent gas are methods belonging to this class.

(2) Those which measure a property of the carrier gas plus

impurity and by suitable balancing out circuits or compensating detectors isolate the excess signal due to the impurity. Examples of this type are the thermal conductivity cell, the gas density comparator and the hydrogen flame detector.

At first sight it might appear that the first type of detector would be the more stable and sensitive and would therefore be the more widely used. This however is not so, since all the detectors of the first type suffer from disadvantages of one sort or another. The simplest and most elegant detector of the first type is that due to Janak [6]. Carbon dioxide is used as carrier gas and after leaving the column is absorbed in 40% potassium hydroxide solution. Other gases apart from acids are then collected in a modified nitrometer and their volumes measured. The characteristic record from this detector is a stepped volume versus time plot. Each step is characteristic of one component. A typical record is shown in Fig. 2. The serious disadvantage of the Janak method is that only substances gaseous at room temperature may be analysed. It is however ideally suited to the analysis of permanent gases,

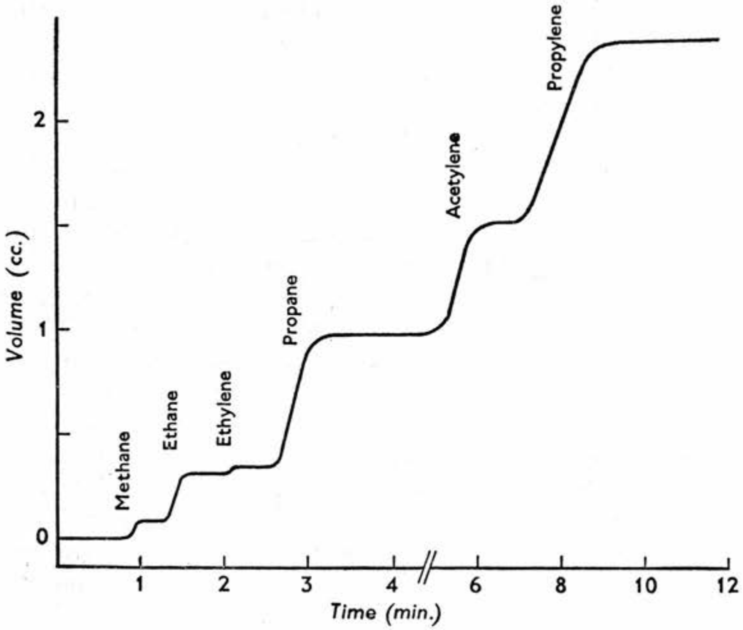

FIG. 2.—Typical volume/time plot obtained by the Janak method. Separation of hydrocarbons on "Alusil."

(*From* Ref. 6.)

mixtures such as "Calor gas" and all hydrocarbons containing up to four carbon atoms per molecule. The method of titration of the eluant gas has been used by Martin and James [2] for the analysis of mixtures of fatty acids and amines. In its more refined form the titration is carried out automatically using a photoelectric cell to monitor the addition of alkali or acid. The method suffers from disadvantages analogous to those of the Janak method. The sensitivity of both methods is somewhat limited, the first by the difficulty of accurate measurement of very small volumes of gas and the second by the difficulty of micro titration.

An ingenious method of detection of the first type for which high sensitivity is claimed is described by Martin and Smart [7]. Nitrogen is used as carrier gas and the mixture emerging from the column is passed through a small combustion chamber containing heated copper oxide. The emergent mixture, which contains carbon dioxide, is then passed through an infra-red analyser which measures carbon dioxide concentration. The noise level of this detector is very low and corresponds to about 1 part of carbon dioxide in 10^6 of nitrogen. Another detector of this type which may prove of high sensitivity is the flame luminosity detector. Hydrogen diluted with nitrogen is used as carrier gas and the mixture burnt in a light-tight container. The luminosity of the pure hydrogen flame is exceedingly low and increases greatly when a few parts per thousand of a carbon-containing compound is added to the gas stream. Preliminary experiments by the Author show that by using a photomultiplier cell it is possible to detect as little as 1 mole of benzene in 10^5 of carrier gas without any elaborate experimental precautions.

The majority of well-tried detectors are however of the second type and by far the most popular is the thermal conductivity cell [4, 8]. High stability is achieved by using two gauges in opposition. One gauge is placed in the pure carrier gas stream and the other in the stream emerging from the column. The gauges are made from 10-cm. lengths of fine platinum or tungsten wire (44–50 S.W.G.) which are mounted in two channels drilled close together in a large copper or brass block (usually some 8 cm. diameter and 10–15 cm. long). These two gauges form the adjacent arms of a Wheatstone bridge. By adjustment of the resistance of the other two arms the bridge is balanced when the pure carrier gas is passing through the column. The presence of an impurity in the gas stream from the column changes the thermal conductivity. This in turn alters the temperature of the fine wire and hence changes its resistance. The passage of impurity through the gauge thereby sets up an off-balance potential across the bridge. This potential is supplied to a sensitive galvanometer or a millivolt recorder. The typical record for this type of detector is a series of peaks, such as shown in Fig. 3, each peak being characteristic of one separated component in the mixture. The thermal conductivity detectors now in use have a noise level, with nitrogen as carrier gas, equivalent to about 1 mole of impurity in 10^5 moles of carrier gas.

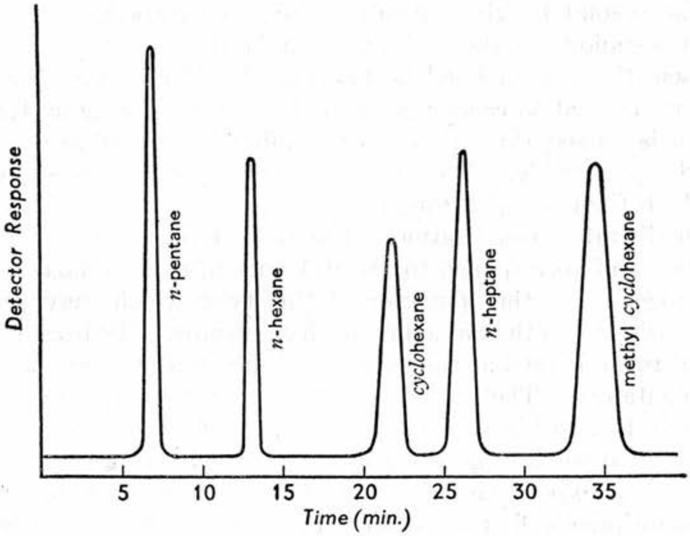

FIG. 3.—Separation of hydrocarbons using a thermal conductivity detector. (*From* Ref. 15 by kind permission of *Analytical Chemistry*.)

The gas density comparator of James and Martin [9] also compares in sensitivity with the thermal conductivity detector. This detector is an ingeniously contrived device which continuously measures the difference in density between the pure carrier gas and the gas emerging from the column. The density difference sets up a pressure differential across a small horizontal channel in the detector. This channel houses an electrical anemometer whose output is supplied to a recorder. Very high sensitivity has been claimed for the density balance, but data so far available indicate that with nitrogen as carrier gas the noise level is equivalent to a density change of about 5 parts in 10^5 [10]. A third detector now being used was first described by Scott [11] at the Vapour Phase Symposium held at Ardeer in 1955. In a modified form

[12, 13] nitrogen is used as carrier gas for the chromatography proper and a stabilised stream of hydrogen is mixed with the gas emerging from the column. The resulting mixture is burnt at a jet in contact with a thermocouple. When any impurity passes through the flame the temperature rises in proportion to the heat liberated and the resulting change in the e.m.f. of the thermocouple is supplied to a recorder. This detector has a sensitivity comparable with that of the others and the noise level corresponds to a heat output change in the flame of about 5 parts in 10^5.

It appears from these figures that the thermal conductivity detector is the most sensitive. It must however be remembered that, while the sensitivity per mole of the thermal conductivity detector is approximately constant, that of the density balance and the flame detector increases with molecular weight and heat of combustion respectively. Thus in terms of benzene, for example, the density balance has a noise level equivalent to 2×10^{-5} molar and the flame detector a noise level equivalent to about 3×10^{-6}. In this particular case the flame detector is the most sensitive. The sensitivity of the conductivity detector can however be increased about sevenfold if hydrogen is used as carrier gas instead of nitrogen and that of the density balance about twice. Nevertheless the flame detector is probably the most sensitive for high molecular weight substances with large heats of combustion and it has the advantage that the sensitivity per gram of substances of similar composition is approximately constant.

As can be seen, all these detectors possess the necessary sensitivity for the detection and measurement of quantities of the order of 500 micrograms with an accuracy of about 1% and it does not appear likely that any great increase in sensitivity can be achieved by further refinements. Detectors based on the first principle mentioned above do not however have the inherent disadvantage that their noise level is determined by the carrier gas, and there seems no reason why extremely sensitive detectors of this type should not be constructed to deal with analyses on the microgram and sub-microgram scale.

While it is important that detectors in gas chromatography should have a high signal to noise ratio, it is also essential that their response should be linear with respect to concentration. This has been shown to be the case for all the detectors mentioned above. Each detector has however its own peculiarities of calibration. The very simple detectors based on volume measurement and titration are by far the most accurate and it is claimed for the Janak method that an accuracy of ± 0·1% can be achieved. The other methods, while more versatile, are unfortunately as yet less accurate and ± 1% is the best that can be claimed. The gas density balance is in principle the simplest detector to calibrate and, once the identity of the emergent band is known, the calibration factor follows immediately from the difference between the molecular weight of the substance in question and that of the carrier gas. The flame detector has been shown to be reasonably linear in response to the heat liberated in the flame [13] and for rough quantitative work calibration factors are simply proportional to the heats of combustion of the substances being determined. The thermal conductivity detector requires more extensive calibration since differences in thermal conductivity, while a linear function of concentration at low concentrations, are not simply related to the molecular weight of the substance added but depend upon the temperature of the wire and surroundings of the gauge [14]. Calibrations must therefore normally be made with standard substances if high accuracy is required. Fortunately this rather unsatisfactory position can be substantially remedied if hydrogen is used as carrier gas. Hydrogen has a thermal conductivity some ten times that of most organic substances and an error of not more than 2% is introduced if it is assumed that equal molar concentrations of all organic substances produce the same change in thermal conductivity when added to hydrogen [15].

Reproducibility of analyses using the more indirect detectors is normally of the order of 1–2% if peak areas are measured. For many purposes however a slightly lower accuracy is satisfactory and it is sufficient to measure peak heights which are approximately proportional to amount. Unfortunately peaks tend to broaden slightly as the quantity in the band increases and strict linearity is not maintained. Peak heights as a measure of quantity also suffer from the disadvantage that simple methods of working out calibration factors cannot be applied unless a value is assumed for the peak width. It is furthermore essential, when using peak heights as a measure of amount, to employ a standard injection procedure, since any irreproducibility in the time taken to vaporise the sample will appear as a change in width and hence height of the peak [16]. Accuracy from peak height measurement is between 2% and 10% depending upon the care taken in calibration and injection procedure.

In the foregoing we have been concerned mainly with the maximum sensitivity and reproducibility of gas chromatography. It may well be asked, at the other end of the scale, how large a sample can conveniently be separated into its components by the technique.

To date several papers have appeared on the subject in connection with the preparation of highly pure organic compounds on the gram scale. With a column 10 mm. in diameter it is possible to separate up to about 1 gm. of substances boiling not too close together, although the efficiency of such a column decreases rapidly as the size of sample exceeds 0·1 gm. [17]. With larger columns the maximum loading is roughly proportional to the cross-sectional area. Evans and Tatlow, for example, have used a column 30 mm. in diameter for separation of up to 10 gm. of various fluorine compounds [18]. The quantitative recovery from such large-scale columns has been shown to be better than 0·5% and simple weighing of condensed fractions has been used as one of the most accurate quantitative methods of analysis [19].

On an even larger scale an industrial method has recently been described for the separation of 90,000 cubic metres of carbon dioxide from acetylene per day [20]. The mixture is introduced into the centre of the column packed with carbon. This packing is progressively shaken down the column at a carefully controlled rate so that the carbon dioxide emerges from the top of the column and the acetylene from the foot. The purity claimed for the two fractions is 99%.

Having described in some detail the essential features of the apparatus used for gas chromatography, it is of some importance to consider the various factors which influence the degree of separation which can be achieved with a given mixture and to indicate briefly what conditions of column temperature, choice of liquid phase, packing, flow rate and so on will lead to the most efficient separation of any pair or series of substances.

In general two quite different effects must be distinguished from the start. The separation of two components by a column will depend firstly upon the relative separation of the peak maxima, given for example by the quotient of the times taken for the peak maxima to appear, and secondly upon the widths of the two peaks relative to the separation of the maxima. The first of these, that is the relative separation of the peak maxima, is determined entirely by the thermodynamics of the process of chromatography, and the second, that is the relative widths of the peaks, by the kinetics of the process, the rates of attainment of equilibrium, the rates of diffusion in the two phases, etc.

The thermodynamics of the chromatographic process will be considered first. The rate at which any band of a component X moves down a chromatographic column depends simply on the solubility of the component in the liquid phase and is given by:

$$\frac{\text{Rate of movement of band}}{\text{Rate of movement of carrier}} = \frac{\text{Amount of X per cm. column length in gas phase}}{\text{Total amount of X per cm. column length}}$$

The ratio on the right-hand side of the equation is directly related to the solubility of the component in the liquid phase and the relative cross-sectional areas of the liquid and gas phases of the column. Usually in discussing the movement of bands in a column it is desirable to eliminate the time element and to use the concept of the "retention volume." The "retention volume per gram of liquid phase" for any substance is defined as the volume of eluting gas which must pass into the column in order to elute the band of the substance through a length of column containing 1 gram of liquid phase. "The net retention volume per gram" is this quantity reduced by the free volume of the appropriate length of column. Net retention volumes are normally measured experimentally at the temperature and pressure of the column and will be denoted by V_r^T. In a theoretical treatment it is however often convenient to use retention volumes reduced to NTP. Such retention volumes will be denoted by V_r^{NTP}. By simple manipulation of the basic equation above it can be shown that the net retention volume per gram at the column temperature and pressure is related to the solubility of the component in question by the equation

$$V_r^T = s/d$$

where $s = \text{solubility} = \dfrac{\text{(moles X per c.c. of liquid phase)}}{\text{(moles X per c.c. of gas phase)}}$;

d = density of liquid phase.

Now the solubility of a vapour may be written in terms of its saturation vapour pressure and its activity coefficient in the solvent. This substitution then gives the following relation for the net retention volume reduced to NTP:

$$V_r^{NTP} = \frac{1}{f \cdot p^0} \times \frac{22{,}400 . P}{M_s}$$

where p^0 = saturation vapour pressure of the pure component X;
f = the activity coefficient of X in the column solvent ($f = 1$ for pure substance);
22,400 = gram molecular volume of an ideal gas in c.c. at NTP;
P = column pressure;
M_s = molecular weight of column liquid.

If this equation is now differentiated with respect to temperature one obtains:

$$\frac{d \ln V_r^{NTP}}{d(1/T)} = -\frac{d \ln p^0}{d(1/T)} - \frac{d \ln f}{d(1/T)}$$

$$= (1/R)[\Delta H_{vap} - \Delta H_m] = -\Delta H_s/R$$

where ΔH_{vap} = latent heat of vaporisation of X per mole;
ΔH_m = heat of mixing of X with column liquid;
ΔH_s = heat of solution of X in column liquid.

For the very dilute solutions with which we are concerned the heat of mixing is approximately independent of temperature and we can therefore write

$$\Delta H_s = -a \times \Delta H_{vap}$$

$$\ln V_r^{NTP} = -a \ln p^0 + \text{const.}$$

Plots of $\ln V_r^{NTP}$ against $1/T$ should thus give straight lines whose gradients give heats of solution [21] and plots of $\ln V_r^{NTP}$ against $\ln p^0$ should give straight lines whose gradients give the ratio of the heat of solution to the heat of vaporisation. Plots of this type are given by Purnell [22]. Ideal solutions show values of $a = 1$ while those exhibiting positive and negative deviations from Raoult's law have values of 'a' respectively less or greater than unity.

It is also found that with homologous series forming ideal solutions the $\ln V_r^{NTP}$ versus $\ln p^0$ plots for different members are coincident so that differences in retention volumes are the result purely of differences in vapour pressure. The chromatographic separation is thus equivalent to very efficient distillation. With a series forming non-ideal solutions a series of lines is normally obtained [23] (*see* Fig. 4), the lines being approximately equally spaced from each other. The irregularities of solution may therefore either enhance or reduce the effect of vapour pressure differences on the relative retention volumes of substances. Fig. 4 illustrates the former, where a better separation is obtained with the column in question than would be if the solution were ideal.

Retention diagrams of the above type are of use in predicting the type of liquid phase best suited for a given separation, since they enable one at a glance to read off retention volume differences for any two members of a series at any temperature. The diagrams can be constructed using relatively crude apparatus and it is normally necessary to experiment with only two members of a series at a few temperatures since intermediate members can be interpolated on the basis of equal spacing of the lines.

The above considerations relate only to the thermodynamics of the chromatographic process treated as a dynamic equilibrium. No information can be obtained from this type of treatment about the actual separating efficiency of a chromatographic column. If chromatography were an ideal process, that is

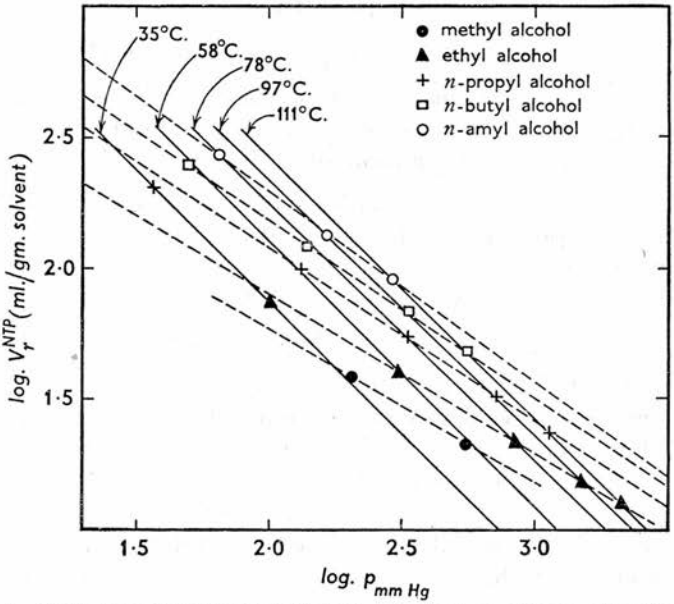

FIG. 4.—Retention diagram for aliphatic alcohols on silicone oil D.C. 710. (*From* Ref. 23.)

(*a*) if there were no diffusion in either liquid or gas phases in the direction of flow,

(*b*) if equilibrium between the gas and liquid phases were attained instantaneously (a condition contradictory to (*a*) above)

(*c*) if all conceivable paths in the column were of equal length, *i.e.* if there were no "eddy diffusion," and

(*d*) if the solution isotherms were linear,

then any band would emerge from the column with its original contours unchanged and perfect separations could be obtained, provided that the bands originally introduced on to the column were sufficiently sharp. In practice only the last of these conditions holds even approximately and, as a result, initially sharp bands become increasingly diffuse as they proceed along the column. The "efficiency" of any column, apart from thermodynamic considerations, should clearly be related to this smudging of the bands, and it is most simply given by the ratio of the retention volume at the peak maximum (V_r^T) to the peak breadth (β) at a height $1/e$ of the peak maximum.

In many ways the process of chromatography is analogous to that of distillation and it has been found that a most useful concept in describing column efficiency is that of the theoretical plate. The concept was first introduced to chromatography by Martin and Synge [1] who treated the process as one of extractive distillation. The column was imagined to consist of a series of identical plates in each of which there was equilibrium between the liquid and gas phases, and in each of which the concentrations in the two phases were uniform. The process of chromatography was then imagined to proceed by the successive addition of equal small volumes δv of solvent or gas to the column. After each addition the column was allowed to rest so that equilibrium and uniformity of concentration could be re-established in each plate. Repetition of this discontinuous process results in the gradual movement down the column of a charge originally on the first plate, and the amount of substance on each plate after n such additions is given by the size of successive terms in the expansion of

$$[(1 - \delta v/V) + (\delta v/V)]^n$$

where $(\delta v/V)$ is the fraction of charge on any plate transferred to the next plate by the addition of a volume δv to the top of the column. When n tends to infinity and $\delta v/V$ becomes very small this binomial distribution tends to the normal error distribution curve. The maximum of the curve is found either by differentiation or by picking out the largest term in the above expansion. The serial number of this term then gives the plate number at which the peak maximum is to be found after n additions of volume δv. By this more elaborate derivation it is found that the peak maximum moves down the column at the rate given by the first equation in this section. It is however also possible to derive a value for the width of the peak at a height $1/e$ of the maximum. Gluckauf [24] has given a similar treatment of the problem in which the addition of liquid to the column is regarded as a continuous process rather than a stepwise one. He finds that this treatment gives essentially the same result as the discontinuous treatment, although the bands are slightly more diffuse by the continuous treatment in a column of the same plate efficiency. The equation given to a first approximation by both treatments for the relation between retention volume, band width and plate number N is:

$$N = 8(V_r^T/\beta)^2$$

or

$$\text{Column efficiency} = V_r^T/\beta = (N/8)^{1/2}$$

Since the number of plates in any column is proportional to its length, other factors being equal, the efficiency of any column increases as the square root of the length and it is not normally practicable to increase the efficiency of a column very greatly by increase in its length. Under any experimental conditions the efficiency and plate number of any column can readily be evaluated simply by measurement of the retention volume and the peak breadth β.

Theoretical calculations as to how the plate efficiency of columns depends upon flow rate, particle size, temperature, nature of the liquid phase and carrier gas, etc., have been made by Klinkenberg *et al.* [25]. They have shown that the main disturbing features in gas chromatography are eddy diffusion, gas diffusion and resistance to mass transfer between the fixed and mobile phases. Each of these factors contributes a substantially independent term to the height equivalent to a theoretical plate (HETP). Their theoretical equation is:

$$\begin{aligned}(\mathrm{HETP}) &= 2\lambda d_p + \gamma \mathrm{D}_{gas}/u + \frac{8}{\pi^2}\times\frac{k'}{(1+k')^2}\times\frac{d_f^2}{\mathrm{D}_{liq}}\times u\\ &= \underset{\substack{\text{Eddy}\\ \text{diffusion}\\ \text{term}}}{\mathrm{A}} + \underset{\substack{\text{Gas phase}\\ \text{diffusion}\\ \text{term}}}{\mathrm{B}/u} + \underset{\substack{\text{Resistance to}\\ \text{mass transfer}\\ \text{term}}}{\mathrm{C}.u}\end{aligned}$$

where u = linear flow velocity of gas through column;
λ = constant depending upon regularity of packing;
γ = constant depending upon tortuosity of paths in column;
d_p = diameter of particles; d_f = thickness of liquid film on particles;
D_{gas}, D_{liq} = diffusion coefficients of the component in gas and liquid phases;
k' = column partition coefficient

$$= \frac{\text{(moles component per unit length of liquid phase)}}{\text{(moles component per unit length of gas phase)}}.$$

The variation of the HETP with flow rate is summarised in the second equation above. At low flow rates diffusion in the gas phase is the most important term, while at high flow rates this contribution is negligible and the resistance to mass transfer, representing the difficulty of attaining proper equilibrium between the liquid and gas phases, becomes the main contributing term. Eddy diffusion, resulting from the unequal lengths of the various paths round the particles of column packing, contributes a constant amount independent of flow rate. The value of HETP thus falls from a high value at low flow rates to a minimum at $u = (B/C)^{1/2}$ and then rises again more or less linearly. When using any particular column it is thus important to choose the flow rate such that the optimum efficiency is obtained. This generally occurs at a linear flow rate of about 2 cm./sec.

In addition to choosing a suitable flow rate it is clearly advantageous to choose column packing, liquid phase, temperature, etc., so as to minimise the constants A, B and C. The first term in the equation for HETP, the contribution of eddy diffusion, may be reduced by reduction in particle size. Unfortunately this cannot be taken too far since it becomes increasingly difficult to pack columns evenly with decrease in particle size and the constant λ rises rapidly with decrease much below 100 mesh. In practice the constant A has a minimum value for particles between 30 and 80 mesh (approx. 550–200 μ diam.). The term B/u arises from the contribution of gaseous diffusion and can be reduced by decrease of D_{gas}. This may be achieved either by using a denser gas as carrier (nitrogen and carbon dioxide in place of hydrogen or helium), by lowering the temperature of the column or by increasing the pressure. The quantity γ depending upon the tortuosity of the path is usually between 0·5 and 1·0.

The final term in the equation gives the contribution of resistance to mass transfer, and it may be reduced in a number of ways. The use of a non-viscous liquid as stationary phase will increase D_{liq} and so reduce C; a decrease in the thickness of the liquid film d_f will also decrease C. This decrease may be brought about in two ways, either by decreasing the size of the particles or by cutting down the liquid/solid ratio. The first expedient will however lead to an increase of A unless the particle size is kept above 80 mesh. A decrease in the liquid/solid ratio is therefore a more satisfactory way of decreasing C. The amount of liquid cannot however be cut much below 10% since the column then becomes increasingly easy to overload. In practice it is found that little advantage is gained if less than 20% of liquid phase is used. The quantity $[k'/(1 + k')^2]$ may be reduced by increase in k' (which has a value between 1 and 100 for most systems). This may be achieved either by increasing the amount of liquid phase in the column or by increasing the solubility of the component in the liquid phase. The former does not however bring about the desired result since the thickness of the film is necessarily increased and the net result is an increase in C. Lowering the temperature will generally lower the resistance to mass transfer by increasing the solubility but if taken too far may so increase the viscosity of the liquid phase that an overall increase in C occurs. Such a situation will only arise however if the liquid phase becomes glassy or crystalline. Decrease of temperature will therefore nearly always reduce the constant C; it furthermore decreases D_{gas} and so is favourable to the reduction of the constant B also.

For optimum efficiency of a gas chromatographic column the following points should therefore be borne in mind:

(*a*) Particle size should be between 30 and 80 mesh.
(*b*) A non-viscous liquid phase in the ratio of about 20% by weight to solid support should be used.
(*c*) The carrier gas should be of high molecular weight, although the value of increased sensitivity which may result from the use of hydrogen or helium must be weighed against this.
(*d*) No advantage is gained by use of reduced pressure for column operation either on thermodynamic or kinetic grounds.
(*e*) Column temperatures should be as low as is consistent with obtaining separations in a reasonable time but not so low that the liquid phase becomes glassy or crystalline.
(*f*) Linear flow rates of about 2 cm./sec. should be employed.

Bearing all the above points in mind it is possible to build a column with a plate height of about 0·2 cm. A 2-metre column will thus have a plate efficiency of about 1000 and with such a column it is possible to separate almost completely substances whose solubilities differ by a factor of 1·20. If the substances being separated formed ideal solutions in the liquid phase, then separation could be obtained of substances boiling 5° C. apart. Since columns up to 20 metres in length are now in regular use, it is possible to separate substances boiling 1·5° C. apart or with solubilities differing by about 6%. In most simple cases, where only a few compounds are to be separated, it is more convenient to choose a solvent where the irregularity of solution will enhance vapour pressure differences than to use excessively long columns, but in the analysis of very complex hydrocarbon mixtures solvent variation is not suitable and it is now becoming customary to employ very long columns for these difficult analyses.

The great power and appeal of the method of gas chromatography evidently lies in a combination of features. It is a method of analysis of very wide applicability and of high efficiency; it is cheap, rapid and accurate; it is a micro method and requires only a minimum amount of skill in operation and interpretation. To date, the technique has been most widely used in the petroleum industry, but it is now being rapidly extended to the analysis of all types of organic mixtures. In addition to its use as a routine analytical tool for control of industrial processes, it is finding important applications in the field of pure preparative organic chemistry and is already recognised as an ideal analytical method for use in connection with experiments in chemical kinetics. These experiments normally yield only minute amounts of product, since it is advantageous to work with low concentrations of reactants and low percentage conversions. In the past analyses of the complex product mixtures has often been impossible but with an instrument capable of analysing milligram amounts of complex mixtures the range of kinetic experiments which can be tackled by the analytical method is greatly increased. It is probably true to say that within the next few years apparatus for gas chromatography will find an essential place in almost every physical chemical laboratory concerned with chemical kinetics and will form an integral part of the equipment of any organic laboratory concerned with the micro analysis of organic mixtures in general.

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GAS CHROMATOGRAPHY

J. H. Knox

METHUEN'S MONOGRAPHS ON
CHEMICAL SUBJECTS

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GAS CHROMATOGRAPHY

Gas Chromatography

John H. Knox

Lecturer in Chemistry in
the University of Edinburgh

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Contents

Preface

Gas Chromatography is a subject whose development has been extraordinarily rapid since Martin and James described the first successful experiments on partition gas chromatography in 1952. In 1956 Phillips published the first book devoted entirely to gas chromatography. His book was followed a year later by Keulemans and Verver's *Gas Chromatography*, and this was revised in 1959. Keulemans and Verver has become the standard work on the subject but it is already somewhat out of date and there is a need for a monograph which is orientated to take account of recent trends, and in particular deals in some detail with capillary columns and ionization detectors.

The aim of the present volume is to give an adequate coverage to these new aspects and at the same time to present the basic principles of gas chromatography in a simple way. Sufficient detail of apparatus has been included to enable a reader with access to a workshop to construct much of his own equipment. The sections on theory assume a knowledge of elementary physics, chemistry and mathematics and it is hoped that their understanding will enable users of gas chromatography to improve the performance of their equipment, to obtain more efficient resolution of mixtures and faster analyses.

In a short book about a technique as widely used as gas chromatography there are bound to be omissions, and in particular any examples of specific applications are likely to be illustrative. Apart from noting some general principles to be followed in the selection of the best operating conditions for any particular analysis no attempt has been made to deal with this field comprehensively. For such details the reader is asked to consult the original literature and he cannot do better than refer initially to *Gas Chromatography Abstracts*, an annual publication which contains short abstracts of all papers on gas chromatography published during the preceeding year. The really valuable feature of *Gas Chromatography Abstracts* is its extensive classified subject index which enables one to discover very rapidly all papers relevant to any particular topic.

ACKNOWLEDGEMENTS

I am very much indebted to the many workers in gas chromatography with whom I have had contact from time to time, and in particular to Dr Lovelock, Dr Scott and Dr Purnell whose combined researches have had such a major influence on the field.

I am also indebted to Prof. Trotman-Dickenson for many stimulating discussions at Edinburgh and also for his part in the early stages of writing this book which was originally planned as a joint work.

I should finally like to thank Mr W. B. Brown for the useful suggestions he made on reading the original manuscript and for his help in proof correcting.

September 1961 JOHN H. KNOX

CHAPTER 1

Introduction

Chromatography is one of the most widely used general methods for separating the components of mixtures. It depends upon differences in the distribution coefficients of the components between a fixed and a mobile phase. In the early chromatographic experiments of Tswett in 1906 a small quantity of a solution of plant pigments was placed on the top of a column containing powdered chalk and was then washed down the column by means of light petroleum. The various components of the original mixture were observed to separate into coloured bands which moved down the column at different speeds and eventually became completely separated. The name 'chromatography' derives from this original experiment. However, the process of separation in no way depends upon the substances being coloured, and from 1930 onwards the method of elution chromatography, as it is now called, became increasingly used for the separation of uncoloured as well as coloured substances. The position of the bands of uncoloured substances could be discovered by extruding the column and cutting it into sections which were then individually analysed. However, a much more satisfactory method of collecting separated substances is to elute them from the column and collect fractions of the emergent solution. These fractions can then be worked up and analysed, and the column used again.

The process of elution chromatography can be represented formally as shown in Figure 1.1. The column may be imagined to consist of a mobile phase of average cross-sectional area a_m, and a fixed phase of average cross-sectional area a_f. When a sample of a single substance is placed on the top of the column it will distribute itself between the two phases according to its equilibrium distribution coefficient and the relative amounts of the two phases. In the early chromatographic experiments the fixed phase was an adsorbent solid and the amounts of a given substance in the two phases were governed by its adsorption coefficient. In 1941 Martin and Synge[1] brought about a great advance in chromatography by showing that a liquid supported upon a solid could be used as the fixed phase. Originally they used water supported on silica gel as the fixed phase and chloroform as mobile phase for the separation of acetylated amino acids. Later they invented the powerful technique of paper chromatography where the water bound in filter paper is the fixed phase. In liquid/liquid chromatography the amounts of a substance in the two phases are determined by its relative solubility in the two phases.

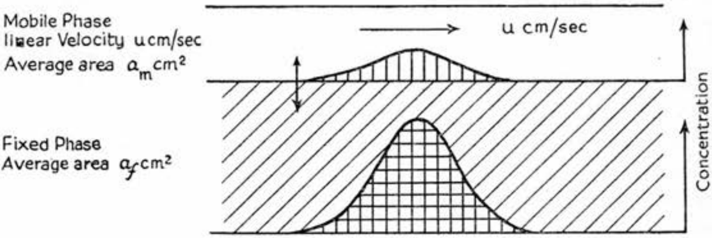

FIG. 1.1. Formal representation of elution chromatography, showing concentration distribution in mobile and fixed phases.

When the eluting liquid or mobile phase is passed through the column only those molecules of the sample which are in the mobile phase at any instant can move down the column. However, since there is a dynamic equilibrium between the fixed and mobile phases no single molecule will remain for long in any one phase and the rate of movement of a band of any substance will be the same as the average rate of movement of the individual molecules. Thus

$$\frac{\text{Rate of movement of band}}{\text{Rate of movement of mobile phase}} = \begin{array}{l}\text{Fraction of molecules}\\ \text{of substance in mobile}\\ \text{phase at any instant}\end{array}$$

Since this fraction is determined only by the distribution coefficient and the amounts of the two phases, substances with different distribution coefficients will move at different speeds and can therefore be separated. However any band inevitably broadens as it moves along the column and it is therefore more difficult to separate compounds whose distribution coefficients are similar than those whose distribution coefficients differ widely.

Martin and Synge in their original paper also suggested in passing that it might be possible to use a gas as the mobile phase. This suggestion was not followed up for several years. This was partly due to the fact that the original paper was published in the *Biochemical Journal* and the suggestion of gas chromatography was not noticed by the chemists who were most likely to use it, but also partly because of the obvious experimental difficulties in detecting and measuring the very small concentrations of eluted vapours in the gas emerging from the column. The first successful gas chromatographic experiment was carried out in 1952 by James and Martin[2] who separated mixtures of fatty acids on a column containing silicone oil supported on kieselguhr. They determined the amounts of the separated acids as they emerged from the column by means of an automatic titration

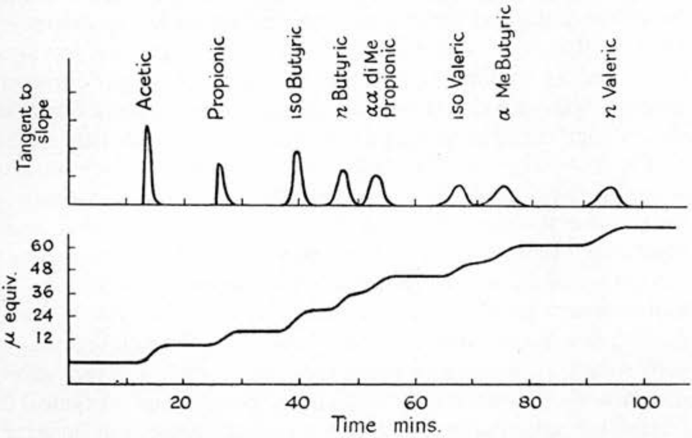

FIG. 1.2. Gas chromatogram of fatty acids by James and Martin. Column length = 11 ft; temperature = 137°C; liquid phase = silicone oil + 10 per cent stearic acid; detection by titration (taken from James and Martin (1952) *Analyst* 77, 915).

device. One of their original chromatograms, a plot of titre against time, is shown in Figure 1.2. This type of stepped chromatogram where the height of each step is a measure of the quantity of each separated substance is known as an integral chromatogram. The more usual differential chromatogram is obtained from it by plotting the tangent to the curve as a function of time.

James and Martin's method of detection had obvious disadvantages and gas chromatography cannot be said to have become a general technique until Ray[3] introduced the katharometer as detector in 1954. Katharometers or thermal conductivity gauges had previously been used by Phillips as detectors in displacement gas chromatography. Although this technique was developed slightly before the elution method it has serious disadvantages as an analytical method and is now little used. The katharometer consists of an electrically heated wire placed in the gas stream. Changes in the composition of the gas alter the thermal conductivity and hence the temperature and resistance of the wire. By recording the change in resistance the elution of substances from the column can be followed. Since the katharometer measures the instantaneous concentration of the gas passing over it the chromatogram obtained is of the differential type consisting of a number of peaks the area of each of which gives a measure of the amounts of the separated components. A typical differential chromatogram obtained with a katharometer as detector is shown in Figure 1.3.

The application of the katharometer to gas chromatography solved many of the initial problems and the basic design of the equipment has changed little since that time. The essential features of any gas chromatography apparatus are shown in Figure 1.4. Carrier gas from a cylinder or other convenient source is passed through a pressure reducing valve and a drying tube into a flow regulator which ensures that an even flow of carrier gas passes to the column. The gas then passes the injection point where it picks up the sample for analysis. The injection should be as nearly instantaneous as possible. The carrier gas + sample pass into the column where the components of the mixture are separated. The column is often made up of one or more U tubes each about 3 ft in length and is thermostatted. The gas emerging from the column flows through the detector which measures

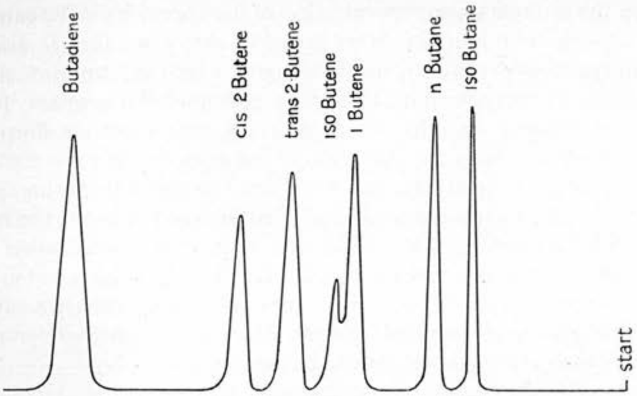

FIG. 1.3. Differential chromatogram showing the separation of C_4 hydrocarbons on a packed column using katharometer detection (by kind permission of Perkin-Elmer Corp.).

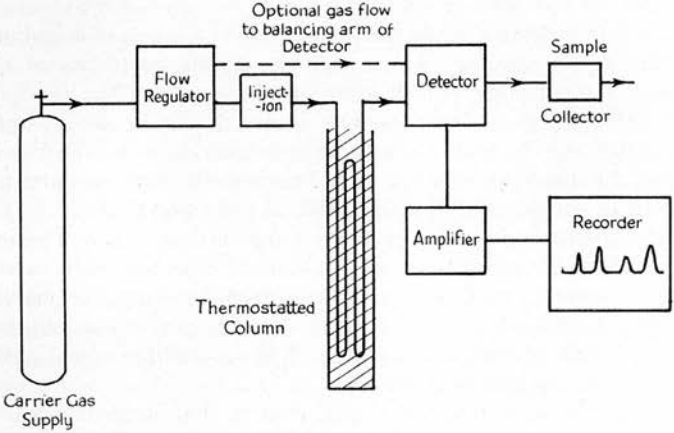

FIG. 1.4. Basic gas chromatography apparatus.

either the instantaneous concentration of the impurities in the carrier gas or their total amount. Most detectors are of the former differential type and provide an electrical signal which is proportional to the impurity concentration. This signal is amplified if necessary and fed to a suitable recorder which generally draws out the finished chromatogram. After passage through the detector the gas stream is either vented to the atmosphere or passed through a trap where the vapours in the carrier gas can be collected for identification. The best identification methods are those which depend upon molecular structure for example, nuclear magnetic resonance, infra-red or mass spectrometry. With the possible exception of the electron capture detector no detector can itself identify substances except in so far as it enables their retention volumes to be measured.

Since 1954 two major developments in gas chromatography have occurred. Although the katharometer is an excellent general detector it cannot detect concentrations of impurity below about one part in 10^6 of carrier gas. By about 1958 the need for more sensitive detectors was becoming pressing. The main reason for the limited sensitivity of the katharometer is that it measures a common property of all components of the column gas and its ultimate limit of sensitivity is set by the stabilities of the carrier gas stream and of the electrical supply. In order to increase sensitivity by several orders of magnitude detectors are required which measure specific properties of the eluted vapours and give little or no signal from the carrier gas itself. In 1958 two such detectors were invented, the Lovelock argon detector[4] and the McWilliam flame ionization detector.[5] They were some 10^3 times as sensitive as katharometers. Both measure the electrical conductivity of weakly ionized gases and they depend for their high sensitivity upon the fact that organic molecules or products from them are much more readily ionized than the usual carrier gases – helium, argon, hydrogen and nitrogen. Their invention has led to great increases in column efficiency since one can use much smaller samples and columns containing much lower loadings of stationary phase than was previously possible.

About the same time Golay[6] described the first successful use of a coated capillary as a gas chromatographic column. This idea had originally been suggested by Martin in 1956. Only minute samples can be retained on these columns since the liquid phase loading is very low, and the invention of the ionization detectors was most timely. It was soon evident that highly efficient analyses could be performed on capillary columns much faster than had previously been possible with packed columns. A typical separation on a capillary column is shown in Figure 1.5. It was at first believed that capillary columns had an intrinsically higher resolving power than packed columns. However, recent theoretical and practical work has indicated that the two types of column, if constructed in equivalent ways and operated under equivalent conditions, should have approximately the same speed. Nevertheless each type of column has its own valuable features and neither can be dispensed with.

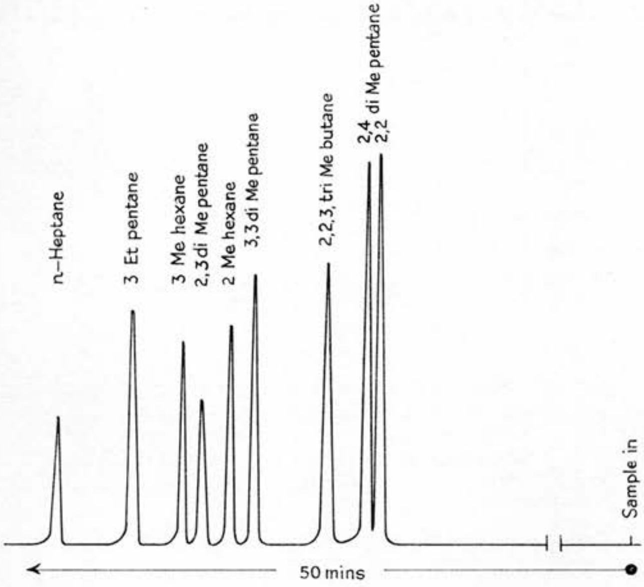

FIG. 1.5. Separation of C_7 hydrocarbons on a 250 ft long, 10 thou. diameter, capillary column. Liquid phase = squalane; column temperature = 72°C (from Desty, Goldup and Whyman (1959) *J. Inst. Petr.* **45**, 287).

Today the range of gas chromatography is wide. It can be used for the analysis of hydrogen isotopes or compounds such as natural waxes containing components boiling above 400°C. Illustrative chromatograms are shown in Figure 1.6 and 1.7. The upper range of gas chromatography is set not so much by the involatility of the substances to be analysed as by their thermal instability at the high temperatures which are required for their analysis. With the increase in the sensitivity of detectors and the possibility of using lower analysis temperatures and faster columns, the upper range is continually being extended. There seems no ultimate reason why gas chromatography should not be used for the determination of the molecular weight distribution of polymers and for the analysis of inorganic salts boiling above 1,000°C.

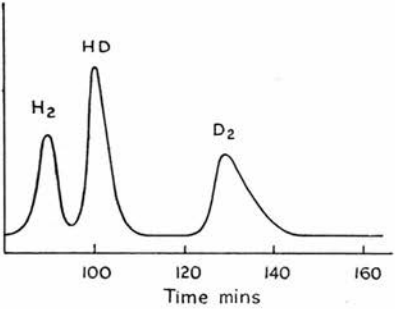

FIG. 1.6. Separation of hydrogen isotopes on a chromia/alumina catalyst at −196°C with neon as carrier gas (taken from Hunt and Smith (1961) *J. Phys. Chem.* **65**, 87).

The sample size in analytical gas chromatography may be between 10^{-8} and 10^{-2} g and by using large diameter columns preparative scale gas chromatography can be carried out with samples up to 100 g. The total quantitative range thus covers ten orders of magnitude. The analysis time may vary considerably, from several hours for a complex mixture to a few seconds with a simple mixture using high-speed columns. The accuracy of gas chromatography is of the order

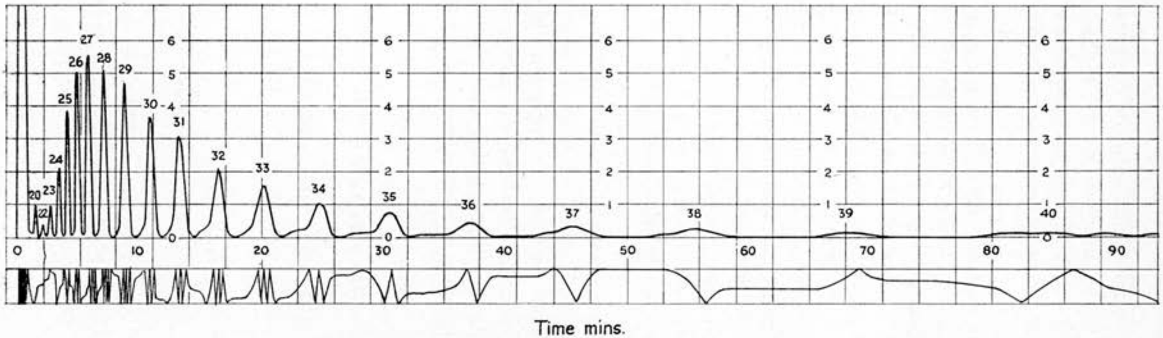

FIG. 1.7. Chromatogram of a naturally occurring wax containing C_{20} to C_{40} straight chain hydrocarbons. Stationary phase = silicone rubber; temperature = 286°C. Lower trace gives integrated peak area (taken from Aerograph *Gas Chromatography Notebook*, publ. by Wilkens Instrument and Research Inc.).

of 1 per cent on the amount of any substance separated. It is thus possible to determine the quantity of a trace component with the same relative accuracy as that of a major component in a mixture since the sensitivity of the detecting devices can normally be altered by many powers of ten.

Gas chromatography thus compares favourably in speed, sensitivity, versatility and accuracy with other general methods of analysis. The feature that gas chromatography yields a single peak for each separated component is of tremendous value when analysing complex mixtures, but has the inevitable drawback that identification of separated components is difficult. Ideally therefore gas chromatography should be supplemented by identification methods which give several peaks for each component. Such methods are nuclear magnetic resonance, infra-red and mass spectroscopy. Probably one of the most powerful analytical devices yet devised is a gas chromatography apparatus used in direct conjunction with a time of flight mass spectrometer which gives a mass spectrum for each component as it emerges from the column.

A final but important advantage of gas chromatography over comparable methods of analysis is that the equipment is relatively cheap. The most expensive single part of any apparatus is generally the electronic recorder. Commercial instruments complete cost about £1,000 but apart from the recorder (costing £150–300) a home-made gas chromatography apparatus can often be constructed for less than £100.

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CHAPTER 2

Theory of Gas Chromatography

Definitions

Before developing the theory of gas chromatography a number of relevant terms must first be defined. The majority of chromatograms are of the differential type and since this form is more simply related to the theory of chromatography we shall confine our attention to it. An integral chromatogram is always derivable from any differential chromatogram.

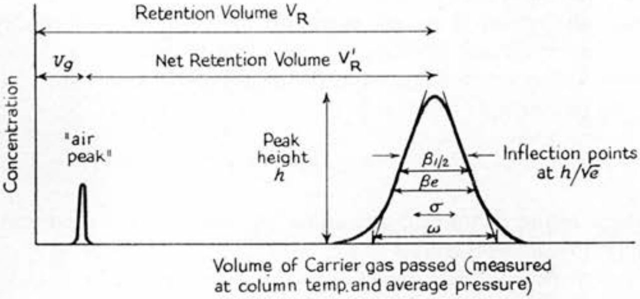

FIG. 2.1. Differential chromatogram of a pure substance containing a trace of air.

Figure 2.1 illustrates a typical chromatogram of a pure substance containing a trace of an insoluble impurity (for example air) which moves along the column at the same rate as the carrier gas.

The volume of carrier gas passed between the point of injection of the sample and the peak maximum, and measured at the average pressure and temperature of the column is termed the true retention volume of the substance and is denoted by V_R. V_R is related to the retention time (the time between injection and peak maximum), t_R, by the equation

$$t_R = V_R/f_{\text{av}}$$

where f_{av} is the average flow rate through the column. Owing to the compressibility of the carrier gas this average flow rate differs from the outlet flow rate f_{o}. If p_{i}, p_{o} and p_{av} are respectively the inlet, outlet and average pressures in the column then

$$p_{\text{av}}/p_{\text{o}} = f_{\text{o}}/f_{\text{av}} = \frac{2}{3}\cdot\frac{(p_{\text{i}}/p_{\text{o}})^3-1}{(p_{\text{i}}/p_{\text{o}})^2-1} \tag{2.1}$$

For $p_{\text{i}}/p_{\text{o}}$ between 1·0 and 1·5 the difference between p_{av} and the mean column pressure $p_m = \frac{1}{2}(p_{\text{i}}+p_{\text{o}})$ is less than 2 per cent and the two may be taken as equal for practical purposes. For larger ratios the difference is more serious as can be seen from Figure 2.2.

Since the retention volume is usually measured experimentally at the temperature and pressure of the laboratory the true retention volume has to be obtained from the experimental retention volume V_{exp} by the formula

$$V_R = V_{\text{exp}}(Tp_r)/(T_r p_{\text{av}}) \tag{2.2}$$

where T is the column temperature; T_r and p_r are the laboratory temperature and pressure.

The retention volume of air equals the volume of gas in the column (if measured at the average column pressure) and is denoted by v_g. It is often called the dead volume of the column. The net retention volume V_R' is the true retention volume less the dead volume of the column, that is

$$V_R' = V_R - v_g \tag{2.3}$$

As a band of vapour X moves down the column it spreads out owing to a number of perturbing factors, and the narrowness of any band relative to the retention volume is a measure of the efficiency of the column. When the sample size is not too large the distribution coefficient of X between the fixed and mobile phases is independent of the concentration of X and the chromatographic peaks are symmetrical. They should theoretically follow the Gaussian error curve

$$y = h . e^{-x^2/2\sigma^2} \tag{2.4}$$

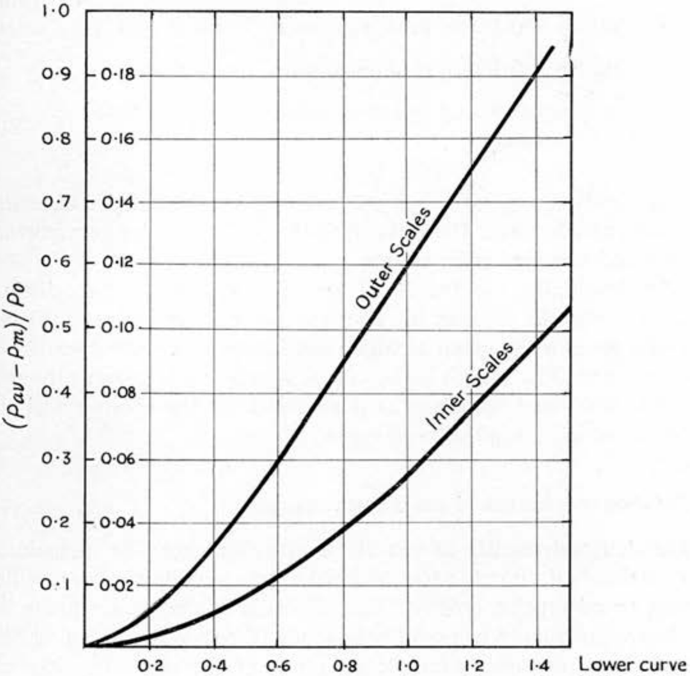

FIG. 2.2. Difference between average and mean column pressures.

where y is the peak ordinate at any distance x from the centre. The curve has inflection points at $y = h/e^{1/2}$. The breadth of the peak at a height h/e (that is 0·368 of the peak maximum) is $\beta_e = 2\sqrt{(2)}\sigma$. V_R/β_e

may be taken as a convenient measure of column efficiency. However, it is sometimes simpler to measure the peak width at half the maximum height or the width obtained by drawing tangents from the inflection points to the base. The three measures of peak width are related to the standard deviation, σ, as follows:

$$\left.\begin{array}{ll}\text{Width at 0·368 of peak maximum} & \beta_e = 2\sqrt{(2)}\sigma \\ \text{Width at 0·500 of peak maximum} & \beta_{1/2} = 0{\cdot}834\beta_e \\ \text{Base width found by extrapolation} & w = 0{\cdot}414\beta_e \\ \quad\text{of tangents} & \end{array}\right\} \quad 2.5$$

Any of the quantities V_R/β_e, $V_R/\beta_{1/2}$ and V_R/w can be used as measures of column efficiency. The units of V_R and peak width are unimportant provided that they are the same.

In developing the theory of gas chromatography two distinct aspects must be considered. The first is the thermodynamic aspect which governs the speed at which any band of vapour moves down the column. The second is the kinetic aspect which governs the rate at which a band broadens as it moves down the column and the factors which cause this broadening.

The thermodynamics of gas chromatography

The thermodynamics of gas chromatography may be considered most simply if the column is assumed to be a partition column rather than an adsorption column. The extension of the arguments to an adsorption column can readily be made. We therefore imagine that the column contains a mobile gas phase of average cross sectional area a_g, and a fixed liquid phase of average cross-sectional area a_l. The liquid is supposed to be supported on a finely divided inert support such as firebrick, Celite or glass beads, or on the walls of a capillary tube. As has already been shown in the Introduction the speed at which any band moves in the column relative to the carrier gas is equal to the fraction of the component in the gas phase. The volume of gas required to elute any vapour is therefore inversely proportional to this fraction. That is:

$$\frac{\text{Speed of band}}{\text{Speed of carrier gas}} = \text{Fraction of vapour in gas phase}$$

$$= v_g/V_R$$

or

$$V_R/v_g = 1+\frac{\text{Quantity of vapour in liquid}}{\text{Quantity of vapour in gas}}$$

$$= 1+K$$

Hence

$$V'_R/v_g = K \qquad 2.6$$

Where K is a constant for any column and any substance and is called the column capacity coefficient. The column capacity coefficient is related to the solubility coefficient α of the vapour by the relation

$$\alpha = \frac{\text{Concentration of vapour in liquid}}{\text{Concentration of vapour in gas}}$$

$$= K(a_g/a_l) = K(v_g/v_l)$$

$$= V'_R/v_l \qquad 2.7$$

where v_l is the volume of liquid phase in the column. Solubility is most conveniently expressed in terms of the vapour pressure equation for any solution

$$p = p^0\gamma X$$

where p^0 is the vapour pressure of the pure substance being chromatographed and p is its pressure over the solution in the column liquid phase, X is the mole fraction of the substance and γ its activity coefficient. The concentrations in the liquid and gas phases are then given respectively by

$$c_l = \rho X/M_s \text{ (moles/ml)}$$

$$c_g = p/RT$$

where M_s = molecular weight of solvent; ρ = density of solvent in g/ml and T = column temperature. Hence

$$\alpha = c_l/c_g = V'_R/v_l$$

$$= \rho XRT/M_s p = \rho RT/M_s p^0\gamma$$

and

$$V'_R = RTm/p^0 M_s\gamma \qquad 2.8$$

where m = weight of solvent in column. The net retention volume is thus proportional to the weight of liquid phase in the column. For this reason it is most convenient to tabulate retention volume data in terms of the retention volume per gram. The true net retention volume per gram is called the specific retention volume and is denoted by V_r^T; it is given by

$$V_r^T = RT/p^0 M_s \gamma \tag{2.9}$$

This specific retention volume is measured at the temperature T and the average pressure of the column. It is convenient to reduce specific retention volumes to 0°C so that

$$V_r^{273} = 273R/p^0 M_s \gamma$$

$$V_{r(\mathrm{cm}^3)}^{273} = (1{\cdot}703 \times 10^6)/[p^0_{(\mathrm{cm\,Hg})} M_s \gamma] \tag{2.10}$$

If the experimental net retention volume is measured at the temperature and pressure of the laboratory then the standard specific retention volume is obtained from the formula

$$V_r^{273} = V'_{\mathrm{exp}}(273\, p_r)/(mT_r p_{\mathrm{av}})$$

The effect of temperature change on the retention volume of any substance is obtained by differentiating equation 2.10

$$\begin{aligned} d(\ln V_r^{273})/dT &= -d(\ln p^0)/dT - d(\ln \gamma)/dT \\ &= -L/RT^2 + \Delta H_m/RT^2 \\ &= \Delta H_s/RT^2 = -bL/RT^2 \end{aligned} \tag{2.11}$$

where L = molar latent heat of vaporization of the substance; ΔH_m = partial molar heat of mixing of substance with column liquid phase; ΔH_s = molar heat of solution of vapour in column liquid, and $b = -\Delta H_s/L$ is approximately constant over a moderate temperature range. For ideal solutions $b = 1$.

A plot of $\log_{10} V_r^{273}$ against $1/T$ should therefore be a straight line of gradient $-\Delta H_s/4{\cdot}57$; a plot of $\log_{10} V_r^{273}$ against $\log_{10} p^0$ should be a straight line of gradient $-b$. A typical plot of $\log_{10} V_r^{273}$ against $1/T$ is shown in Figure 2.3. The data are amongst the most accurate retention volume values so far measured.

Very often it is possible to construct linear plots of $\log V_r^{273}$ against the boiling point or the carbon number of the members of any homologous series. For any such series the ratio L/RT_b, where T_b is the boiling point, will be nearly constant and approximately 10·5 (Trouton's rule). We can therefore write the integrated Clapeyron–Clausius equation in the form:

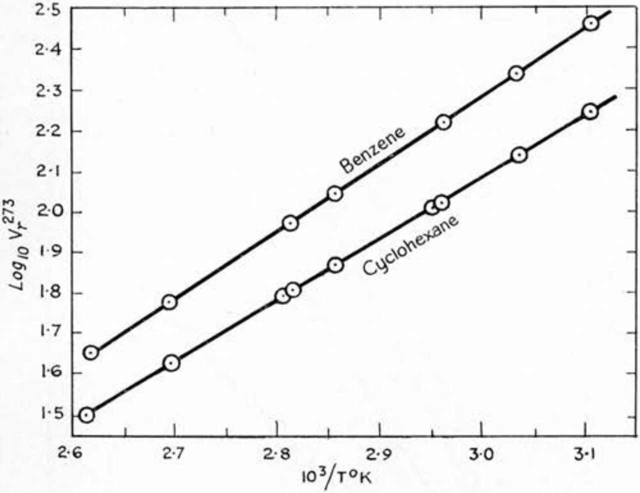

FIG. 2.3. Variation of specific retention volume with temperature for benzene and cyclohexane on dinonyl phthalate. Plotted from data of Adlard, Khan and Whitham (1960) *Gas Chromatography 1960* (Ed. Scott, publ. Butterworths), p. 251.

$$\log p^0_{(\mathrm{cm})} = \log 76 - \frac{10{\cdot}5}{2{\cdot}303} T_b(T^{-1} - T_b^{-1})$$

$$= 6{\cdot}4 - 4{\cdot}5(T_b/T)$$

Incorporating this result into equation 2.10 gives

$$\log V_r^{273} = -0{\cdot}2 + 4{\cdot}5(T_b/T) - \log M_s - \log \gamma \qquad 2.12$$

For any homologous series in any given liquid phase, M_s is a constant and the activity coefficient γ will vary regularly and slowly from one member to the next. Thus for a fixed temperature T, $\log V_r^{273}$ should

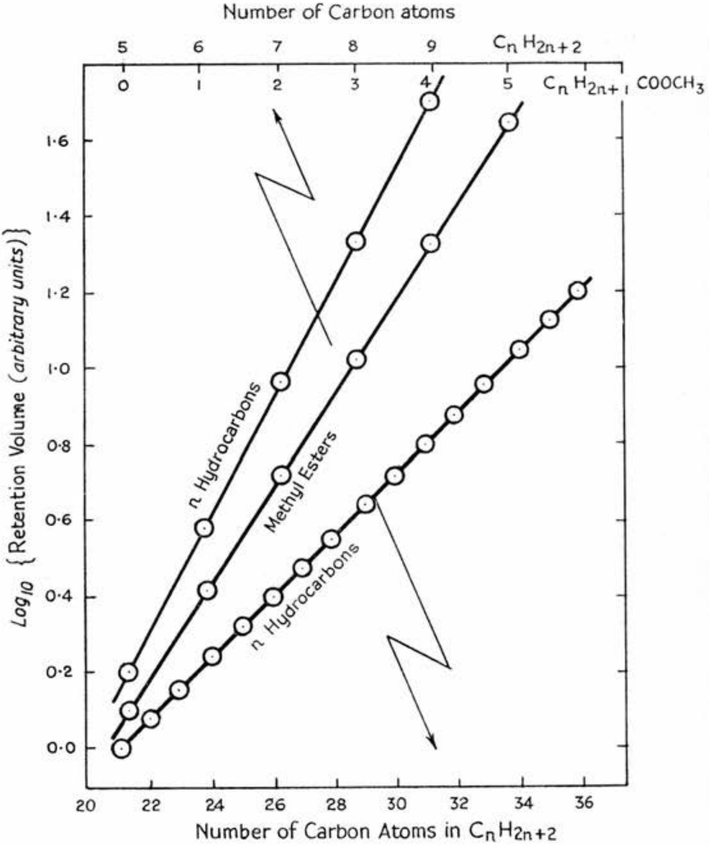

FIG. 2.4. Plots of $\log_{10}$ (retention volume) against carbon number for *n*-hydrocarbons and methyl esters of *n*-fatty acids. Data for C_{21}–C_{36} hydrocarbons from Ogilvie, Simmons and Hinds (1958) *Anal. Chem.* **30**, 25. Other data from Bayer, *Gaschromatographie*, Springer Verlag, Berlin (1959).

increase linearly with the boiling point of the members of any series. Since furthermore the boiling point is usually a linear function of the carbon number in any series plots of $\log V_r^{273}$ against carbon number should also be linear. This is generally true to a surprising degree of accuracy as can be seen from the illustrative plots given in Figure 2.4.

Apart from its analytical and preparative uses gas chromatography can provide a method for determining heats of solution and activity coefficients at extreme dilutions. The solvents which can be used in conventional apparatus are naturally somewhat limited but by incorporating a saturator at the column temperature before the injection point the range of liquids can be considerably extended. The method is accurate provided that care is taken to avoid adsorption of the solute at the surfaces of either the supporting solid or of the liquid. A number of activity coefficients and heats of solution determined by gas chromatography are given in Table 2.1.

TABLE 2.1

Solvent *n*-hexadecane

Substance	25°C γ	40°C γ	$-\Delta H_s$ cal mole^{-1}	L cal mole^{-1}
Methanol	71·5	45	2,940	8,640
Ethanol	47	30·5	3,350	9,750
*iso*Propanol	26·5	18·5	6,150	10,550
t-Butanol	31·5	19·5	6,100	10,900
Acetone	6·3	5·1	4,650	7,260
MeEtKetone	3·8	3·1	4,650	7,250
Ethyl formate	3·17	3·12	6,000	7,680
Ethyl acetate	2·8	2·5	7,200	8,600
n-Pentane	0·89	0·86	5,900	6,200
cycloPentane	0·71	0·71	6,980	6,980
2 Me Pentane	0·85	0·88	7,050	6,720

Activity coefficient data taken from Kwantes and Rijnders (1958) *Gas Chromatography 1958* (Ed. Desty, publ. Butterworths), p. 125; latent heat data from Timmermans, *Physico-chemical Constants of Pure Organic Compounds;* heats of solution calculated from columns 2, 3, and 5.

The kinetics of gas chromatography

Several processes occurring during chromatography lead to the spreading of any sharp band initially injected on to the beginning of the column, and the extent of this spreading is a measure of the inefficiency of the chromatographic process. Although chromatography is a continuous process it is convenient, when considering peak spreading, to introduce the concept of the theoretical plate which derives from an analogous discontinuous process. Any real chromatographic column may be considered to behave like a hypothetical column consisting of a series of distinct units or plates joined together. The process analogous to chromatography is then as follows. The plates of the hypothetical column are initially connected so that the sudden addition of an amount dV of carrier gas (or more generally carrier fluid) to the first plate causes the whole gas phase in the column to move as a plug a short distance down the column and an amount dV to emerge from the last plate. A small fraction of the contents of each plate is thereby transferred instantaneously to the succeeding one. The plates are now disconnected for long enough to allow equilibrium to be re-established in each plate. Finally the plates are reconnected and the whole process repeated. The time interval during which the plates are connected is made so short that no mixing of the contents of adjacent plates can occur by diffusion. If a sample of vapour is now added to the first plate the addition of successive small quantities of carrier gas will elute the vapour down the column until it eventually emerges from the last plate. During elution, however, a band of vapour initially on the first plate will spread. The extent of this spreading, as is shown below, depends only upon the number of plates in the column if dV is sufficiently small. We can thus use the observed spreading in any real column to calculate the number of plates which would be required in a hypothetical plate column to give the same degree of spreading. The 'height equivalent to a theoretical plate', or H.E.T.P., in the real column is then simply obtained by dividing the column length by the number of theoretical plates to which it is equivalent. The H.E.T.P., denoted by H, is the most widely used measure of the efficiency of a chromatographic column.

In developing the theory for a hypothetical column containing N

plates we assume only that the distribution coefficient for any chromatographed vapour between the fixed and mobile phases is independent of its concentration. The qualitative effects of variation of K and α with concentration are considered in Chapter 3.

We denote the amount of any vapour on the rth plate by P_r and consider the effect of the passage of an amount dV of carrier gas through this plate. The change in P_r will result from (*a*) a loss $-dP_{r(1)}$ to the $(r+1)$th plate, and (*b*) a gain of $+dP_{r(2)}$ from the $(r-1)$th plate. These are given respectively by

$$dP_{r(1)} = -P_r \frac{dV}{(1+K).H.a_g}$$

$$dP_{r(2)} = +P_{r-1} \frac{dV}{(1+K).H.a_g}$$

The total change in P_r is thus

$$dP_r = (P_{r-1} - P_r) \frac{dV}{(1+K).H.a_g}$$

If $\lambda = V/(1+K).H.a_g$ and if P_{tot} is initially placed on the first plate, the solution to this equation may be written

$$P_r = P_{\text{tot}}.e^{-\lambda}.\lambda^r/r! \qquad 2.13$$

as can be verified by differentiation of equation 2.13. The maximum P_r which corresponds to the peak maximum concentration is obtained by putting $dP_r/dr = 0$. It is then found that $r = \lambda$. We denote the maximum P_r by P_m and the value of r at this point by r_m.

We can readily show that this gives the same relationship between retention volume and solubility as the simpler arguments given previously. At the peak maximum

$$r_m = \lambda = V/(1+K).H.a_g \qquad 2.14$$

or

$$V/r_m.H.a_g = (1+K)$$

Now $r_m H.a_g$ is the volume of the gas phase in the first r_m plates of the column and V is the volume of carrier gas required to elute the component as far as the r_mth plate. Thus in a column of r_m plates $V = V_R$ and $r_m . H . a_g = v_g$; equation 2.14 thus reduces to

$$V_R/v_g = (1+K) \tag{2.15}$$

The plate theory thus arrives at the same result as the more elementary theory based upon the idea of equilibrium between the total amount of vapour in the gas and liquid phases.

The shape of the peak can be obtained by considering the amounts of component on the different plates. The relative peak height is

$$\begin{aligned} y/h &= P_r/P_m \\ \ln(y/h) &= \ln P_r - \ln P_m \\ &= r \ln r_m - r_m \ln r_m - \ln r! + \ln r_m! \end{aligned}$$

Since r is generally large (say, > 100) Stirling's approximation can be used for $r!$ That is

$$\ln r! = (r+\tfrac{1}{2}) \ln r - r + \tfrac{1}{2} \ln 2\pi$$

Accordingly

$$\begin{aligned} \ln(y/h) &= (\tfrac{1}{2}+r) \ln (r_m/r) + r - r_m \\ &= -(\tfrac{1}{2}+r_m+\Delta r) \ln (r_m+\Delta r)/r_m + \Delta r \end{aligned}$$

where $\Delta r = r - r_m$. When Δr is small with respect to r_m, which is the case for all important values of Δr in a column of reasonable plate efficiency,

$$\begin{aligned} \ln(y/h) &= -(\tfrac{1}{2}+r_m+\Delta r)\left\{\frac{\Delta r}{r_m} - \frac{(\Delta r)^2}{2r_m^2} + \ldots.\right\} + \Delta r \\ &\doteqdot -\Delta r(\Delta r+1)/2r_m \end{aligned}$$

For a column of a large number of plates (say, $> 1{,}000$) $\Delta r \gg 1$ for the majority of important values of Δr and therefore to a good enough approximation

$$y = h . e^{-(\Delta r)^2/2r_m} \tag{2.16}$$

Equation 2.16 is of the same form as the Gaussian error curve given in equation 2.4. It gives the relative amounts of a chromatographed substance on different plates when the peak maximum has reached the r_mth plate from the beginning of the column. When r_m is made equal to N, the number of plates in the whole column, equation 2.16 represents the elution curve of the substance as it emerges from the column. The equation can now be written

$$y = h.e^{-(\Delta r)^2/2N} \qquad 2.16a$$

Generally we examine not the distribution of concentration within the column but in the carrier gas which has emerged from the column. It is therefore convenient to replace plate numbers by equivalent volumes of carrier gas. Equation 2.14 gives the volume of carrier gas required to elute a band of substance through r_m plates. For N plates we therefore have

$$V_R = (1+K)\,Ha_g.N = \phi N$$

The volume of carrier gas required to elute the substance through Δr plates can be written

$$x = (1+K)\,Ha_g.\Delta r = \phi\Delta r$$

Substituting into equation 2.16a then gives

$$y = h.e^{-x^2/2\phi V_R}$$

This equation is directly comparable with equation 2.4 where x, the distance from the peak maximum, is now to be measured as a volume of carrier gas. We can therefore write

$$\sigma^2 = \phi V_R$$

and $$(\beta_e)^2 = 8\sigma^2 = 8\phi V_R$$

Hence $$8(V_R/\beta_e)^2 = V_R/\phi = N$$

The number of plates in a column is thus obtained experimentally by measuring the peak width and the retention volume in the same units and applying one of the formulae

$$N = 8(V_R/\beta_e)^2 = 16(V_R/w)^2 = 5{\cdot}54(V_R/\beta_{1/2})^2 \qquad 2.17$$

Since the ratio of peak width to retention volume is dimensionless the units of V_R and peak width are unimportant provided that they are the same for both quantities.

Resolution, plate numbers and separation numbers

The resolution of any two peaks depends upon the narrowness of the peaks and the separation of their peak maxima. Resolution is most simply defined as the separation of the peak maxima divided by the average peak width. Conventionally the peak width is chosen as the width made by extrapolating tangents rather than either of the β's. For two components 1 and 2

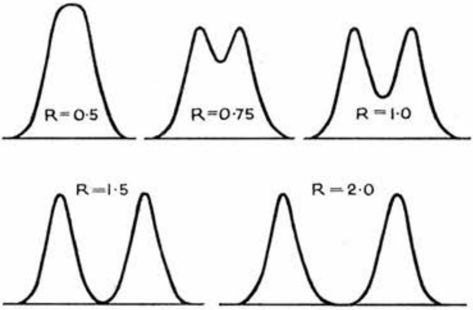

FIG. 2.5. Peak resolution. A resolution R means a separation of the peak maxima by $4R$ standard deviations.

$$\text{Resolution } R_{12} = 2(V_{R1} - V_{R2})/(w_1 + w_2) \qquad 2.18$$

Figure 2.5 illustrates the type of peak resolution obtained for various values or R. Purnell has used the term 'exact separation' for the case when $R = 1{\cdot}5$.

In designing a column for any particular separation one is basically interested in obtaining a certain degree of resolution between various components in the mixture. One can achieve the desired resolution either by arranging for the retention volume ratio of the two substances to be sufficiently different from unity or by arranging that the peaks are sufficiently narrow. The ratio of the retention volumes of any two substances is related to their relative solubilities as has already been shown in equations 2·6 and 2·7.

$$V'_{R1}/V'_{R2} = K_1/K_2 = \alpha_1/\alpha_2 = \alpha_{12} \qquad 2.19$$

Since variation of the column parameters which may increase column efficiency (e.g. particle size, liquid film thickness, column length, nature of carrier gas, etc.) do not in general alter the solubility ratio, it is convenient to express the resolution in terms of the solubility ratio and some measure of column efficiency. For this purpose we introduce a quantity called the separation number (S) defined by

$$S = 16(V'_R/w)^2 \qquad 2.20$$

S is analogous to the plate number N but is derived from the net retention volume rather than the true retention volume V_R.

The resolution can then be written

$$R_{12} = \frac{(V'_{R1} - V'_{R2})}{2\left\{\dfrac{V'_{R1}}{S_1^{1/2}} + \dfrac{V'_{R2}}{S_2^{1/2}}\right\}}$$

$$= \tfrac{1}{2}(\alpha_{12} - 1)\bigg/\left\{\frac{\alpha_{12}}{S_1^{1/2}} + \frac{1}{S_2^{1/2}}\right\}$$

We can assume that S_1 and S_2 will be almost equal for two peaks close together and therefore obtain

$$R_{12} = \tfrac{1}{2}.S^{1/2}(\alpha_{12} - 1)/(\alpha_{12} + 1) \qquad 2.21$$

Finally if the solubility ratio is close to unity as will normally be the case

$$R_{12} = \tfrac{1}{4}(\alpha_{12} - 1).S^{1/2}$$

$$\text{or} \quad S = \{4R_{12}/(\alpha_{12} - 1)\}^2 \qquad 2.22$$

Since the separation and plate numbers are related by the equation

$$N/S = (V_R/V'_R)^2 = (1 + 1/K)^2 \qquad 2.23$$

the plate requirement for any given resolution is

$$N = \{4(1 + 1/K).R_{12}/(\alpha_{12} - 1)\}^2 \qquad 2.24$$

It is clear from this equation that when K is reduced below unity the plate requirement for any given resolution increases very rapidly. In order to make the best use of the plate efficiency of any column one should not therefore work with K values below unity. This fall off in the resolving power of a column as K decreases has to be borne in mind when designing high-performance packed and capillary columns which generally operate with very low percentage loadings of liquid phase with a consequent tendency to give low K values. It can in fact be shown that the best compromise as far as high speed is concerned is to select column conditions such that K lies between 2 and 4. For conventional packed columns K is normally considerably greater than unity and the difference between N and S is unimportant. The effect of changing K on the resolution of two substances for a column of constant N and α_{12} is seen in Figure 2.6.

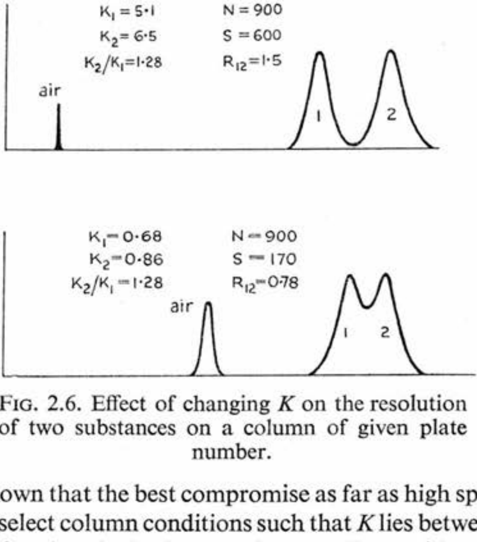

FIG. 2.6. Effect of changing K on the resolution of two substances on a column of given plate number.

Factors affecting column efficiency

Of the two factors affecting peak resolution we consider here the column efficiency and how it may be improved, leaving until Chapter 3 consideration of the relative solubilities of different substances in various stationary phases.

In 1956 Keulemans[1] elucidated the problem of column efficiency by introducing gas chromatographers to the van Deemter equation which relates the HETP to various column parameters. The application of this equation brought about substantial improvements in the efficiency of packed columns. In 1958 Golay[2] worked out an analogous equation for the empty capillary whose walls were coated with liquid phase. Golay's equation differed slightly from the original van Deemter equation and led to modifications making the latter applicable to high-performance packed columns.[3]

The original van Deemter equation is still adequate for what we now term conventional packed columns. Such columns are of moderate efficiency (1,000 to 5,000 plate) and carry some 10–30 per cent stationary phase. They are still used for the great majority of analyses and it is convenient to treat them separately from high-performance columns where maximum speed and separating power are sought. High-performance columns contain only about 1 per cent of stationary phase (measured as a percentage of the gas volume of the column) and they enable analyses of high plate efficiency (up to 100,000) to be carried out rapidly. However, they have attendant disadvantages, the chief of which is that only minute samples can be handled so that it is exceedingly difficult to identify components other than by their retention volumes. Owing to the extreme thinness of the liquid films used surface adsorption becomes important and the retention volumes may be considerably different from those obtained on a packed column where the surface/volume ratio of the liquid phase is much lower.

Conventional packed columns

Van Deemter, Zuiderweg and Klinkenberg[4] showed that the HETP for a packed column could be given by

$$H = 4\lambda r + 2\gamma D_g/u + \frac{8Kd^2}{\pi^2(1+K)^2 D_l} \cdot u \qquad 2.25$$

where λ and γ are constants of the order of unity; r = average particle radius; d = average liquid film thickness; D_g and D_l = diffusion coefficients of vapour being chromatographed in the gas and liquid phases; u = true linear gas velocity in column, i.e. (column length)/(retention time for air peak).

The three terms represent the independent contributions of three disturbing effects: mixing due to unequal paths round particles, often called 'eddy diffusion'; mixing due to longitudinal diffusion in the gas phase; and slowness of mass transfer between the liquid and gas phases. The equation is often written in the simplified form

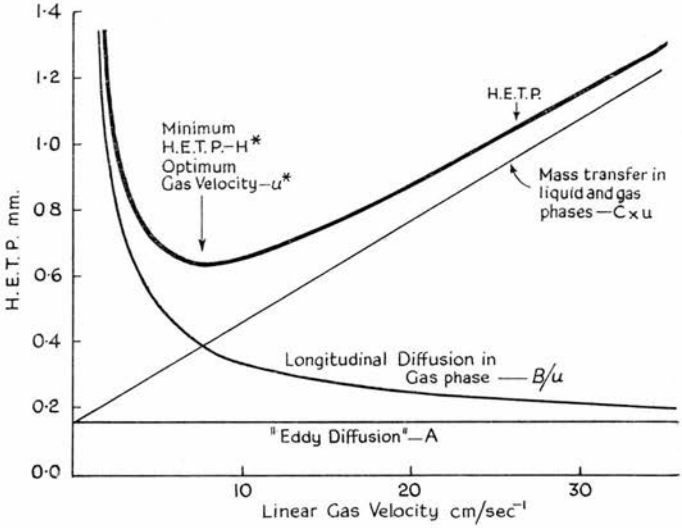

FIG. 2.7. Curve of HETP against gas velocity for $A = 0{\cdot}015$ cm, $B = 0{\cdot}17$ cm^{2}sec^{-1}, and $C = 0{\cdot}0031$ sec.

$$H = A + B/u + Cu \tag{2.26}$$

in which it emphasizes the effect of gas velocity on the HETP. A plot of H against u such as that given in Figure 2.7 exhibits a minimum HETP at a specific gas velocity. It is obviously desirable to work as close as possible to the optimum gas velocity giving this minimum

HETP in order to make full use of the separating power of the column. The values of H and u at the minimum are

$$\begin{aligned} u^* &= (B/C)^{1/2} \\ H^* &= 2(BC)^{1/2} + \mathrm{A} \end{aligned} \qquad 2.27$$

The minimum H usually occurs with nitrogen or argon as carrier gases in the region of 3–6 cm/sec and with hydrogen and helium as carrier gases in the region of 10–20 cm/sec. It is very important when using any column to ascertain the optimum gas velocity by measuring H as a function of u experimentally.

Recently evidence has grown that A is often small. B and C can accordingly be determined by plotting Hu against u^2. Values of B obtained in this way by Bohemen and Purnell[5] are of order of magnitude indicated by equation 2.25.

Particle size

Particle size affects the HETP by altering A and C. C is altered since the film thickness depends upon the radius if columns are made up with the same percentage liquid phase but with different sized particles. Smaller values of H are therefore obtained with smaller particles. However, this may not be of practical value unless the pressure drop across the column can be increased sufficiently to overcome the increased resistance of the column. If the apparatus can develop a maximum pressure drop Δp across the column then the maximum linear gas velocity is given by the Kozeny–Carman equation for any particle size

$$u = \frac{\Delta p r^2}{45 \eta L} \{e/(1-e)\}^2 \qquad 2.28$$

where η is the viscosity of the carrier gas, L = column length, and e = porosity of the packing. For firebrick and glass beads $e = 0{\cdot}38$ and for celite $e = 0{\cdot}45$–$0{\cdot}50$. Roughly then we can write

$$u = \Delta p r^2 / 100 \eta L \qquad 2.29$$

If it is assumed that A is small compared to B/u and Cu one can readily evaluate the number of theoretical plates which can be operated at the optimum velocity for any particle radius by using equations 2.27 and 2.29. The result, which is quite independent of the parameter C, is

$$N_{\text{max}} = L/H^* = \left\{\frac{\Delta p}{400\eta\gamma D_g}\right\}r^2 \qquad 2.30$$

Thus the number of plates which one can operate can only be increased by increasing the column length and the particle radius, if one is already working with the maximum convenient pressure drop across the column. For columns of between 1,000 and 5,000 plates the usual particle sizes are in the range 30–120 mesh.† It is essential however always to use closely graded material with particle sizes differing by not more than 20 per cent.

The carrier gas

Since the HETP depends upon $1/D_g$ through the second term in the van Deemter equation a column of given length will be more efficient if a gas of high molecular weight is used than one of low molecular weight since $D_g \propto 1/M^{1/2}$ on simple kinetic theory of gases. However, if one is working at the maximum convenient pressure drop in any apparatus this gain is largely offset by the increase of viscosity with molecular weight. This is shown clearly by reference to equation 2.30. The carrier gases of higher molecular weight still have some advantage when this is allowed for but generally one can choose the carrier gas on the basis of considerations other than analysis speed.

Column pressure drop

The pressure drop across the column does not enter directly into the van Deemter equation and is only important in so far as it affects the flow rates at different parts of the column. Since linear flow rate is inversely proportional to the pressure of the gas at any point in the column an undesirably large spread of gas velocities will result if p_i/p_o is large. Such a spread will reduce the column efficiency since at least part of the column will be operating at linear speeds differing considerably from the optimum. Keulemans[6] has shown that the

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† British standard mesh sizes are used throughout. The particle radius is readily calculated from the formula r (in mm) $= 6{\cdot}35/$mesh size.

larger part of the pressure drop in a column occurs near the outlet end and therefore in order to obtain the best results the inlet rather than the outlet gas velocity should be close to the optimum.

Operation of the whole column at a uniformly high pressure (by fitting a restriction for example at the outlet end) will reduce D_g since $D_g \propto 1/p$, and hence result in higher column efficiencies. However, it is likely that still higher efficiencies would be obtained by making use of the 'wasted' pressure drop in order to operate a further length of column or a column with smaller particles.

The liquid phase

The properties of the liquid phase affect H via the mass transfer coefficient C. Alteration of the quantity of liquid phase affects both d and K while alteration of its physical properties affects D_l. D_l varies inversely as the viscosity and obviously should be kept as low as possible. Most liquids used in gas chromatography are far below their boiling points and are relatively viscous. While liquids like ethanol, water, acetone, hexane have values of D_l about 10^{-5} $\text{cm}^2\text{sec}^{-1}$, those commonly used as liquid phases have D_l between 10^{-6} and 10^{-7}. While it is not possible generally to effect a major improvement in efficiency by altering the liquid phase it is important to make sure that the liquid phase is reasonably fluid at the temperature at which it will be used. Serious loss of efficiency may occur if the liquid phase becomes very viscous.

Alteration of the loading of stationary phase will have a marked effect upon efficiency. If the particle size is fixed reduction of d will increase efficiency. The effect of change of film thickness on C is however modified by concurrent changes in K. If we assume that each particle is surrounded by a spherical film of thickness d we can write

$$K = 2\pi\alpha r d/a_g$$

With conventional packed columns K is normally much greater than unity and hence

$$\begin{aligned} C &\doteqdot 8d^2/\pi^2 D_l K \\ &= 4d(a_g/\pi^3 D_l r\alpha) \end{aligned} \qquad 2.31$$

C should therefore decrease roughly linearly with the percentage loading. There is however some doubt as to whether the assumption of a uniform thin film is justified and it is possible that the liquid phase forms small globules on the surfaces of some supports. The decrease in film thickness with loading is then much reduced and in the extreme case may not occur at all. If this were the case C would increase as the percentage loading decreased due to the change of K. In practice an intermediate situation exists and, at least down to a certain level, an increase in efficiency results from lower liquid phase loading.

Column temperature

Temperature is the most complex of the variables affecting column efficiency. Change of temperature increases D_l and D_g and decreases K. The variation of D_l and D_g with temperature are not great provided that the liquid phase is not highly viscous. Their effects on column efficiency will tend to cancel out since one appears in the numerator of B and the other in the denominator of C. The major effect of temperature is through K. Any decrease in K tends to increase C and therefore increase of temperature will lower column efficiency. It is therefore desirable on this score to work at low column temperatures. However, the longer retention times may be a disadvantage. The larger specific retention volumes at lower temperatures may of course be countered by using a lower liquid phase loading. The optimum column efficiency is thus obtained by using a low temperature and a low liquid phase loading.

Temperature also has an effect on the solubility ratios and this may have a far more important effect on resolution than any changes in column efficiency. As a general rule however the two effects work in the same direction but this is not always so.

General conclusions for preparation and operation of conventional packed columns

(1) The optimum flow rate for any column should be determined experimentally by measuring the HETP as a function of flow rate, for one of the components of the mixture it is desired to analyse.

(2) Particle size should be as uniform as possible. Larger particles and longer columns should be used for higher efficiencies. It is best to

use the maximum pressure drop across the column if possible without departing from the optimum flow rate.

(3) The pressure drop ratio across the column should preferably not be larger than 2.

(4) The liquid phase in the column should occupy between 5 and 15 per cent of the volume of the gas in the column. With Celite (density about 0·25) this corresponds to 10–30 per cent by weight and with firebrick (density about 0·45) 5–15 per cent by weight. Although higher liquid phase loadings have been used they are not recommended owing to the resultant loss of efficiency.

(5) The lowest convenient temperature should be used. It is generally better to lower temperature and percentage of liquid phase in order to increase column efficiency than to raise them or increase column length.

High-performance columns

When capillary columns were first described by Golay it appeared that much higher plate efficiencies and much faster analyses could be achieved with capillaries than with normal packed columns. It was thought at the time that this difference was an inherent property of the capillary column. An impartial consideration of the differences between packed and capillary columns reveals however that there should be no intrinsic difference between the two, for a packed column is nothing more than a complex network of very short capillaries albeit of somewhat different cross-section to a normal tube. The differences in efficiency and speed were in fact due (*a*) to the use of a capillary much longer than the usual packed column, (*b*) to the very low percentage of liquid phase employed, and (*c*) to the use of very small samples which avoided any possibility of overloading.

Golay's equation for the HETP of a round capillary column of radius r can be written

$$H = 2D_g/u + \left\{\frac{(1+6K+11K^2).r^2}{24(1+K)^2 D_g} + \frac{2K.d^2}{3(1+K)^2 D_l}\right\}u \qquad 2.32$$

The first term is the contribution from longitudinal diffusion and the last term from resistance to mass transfer in the liquid phase. The second term, not present in the original van Deemter equation, is the contribution from resistance to mass transfer in the gas phase. It becomes important when both d and D_g are low, but is probably of minor importance in conventional packed columns. The eddy diffusion term A of the van Deemter equation is absent for obvious reasons. Van Deemter has modified his original equation to take account of the resistance to mass transfer in the gas phase. He obtains[4]

$$H = 4\lambda r + 2\gamma D_g/u + \left\{\frac{K^2 r^2}{25(1+K)^2 D_g} + \frac{2Kd^2}{3(1+K)^2 D_l}\right\} u \qquad 2.33$$

The second and last terms are effectively the same as the first and last terms in the Golay equation. The third term, the contribution of resistance to mass transfer in the gas, is smaller than the equivalent term in the Golay equation. This is because the effective radius of the channels in a packed column is considerably less than the radius of the particles themselves. By comparing the Kozeny–Carman equation with the Poiseuille equation it can readily be shown that the dynamic channel radius in a column of packed spheres is about 0·27r. If r in equation 2.33 is replaced by $r'/0{\cdot}27$ (where r' = dynamic channel radius) the third term in equation 2.33 becomes almost identical to the second in equation 2.32, at least at high K values. The equations differ at low values of K since the modified van Deemter equation takes no account of mixing due to lateral diffusion across a gas stream whose velocity is not uniform. Otherwise the two equations are similar and, if one discounts the 'eddy diffusion' term for packed columns as being small, the Golay equation should enable one to derive approximate conditions for the highest performance which could be expected from any packed column.

So far no one has succeeded in making a packed column whose performance approaches the theoretical within a factor of ten, but for capillaries the experiments of Scott[7] and Desty[8] have gone far to verify the Golay equation both qualitatively and quantitatively.

The 'performance' of any column may be defined roughly as the speed at which separation can be attained. In seeking high performance one might therefore enquire into the minimum time required to obtain a given resolution of two substances with a given solubility ratio. Equations 2.21 and 2.22 show that this implies a given separation number S. Now it is not difficult to show that the speed of analysis will increase as the pressure drop across the column increases. This is simply the converse of the argument developed in the section on particle size on p. 29. It is therefore necessary to regard the maximum permissible pressure drop across the column as a limiting factor in the attainment of performance. The problem is therefore to determine the maximum speed at which a substance can be eluted with a separation number S when the pressure drop across the column has a certain fixed value Δp.

In order to make use of these two restrictions we write H in terms of the column length, L, the column capacity coefficient, K, and the separation number S. We also replace u by the value given in the Poiseuille viscosity equation. That is:

$$H = LN^{-1} = LS^{-1}[K/(1+K)]^2 \qquad 2.34$$

$$u = \Delta pr^2/8\eta L = r^2/DL \qquad 2.35$$

where $D = 8\eta/\Delta p$. The time of elution of a vapour whose column capacity coefficient is K is

$$t = (1+K)L/u \qquad 2.36$$

Thus substituting into equation 2.32 we obtain

$$S^{-1} = 2D_g(1+1/K)^2\, D/r^2 + \left\{\frac{(1+6K+11K^2)r^2}{24K^2 D_g} + \frac{2d^2}{3KD_l}\right\}\frac{1+K}{t} \qquad 2.37$$

If we consider first of all columns with a fixed percentage of liquid phase we can put $d/r =$ constant. We denote this ratio by ρ. For a capillary it may be noted $\rho = \frac{1}{2}v_l/v_g$. 2.37 can then be written

$$S^{-1} = P/r^2 + Qr^2(1+K)/t \qquad 2.38$$

where

$$P = 2D.D_g(1+1/K)^2$$

$$Q = \frac{1+6K+11K^2}{24K^2 D_g} + \frac{2\rho^2}{3KD} \qquad 2.39$$

If the liquid phase loading is constant then K will be constant for any column liquid and column temperature. The optimum conditions for a given ρ and K can thus be obtained by differentiating equation 2.38

regarding P, Q and K as constants. The minimum time is obtained by putting $dt/dr = 0$

$$t_{\min} = Q(1+K)r^4/P$$

Substitution into equation 2.38 then gives

$$\begin{aligned} t_{\min} &= 4PQ(1+K).S^2 \\ r_{\min} &= (2PS)^{1/2} \end{aligned} \qquad 2.40$$

Other column parameters may be evaluated using equations 2.34–2.36. In particular it can be shown that the gas velocity for the minimum analysis time at fixed pressure drop is given by

$$\begin{aligned} u^2_{\min} &= (2DSQ)^{-1} \\ &= 2D_g(1+1/K)^2/Qr^2 \\ &= B/C \end{aligned} \qquad 2.41$$

where B and C are the coefficients of $1/u$ and u in the Golay equation as in the original van Deemter equation (2.26). This value for $u_{\min}$ is that which gives the minimum HETP for the column of the chosen radius. If therefore one is free to chose a column of exactly the correct radius the fastest analysis is obtained when the optimum gas velocity is achieved with the maximum pressure the apparatus can develop.

The minimum analysis time given by equation 2.40 will of course depend upon the values of ρ and K. It can readily be seen that if K is maintained constant $t_{\min}$ can always be reduced by reducing ρ. The ultimate minimum is found to occur for $\rho = 0$, $K = 2$. This however is unattainable in practice since it implies that the solubility is infinite. A compromise must therefore be accepted. For $\rho = 0{\cdot}003$ (corresponding to a 0·6 per cent by volume coating of liquid phase) the ultimate minimum can be approached within a factor of two if $K = 3$–4.

The fastest analysis for a given S and Δp is thus obtained by using a column containing about 0·6 per cent by volume of liquid phase at its optimum gas velocity and by arranging that the K value of the components being separated is about 4.

As can be seen from equation 2.40 the minimum analysis time increases as the square of the separation number required. This emphasizes the importance of selecting a column liquid which gives the most favourable solubility ratio and demands the lowest separation number for a given degree of resolution of any two substances. The way in which the various column parameters necessary for the fastest analysis vary with the required separation number is illustrated in Table 2.2. The values have been calculated for $k = 3{\cdot}3$ $\rho = 0{\cdot}003$ and a pressure drop of 76 cm Hg. Nitrogen has been taken as the carrier gas and the liquid phase has normal properties for a gas chromatographic liquid. The conclusions reached above and the figures in the table can be taken to apply approximately to packed columns provided that it is borne in mind that a rather lower efficiency is expected in view of the neglect of the eddy diffusion term. The mesh sizes quoted in the table are based upon the assumption that A is zero.

TABLE 2.2

Capillary column parameters for minimum analysis times

Carrier gas – nitrogen; pressure drop 76 cm Hg; liquid phase loading 0·6 per cent v/v.

Separation Number	*Elution time (sec)*	*Column diameter (mm)*	*Mesh size (packed)*	*Column length (cm)*	*Gas velocity (cm/sec)*
100	10^{-3}	0·006	400	0·1	650
1,000	0·1	0·02	130	3	200
10,000	10	0·06	40	100	65
100,000	1,000	0·2	13	3,000	20
1,000,000	100,000	0·6	4	100,000	6·5
S	$10^{-7}S^2$	$6\times10^{-4}S^{1/2}$	$4\times10^3 S^{-1/2}$	$10^{-4}S^{3/2}$	$6.5\times10^3 S^{-1/2}$

The figures in Table 2.2 have not so far been attained in practice although they have approached for the longer capillaries within a factor of less than ten. However few workers have specifically attempted to obtain the highest possible speed and much progress is to be expected in this direction in the near future.

Experiments by Scott, with capillary columns, and Purnell with packed columns indicate that high speeds such as those indicated in the table are certainly possible. However, with the shorter columns serious practical difficulties arise in making the injection systems and detectors of sufficiently small volume. Owing to the much smaller gas volume in a capillary than in a packed column of equivalent dimensions it is probable that high performance packed columns will be more useful for low separation requirements (say, below 10,000) while the capillary column with its advantages of compactness will be used for higher separation numbers.

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CHAPTER 3

Columns and Column Packings

In Chapter 2 we have considered from a theoretical standpoint the effects of various column parameters on column efficiency. We now consider the practical details of column design, the uses and the selection of various supports and liquid phases.

Materials for packed columns

The stationary phase and its support for a packed column are usually contained in a tube some 2–10 mm in diameter and from 20 cm to 20 metres in length depending upon the size of sample to be analysed and the plate efficiency required. For most analyses columns of intermediate dimensions are used, 3–4 mm in diameter and 2–4 metres in length. Columns may be made of glass, metal or plastic tubing. Glass columns are usually straight or in the form of one or more U's, each arm of the U being about 100 cm long. Such columns require long tubular thermostats (see Chapter 5). Metal or plastic columns are easily coiled and can more readily be accommodated. Coiled glass columns can be used but they are a little difficult to fill. Metal columns can be made of copper, cupronickel or stainless steel. Plastic columns can be made from polythene or nylon. One must however be careful that the liquid phase does not dissolve in the plastic at the temperature of operation which must be relatively low. The great advantage of plastic tubing is the ease with which it can be coiled and uncoiled.

The diameter of the chromatographic column does not enter into any of the simpler theoretical equations since it is assumed that the packing is completely uniform. This cannot of course be strictly true and any irregularities in packing will result in loss of efficiency. In order to avoid this the column diameter should not be more than about twenty times the particle diameter and the supporting material should be closely graded with a maximum range of particle diameter of 20 per cent. In practice a lower limit to the column diameter is set by the size of sample it is desired to analyse and by the volume of the injection system, detector and ancillary tubing. The combined volume of these parts of the apparatus should be less than half the gas phase volume in the column if loss of resolving power is to be avoided. When using katharometers or standard argon detectors which have volumes of a cubic centimetre or more the column diameter should be at least 3 mm for a 100 cm length.

Column length has to be selected along with particle radius from consideration of the plate efficiency required and the practicable pressure drop across the column. Convenient particle sizes for columns of different lengths to be operated with a pressure drop of about half an atmosphere are: 100 cm, 120–140 mesh (see footnote to p. 30); 200 cm, 80–100 mesh; 5 metres, 50–60 mesh; 10 metres 35–45 mesh. A maximum plate efficiency of about 10,000 is obtainable with the longer columns and about 10–20 per cent loading of stationary phase. For higher plate efficiencies pressurized columns must be used with small particles or high-performance columns. For most applications however, plate efficiencies of between 1,000 and 5,000 are adequate and columns between 1 and 5 metres may be used.

Columns are generally packed straight or in U form and coiled if necessary later. However, it is not difficult to pack coiled columns up to 3 metres in length if the packing is driven in by compressed air. The column packing after preparation should appear quite dry and it is generally poured into the column while it is continuously tapped longitudinally and laterally. Tapping is continued until no more settling of the packing occurs. The column may be tapped sideways with any light wooden object or it may be held against an eccentrically rotating spindle. In order to pack a coiled column the packing should be placed in a wide tube attached to one end of the column and blown into the column by means of compressed air at about 10–20 p.s.i.g. While the packing is entering the column the spiral should be tapped continuously until no further settling occurs. This procedure can of course be applied to any type of column and generally speeds up the filling procedure without impairing efficiency.

After packing the column, the open ends are plugged with cotton wool, glass wool, or asbestos wool and the columns are attached to the apparatus by means of any suitable leak proof joint. Rubber tubing, plastic tubing, ground glass joints, and metal unions have all been used successfully.

Adsorption columns – preparation of packings

Adsorption chromatography is chiefly used for the analysis of gases and the only widely used adsorbents are charcoal, silica gel, alumina and Linde molecular sieves. These materials all tend to adsorb water and must be activated before use. Apart from charcoal the adsorbents are activated by heating to a dull red heat in a crucible with occasional stirring and allowing them to cool in a desiccator. Carbon must be activated by heating under vacuum or in a stream of inert gas to avoid oxidation. The carbon is placed in a round bottomed flask attached to a pump and heated to about 200°C until all 'boiling' ceases. This indicates that all adsorbed material has come off. Sometimes after activating an adsorbent it is necessary to resieve it in order to remove fines which have been formed during the activation procedure. The sieving should be done quickly to avoid loss of activity by adsorption of water vapour from the air.

Very often adsorbents prove either to be too active or to give misshapen peaks. Both of these undesirable effects can be countered by coating the adsorbent with a small percentage (0·5–2 per cent) of an involatile liquid such as squalane or dinonyl phthalate. This type of coating is often referred to as a tailing reducer. The effect of the addition of a tailing reducer to alumina is shown in Figure 3.1. Unsymmetrical peaks result from a dependence of the column capacity coefficient K on concentration, or, in other words, from non-linearity of the adsorption isotherm. If, for example, the activity of the sites on the adsorbent varies, the molecules adsorbed first will be more strongly held than those adsorbed later. K, and hence the retention time, will thus decrease as the concentration increases. The rear part of any band will thus be more strongly held than the rest of a band and so will move ever more slowly the more dilute it becomes. This means that the band will have a sharp leading edge and a long-drawn-out tail. If, on the other hand, adsorption becomes stronger as the concentration increases the peaks will have slowly rising leading edges. This occurs when the adsorbed material tends to

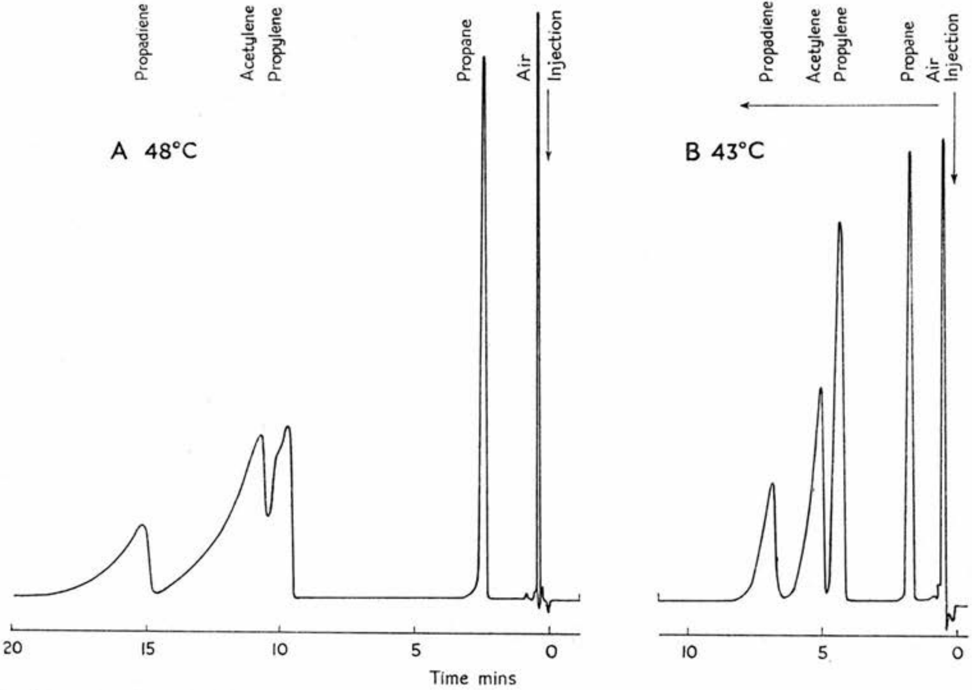

FIG. 3.1. The effect of a 'tailing reducer' on activated alumina. Separation of approx. 0·1 mg of a mixture of air, propane, propylene, acetylene and propadiene (allene): (A) on untreated activated alumina at 48°C and (B) on activated alumina poisoned with 2 per cent of dinonyl phthalate at 43°C. Both columns 150 cm long. Carrier gas – hydrogen. Detection by katharometer.

liquefy in the pores of the adsorbent, or with partition columns when the substances being chromatographed tend to associate in solution. The qualitative correlation between peak shape and the adsorption isotherm is illustrated in Figure 3.2.

The first type is typical of adsorbents even at the lowest coverages. The activity of the sites progressively declines as the coverage increases. The simplest way to induce linearity is to deactivate the most active sites so that those remaining have roughly the same, although lower, activity. 'Poisoning' is therefore a useful method of extending the range of adsorbents. The poison, or tailing reducer, is applied by dissolving the calculated amount in a volume of a volatile solvent (methylene chloride, pentane, ether) equal to that of the absorbent it is desired to treat. The solvent is then driven off under vacuum or by heating.

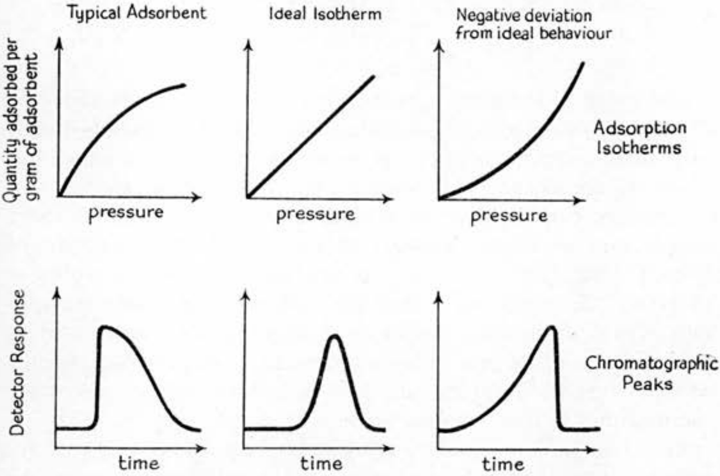

FIG. 3.2. Correlation between peak shapes and isotherms.

Poisoning is particularly useful when the mixture to be analysed contains olefins or acetylenes.

Uses of adsorption columns

Adsorption columns are of special value for the analysis of gases since there are few partition columns which can retain substances boiling below $-80°C$ sufficiently for them to be separated above room temperature. The gases which can usefully be separated at 25°C on the four main adsorbents unpoisoned are:

Activated carbon	H_2, O_2+N_2, CO, NO, CH_4
Silica gel	CH_4, C_2H_6, CO_2, C_2H_4
Alumina	C_2H_6, C_2H_4, C_3H_8, C_3H_6, cycloC_3H_6
Linde sieve 5A	H_2, O_2, N_2, CH_4, CO, C_2H_6

The range of these adsorbents can be considerably extended as already mentioned by adding a tailing reducer. Heating the adsorbents will enable compounds of higher molecular weight to be eluted but the peaks are often tailed. Alumina poisoned with a few per cent of squalane can be used for C_3 mixtures and acetylene at room temperature or slighty above, and poisoned with 3 per cent of di-nonyl phthalate can be used to separate C_4–C_6 hydrocarbons at 75–100°C. Generally the higher the molecular weight of the substances to be determined and the more unsaturated they are the more poison is required to give symmetrical peaks. Even poisoned alumina retains oxygenated compounds and carbon dioxide very strongly and it cannot be used for their analysis.

Activated carbon and silica gel can also be poisoned and used for higher hydrocarbons. Naphthenes, for example, appear before the saturated analogues on carbon poisoned with 1 per cent of squalane but after them on partition columns. Poisoned adsorption columns are particularly valuable in temperature programmed gas chromatography since they can be used over a wider range than partition columns, where the temperature of operation is limited on the one hand by the increasing viscosity and on the other by the increasing vapour pressure of the stationary phase. A recent illustration of the great range of adsorption columns is the separation of high molecular weight hydrocarbons on alumina poisoned with NaOH at 360°C.[1]

The relative retention times of compounds on adsorbents are similar to those on a partition column containing a highly polar liquid phase working at a considerably lower temperature. Unsaturated compounds are retained in proportion to their degree of unsaturation and come well after saturated compounds of the same carbon number. Most cyclic hydrocarbons appear before the corresponding alkanes although cyclopropane is an exception coming on alumina at the same time as propylene.

A disadvantage of all adsorption packings is the difficulty of obtaining reproducible samples of adsorbent with the resulting wide variation in retention times from one batch to the next. They also tend to deteriorate with use due to adsorption of impurities from the carrier gas, particularly water. Generally speaking it is better to use a partition column if one can be found to give the desired separation.

The fourth adsorbent, Linde molecular sieve 5A, is in a class of its own. Linde sieves belong to a wider class of adsorbents made by dehydrating Zeolites. The loss of water leaves an open crystal structure with pores of molecular dimensions. In the 5A sieve the pores are approximately 5 Ångström units across. Other molecular sieves have pores from 3 to 10 Å in diameter. Unlike most adsorbents which take up larger molecules more strongly than smaller ones, molecular sieves will only adsorb molecules that are small enough to enter their pores. Molecules below the critical size are adsorbed more strongly the larger they are, but molecules larger than the critical size are not adsorbed at all. Linde sieve 5A will for example adsorb permanent gases and straight chain hydrocarbons but will not adsorb branched chain hydrocarbons. It is of great value in gas chromatography as it is the only adsorbent which will cleanly separate H_2, O_2, N_2, CH_4 and CO at room temperature in the order given. Unfortunately CO_2 is irreversibly adsorbed. Molecular sieves very quickly adsorb water even when standing in the air for a few minutes. They are thereby greatly deactivated. When using them it is therefore essential to dry the carrier gas thoroughly. This is best done by passing it before use through a tube containing finely divided molecular sieve, or through a trap at $-80°C$ containing firebrick or Celite.

Preparation of partition columns

In gas-liquid partition chromatography the column packing consists of a granulated inert support carrying an involatile liquid phase. The supports commonly used are Celite (a coarse form of Kieselguhr), ground firebrick and less often glass beads. All three can be bought graded with convenient ranges of particle size. However for those who may wish to grade their own material a brief description of the process will be given.

The ungraded material usually contains a high percentage of fines (50–90 per cent). It is first washed in a tall jar by a stream of water delivered from a centrifugal stirrer. The flow is regulated so that all material finer than about 200 mesh is washed away. The larger particles which remain are then filtered off, dried and sieved into fractions. It may then be necessary to treat the graded support in order to eliminate undesirable adsorptive properties.

Celite is normally suitable for use without any further treatment but for the analysis of mixtures containing amines or acids it is sometimes necessary to wash with alkali or acid. Firebricks on the other hand exhibit strong adsorption of nearly all substances except saturated hydrocarbons and other non-polar compounds. Alcohols, amines and carbonyl compounds give badly tailed peaks. Firebricks cannot be significantly deactivated even by prolonged refluxing with concentrated acids. They can however be successfully deactivated by silver plating or polymer coating. Silver plating is carried out by any of the recognized methods. The final product is black. Polymer coating must be carried out by making the polymer *in situ.* Not all polymers are satisfactory, but urea-formaldehyde gives excellent results. A solution of 20 parts by weight of urea is made up in 40 parts of 36 per cent w/w formalin with 1 part of conc. ammonia. It is diluted with water or methanol to give a volume of 80 per cent that of the firebrick to be treated. The firebrick is added and the mixture is heated in an oven and cured at about 130°C for 1–2 days. The final product should be almost odourless and may be used up to a temperature of 150°C. A 20 per cent coating is sufficient to give symmetrical peaks with alcohols and ketones even on non-polar solvents.

Recently it has been claimed that 'Tide' detergent powder treated with light petroleum makes an ideal inactive support which has less adsorptive properties for amines than Celite. 'Tide' untreated apart from drying can be used as a non-polar column packing up to 200°C. It requires no additional liquid phase.

Glass beads may be used as a support only if the quantity of liquid phase to be added is very small. The liquid collects at the points of contact due to the surface tension and a maximum of about 2 per cent by weight can be retained in this way on beads smaller than 100 mesh. They have virtually no adsorptive properties.

Coating of the support with liquid phase is carried out by dissolving the liquid in a volume of solvent approximately equal to that of the support, adding this solution to the support and finally removing the excess solvent by heating or evacuation. The solvent must be much more volatile than the liquid phase. Substances such as low boiling petroleum, methylene chloride, acetone, diethyl ether and chloroform are suitable for most liquid phases.

Liquid phases specially purified for gas chromatography can now be obtained from a number of chemical retailers and it is well worth while paying the rather high prices for these materials in order to avoid troubles resulting from the impurities present in the normal reagents.

Stationary liquid phases

The determination of the best of a number of possible liquid phases for the analysis of a particular mixture is an exceedingly difficult matter. In theory, if one had the necessary data giving the retention volumes of all the components of the mixture on all the liquid phases at all temperatures, one could work out the best liquid phase and the optimum temperature for any desired resolution. These optimum conditions would give the fastest possible analysis. However, even with the necessary data, the mathematical problem would be extremely complex and could not possibly be solved in a reasonable time without an electronic computer. In the great majority of cases the necessary data are not available. The selection of a suitable liquid phases and operating temperature is then more of an art than a science and one must proceed empirically on the basis of a few rather general principles.

Although a hundred or more liquid phases have at one time or another been used in gas chromatography it is neither possible nor desirable to mention more than a few of the more well known. A multiplicity of liquid phases from which to choose only makes the process of selection more tedious without necessarily giving any better result than can be achieved by the intelligent use of a much smaller number.

The effect of change of solvent is mainly to bring about changes in the retention times of one homologous series relative to another. Generally speaking with a non polar liquid phase such as squalane or silicone oil substances are eluted in the order of their boiling points unless complicating features such as hydrogen bonding give rise to unusual boiling points. If the polarity of the solvent is increased the more polar components are held more strongly and the less polar compounds less strongly. These effects can be conveniently summarized by tabulating 'separation factors'. The separation factor for two homologous series is obtained by drawing up plots of log(retention volume) against boiling point. Such plots are generally straight lines which are usually nearly parallel for different series. The separation of the two lines gives the retention volume ratio for hypothetical members of the two series which have the same boiling point. This ratio is the separation factor. An extensive list of separation factors is tabulated by Bayer.[2] By selecting a solvent with a suitable separation factor for two homologous series one can arrange that the peaks of one series appear midway between the peaks of the other series and so on for more complex cases.

Before selecting a liquid phase on the basis of solvent effects two overriding considerations must first be taken into account. The temperature at which a conventional packed column operates is normally not far from the boiling point of the more volatile members of the mixture to be analysed. This operating temperature does not of course determine the liquid phase but it limits the choice. The liquid phase must not be highly viscous at the operating temperature nor must it have an appreciable vapour pressure. In order to avoid loss of column liquid by volatilization the vapour pressure should not exceed about 0·1 mm Hg. However, even as low a vapour pressure as this may not be tolerable to the detector. With katharometers a standing pressure of 0·1 mm of contaminating vapour from the liquid phase will cause no serious effects unless condensation occurs in the gauge, but with the highly sensitive detectors of the ionization type the pressure should not rise above about 10^{-3} mm if noise due to the contaminant vapour is to be avoided. This would at first sight imply that the maximum operating temperature for any stationary phase using an ionization detector should be some 100°C below that for use with a katharometer. However the contamination from a column liquid can be greatly reduced by the simple expedient of filling the last 10 or 20 cm of the column with a support bearing an exceedingly involatile stationary phase such as silicone oil. The volatilized liquid from the first part of the column is then 'chromatographed' on this last short column and having a high molecular weight will have a correspondingly high retention time compared with the components of any mixture analysed on the column. Only after prolonged use will this last section of the column pass stationary phase from the first part of the column.

A stationary phase is normally selected to be chemically similar to the compounds to be separated for this minimizes residual adsorption by the support and ill effects which could result from extreme deviations from Henry's law. With firebrick for example actone gives a skew peak when squalane is used as stationary phase but a symmetrical peak when polyethylene glycol is used. Presumably the latter liquid is itself adsorbed at the sites which would otherwise adsorb the acetone.

Choosing a stationary phase of the correct chemical type may also be important when analysing mixtures containing compounds which are susceptible to hydrogen bonding. Alcohols for example are very insoluble in hydrocarbon solvents and generally give badly shaped peaks on such stationary phases. They also show much lower retention times than one would expect from their boiling points although not lower than might be expected from their molecular weights. This is illustrated by the figures given in Table 3.1. For compounds such as alcohols, amines acids, etc., it is best to use solvents with which they can form hydrogen bonds such as polyethylene glycols, detergent liquids, or glycerols.

If the boiling points of the components of a mixture are well separated and if they do not feature any of the anomalous substances mentioned above, it is probable than an adequate separation will be obtained on a non-polar or slightly polar solvent such as squalane, silicone oil or a phthalate ester. When substances of different chemical type but of similar boiling point are present a non-polar solvent is less likely to give an adequate separation and a polar solvent may be

TABLE 3.1

Relative retention volumes on silicone oil at 50°C compared with boiling points

Substance	*Boiling point*	*Relative retention volume*
n-Pentane	36	1·00 (standard)
Methanol	65	0·35
n-Hexane	69	2·64
Ethanol	78	0·72
Cyclohexane	81	4.64
Isooctane	99	5·98
Water	100	0·72

required. It is then of course necessary to ensure that the change of solvent which improves the resolution of one pair of components does not seriously impair the resolution of another pair. This possibility makes it virtually impossible to give hard and fast rules about the selection of a liquid phase. The more complex a mixture is the more difficult it becomes to use solvent effects. They are chiefly valuable when one is analysing a simple mixture or when one is interested in only one or two specific components, for example trace components, in a complex mixture.

A particularly useful class of liquid phases for the analysis of oxygen and nitrogen containing compounds are the polyethylene and polypropylene glycols. These materials can be used up to about 120°C and are good solvents for alcohols, ketones, aldehydes and halogenated hydrocarbons; they are moderate solvents for ethers and aromatic hydrocarbons and poor solvents for saturated hydrocarbons. Thus decane (b.p. = 174°C) is eluted before methylene chloride (b.p. = 42°C) or acetone (b.p. = 56°C) and carbon tetrachloride is eluted before chloroform (b.p.s = 76 and 65°C respectively). Another liquid of somewhat similar properties is fluorene picrate, an equimolecular complex of fluorene and picric acid.

For giving enhanced separations of acetylenes and olefins from saturated hydrocarbons the highly polar dimethyl formamide or dimethyl sulpholane are useful, but unfortunately they cannot be used above 0°C because of their high volatility.

It occasionally happens that one requires a solvent of intermediate properties between two other solvents. Instead of carrying out a lengthy search for the exact liquid phase required it is much simpler and often equally effective to use a mixed column. There are three ways of making up such a column: (*a*) two columns in series with different packings can be used, (*b*) two packings can be mixed in the desired proportions before filling the column, and (*c*) two liquid phases can be mixed initially before coating the support. The first method is obviously the simplest and the most flexible but one may lose some column efficiency if the separation factors for the two liquids differ greatly. The third method is the best from the theoretical point of view but is inflexible and the liquids may not be miscible in the desired proportions.

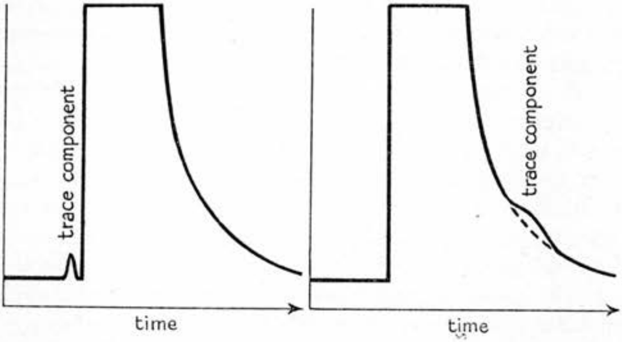

FIG. 3.3. Trace components coming before and after a major component.

Polarity effects may be of particular value in determining trace components in mixtures. Often the peak of a major component swamps the peak of some vital minor component even though equal amounts of the two substances might have been well separated. This is particularly liable to happen when the minor component comes after the major component since any overloading of the column by the major component will usually result in a peak with a sharp front and a long tail. If the trace comes before the major component it is much less likely to be obscured by overloading. This effect is illustrated in Figure 3.3.

If one is interested in determining trace components it is therefore well worth while attempting to use solvent effects to make them emerge before the nearest major components. An additional advantage of eluting trace components early is that their peaks will be sharper and a lower limit of detectability is obtained. One might note that with katharometer detection one cannot hope to detect impurities much below 0·01 per cent except in special circumstances. With the standard argon detector the limit is between 1 and 10 p.p.m. but with the small argon detectors and the flame ionization detector the limits are ten to a hundredfold lower.

The selection of a liquid phase thus depends not only upon the types of substances to be separated but also upon the complexity of the mixture and the relative amounts of the different components. Each analysis must in fact be considered on its own and even the most general rules can sometimes be broken with advantage. The list of commonly used liquid phases and their uses given in Table 3.2 is therefore to be regarded only as a very rough guide. Circumstances can be found where nearly all of the liquid phases mentioned can be used effectively for any of the classes of compounds listed.

In addition to these solvents of general applicability, a number of solvents with special properties have been described. Metal complexes and metallic salts of fatty acids often exhibit super-selectivity for certain specific compounds or groups of compounds. The first such liquid phases were solutions of silver nitrate in ethylene glycol or benzyl cyanide. Below 40°C silver nitrate forms weak complexes with olefines and these are strongly retained compared with their saturated analogues. Ethylene, ethane and the four butenes can be cleanly separated on a single column at room temperature.[3] The field has been greatly extended by Phillips who has used metal stearates to give highly specific separations of amines.[4]

Gas/liquid chromatography is usually carried out at room temperature or above but there is no reason why low temperatures cannot be used to good effect. Low temperature gas chromatography has the advantage over adsorption chromatography that it is much more versatile because solvents of varying polarity can be used. Some solvents which are suitable for analysis at -80°C are listed in Table 3.3. Most of the liquids listed have vapour pressures of 1–5 mm at

TABLE 3.2

Liquid phases and their uses in gas chromatography

Liquid	*Max. temp.* (°C)	*Used mostly for*	*Polarity*
‡Squalane	125	Hydrocarbons, ethers, ketones, halides	Non-polar
Apieson oil	200	High boilers	Non-polar
‡Apieson grease	300	,,	
Polythene	350	,,	
Asphalt	400	,,	
†Silicone oils	200	General purpose	Non-polar
‡Silicone grease	300	,,	
Silicone gums	350	,,	
‡Tricresyl, tritolyl phosphates	170	Hydrocarbons, oxygenates	Slightly polar
†Dinonylphthalate	130	Hydrocarbons, halides,	Moderately
Dinonylsebacate	130	oxygenates	polar
†Polyethylene glycols	120	Alcohols, water, acids, amines, combustion	Hydrogen bonded
Diglycerol	120	products; solubility of hydrocarbons is low	
‡Dimethylsulpholane	20	Low boiling hydro-	Highly
‡Dimethylformamide	0	carbons; olefines from	polar
Nitrobenzene	20	saturates	

† Indicates the three most widely used liquid phases.
‡ Indicates others widely used.

The maximum temperatures are approximate and refer to operation with a katharometer detector. For use with ionization detectors they should be reduced by 50–100°C.

room temperature and care has to be taken in preparing the column packings that the liquid phase is not pumped off with the solvent.

TABLE 3.3

Solvents for gas chromatography at $-80°C$

Liquid phase	*Polarity*	*Uses*
140–160° boiling petroleum	Non-polar	Air, CO_2, C_2H_2, C_2H_4, C_2H_6 up to C_4's
p-Cymene	Slightly polar	$C_2H_4+C_2H_6$, $C_3H_6+C_3H_8$, C_2H_2, Allene, $MeC{\equiv}CH$, C_4's
Ethylene glycol monoethylether	Polar	Olefines after saturates
Dimethylformamide	Highly polar	Olefines after saturates; COS after propylene

For low temperature gas chromatography a spiral column of glass or copper immersed in a large thermos flask is the most convenient column arrangement.

Capillary columns – materials

Capillary columns[5] can be made from nylon, glass, copper, cupronickel or stainless steel tubing. Nylon is cheap but cannot be used above 100°C. Glass capillaries can be purchased or made in a simple apparatus described by Desty[6] but they are fragile and sometimes difficult to coat evenly. Desty's apparatus is however of particular value in that it enables columns of different radii to be made. The range of diameters of commercially available capillary tubing is limited. Metal capillaries are somewhat more expensive than the other two but are robust and can be used at high temperatures.

Capillary columns are usually between 5 and 500 metres in length and from 0·1 to 1·0 mm in diameter (4–40 thou.). They are mounted coiled in a suitable thermostat. With short narrow capillaries very great care has to be taken in the design of the injection system, the detector and all joints between them, that the volume is kept small, preferably much less than the volume of the capillary itself. The plate efficiencies of evenly coated capillaries can range from about 5,000 for the shortest to 1,000,000 for the longest.

Capillary columns can be coated in two ways. The most reliable is probably to fill the column with a 0·5–2 per cent solution of the liquid phase dissolved in a low boiling solvent such as pentane, methylene chloride or ether. One end of the capillary is then closed and the other end fed slowly into an oven at a temperature considerably above the boiling point of the solvent. A reproducible quantity of liquid phase is thereby uniformly deposited on the walls of the capillary. The simpler method is to fill a length of the capillary with an approximately 10 per cent solution of the liquid phase in a volatile solvent and to drive this slowly through the column at not more than 10 cm/min. This gives an even coating of slightly uncertain thickness. The exact thickness can however be calculated by weighing the tube before and after coating. The second method is generally regarded as satisfactory although probably not quite so good as the first. The weight of liquid phase is usually in the region of 1 mg per metre for a 0·5 mm diameter column.

Liquid phases for capillary columns

The quantity of liquid phase used in a capillary column is generally expressed as a percentage of the internal volume of the tube A 1 per cent coating is normal. This is between 5 and 10 times less than is used on a conventional packed column. At any temperature *K*, and hence the retention volume of any substance, will therefore be much lower on a capillary column. This may lead to the danger mentioned in Chapter 2 that *K* becomes less than unity and the resolution of different substances becomes low. However, this is readily corrected by lowering the column temperature. Generally speaking a capillary column will be run some 50–100 degrees lower than the conventional packed column used for the same analysis.

The low loading of stationary phase on a capillary column means that volatilization will lead to much more rapid deterioration than would be expected with a packed column at the same temperature, but the lower operating temperatures of capillary columns largely cancel this out so that packed and capillary columns carrying out the same analysis on the same stationary phase will deteriorate at roughly the same rate. The low loading of liquid phase does however mean that only minute samples can be analysed without overloading. Whereas milligram samples are used for packed columns one cannot use more than a few micrograms with a capillary. This introduces sampling and detection problems which are considered in more detail later.

The stationary phases so far used in capillary columns have been limited to the more involatile liquids mentioned in Table 3.2, and because of the high efficiencies and high speeds readily attainable little attempt had been made to exploit solvent effects. However, with an increasing emphasis on high-speed gas chromatography a wider range of selective liquid phases will certainly come into use.

High-performance packed columns

The main problem to be solved in the development of high-speed, high-performance packed columns is how to reduce the mass transfer coefficient, C. The coefficient A in the van Deemter equation appears to be small or zero, and the coefficient B is of the order of magnitude of a diffusion coefficient as predicted by the theory. Thus little improvement in column performance can be expected from attempts to reduce A and B, or at least to make them closer to the theoretical values. However, the values of C for the packed columns which have so far been constructed are much larger than those given either by the modified van Deemter or the Golay equations. This is probably due to two factors. Firstly, with supports such as firebrick and Celite the liquid phase must be partly held in pores and cracks running inwards from the surface of the support, and even if the surface area is large, the root mean square thickness d of the liquid layer will almost certainly be greater than that for an evenly coated sphere. Secondly, experiments on the spreading of air peaks show that even with spherical glass beads the gas phase mass transfer coefficient is much greater than the equations would suggest. The reason for this is probably that in any normal packed column there are regions of stagnant or semi-stagnant gas in and out of which molecules can diffuse. The effect of the velocity distribution in a capillary is thus exaggerated. Thus the quantity r which appears in the coefficient C

of the modified van Deemter equation may be much greater than the particle radius.

In order to construct a high-speed packed column it will probably be necessary to use a 'tailor-made' support for the liquid phase. The support will have to be a porous structure which can be evenly coated with a liquid layer and also one whose surface is highly accessible to the moving gas, so that the effective channel radius for mass transfer is close to the dynamic channel radius of the packing.

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CHAPTER 4

Detectors

The development of gas chromatography has followed closely upon the adaptation or invention of suitable detectors. The earliest detectors were of the integral type and are typified by the titration device of James and Martin[1] and by the Janak nitrometer.[2] These detectors were followed by the application of the thermal conductivity gauge by Phillips[3] and Ray[4] and more recently by the invention of the argon and flame ionization detectors by Lovelock[5] and McWilliam.[6]

The Janak nitrometer

The gas chromatographic method invented by Janak is one of great simplicity and is still probably the most accurate. It is unfortunately applicable only to gases or to very volatile liquids and is of low sensitivity. Carbon dioxide is used as the carrier gas and is absorbed after emerging from the column in 30 per cent potassium hydroxide solution. Eluted gases which are unabsorbed are collected in a calibrated gas burette at atmospheric pressure. Details of the apparatus are shown in Figure 4.1. Gases emerging from the column bubble through a small jet (A) whose outlet is just below the surface of a pool of mercury. The jet is made fine so that the bubbles are small and do not disturb the manometer levels. The absorption of the carbon dioxide is an exothermic reaction and it is best to cool the solution by means of the coil (B) through which cold water passes. Even so there is a slight increase in the volume of the solution since potassium carbonate has a slightly larger partial molar volume than the potassium hydroxide from which it is formed. The filling tube (C) is therefore made much wider than the arm (E) of the gas burette and is left open. Any small change in the volume of the liquid is mainly taken up by rise of the liquid in the filling tube.

At the start of an analysis the tap (F) is closed and the eluted gases collected in E whose right-hand limb, conveniently made from a 5 or 10 ml semi-micro burette, is graduated in 0·01 ml divisions. Each time a reading is to be taken the pressure is adjusted to atmospheric by

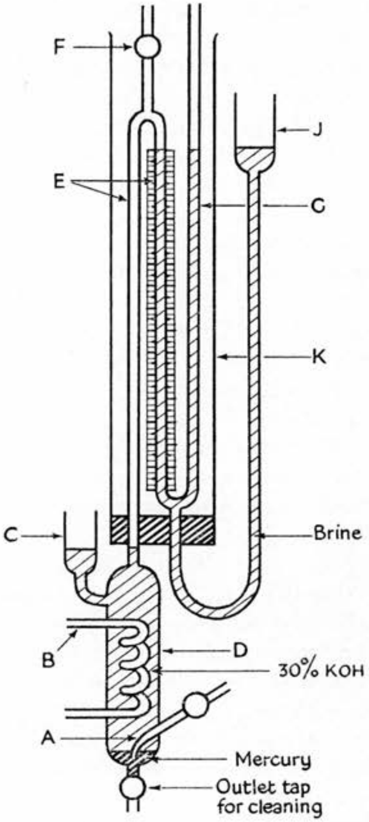

FIG. 4.1. The Janak nitrometer detector.

raising or lowering the reservoir (J) so that the levels in E and G are the same. Brine is used as the containing liquid in E and G because of its low vapour pressure. The three tubes making up the measuring system are thermostatted by immersing the whole in a water jacket (K).

An accuracy of better than 0·005 ml is attainable with the nitrometer detector and thus components can be determined to about 0·1 per cent on samples of 5 ml. In order for the high potential accuracy to be realized, however, the bands of different components must be sharp and well separated so that the small drift rate due to impurities in the carbon dioxide can be accurately allowed for. If well-weathered solid carbon dioxide (Cardice) is used as the source of carrier gas a drift rate as low as 0·01 ml per minute at a flow rate of 100 ml/min can be realized. Cylinder carbon dioxide is not sufficiently pure to be used as the carrier gas. The crushed Cardice should be placed in a wide tube (say, 30–40 mm diameter) which can be partially immersed in a thermos flask. The rate of evaporation can then be roughly controlled by raising or lowering the tube in the thermos flask. Exact control of flow rate is unimportant with the nitrometer and one requires only a simple blow-off in order to vent excess carbon dioxide and maintain a roughly constant pressure across the apparatus.

The nitrometer detector is relatively cheap and is simple to construct, but it is seriously limited because only gases can be analysed and because a rather large sample is required. The first limitation can be alleviated by heating the gas burette and measuring the gas under conditions of constant volume rather than constant pressure, but a more satisfactory solution is to employ a vapour converter (see Chapter 5) which converts any organic material emerging from the column into a single substance such as hydrogen. A vapour converter also increases the sensitivity.

The large sample required by the nitrometer detector means that columns are likely to become overloaded and therefore give worse separations than would be obtained with smaller samples. This disadvantage is partially overcome by using 8–10 mm bore columns instead of the more usual 2–4 mm bore columns, but the flow rate and drift rate are also increased proportionately.

Katharometers

Katharometers or thermal conductivity gauges are at present the most widely used detectors and they are regarded as the standard against which any other detector is assessed. The katharometer is basically a very simple device consisting of a fine wire mounted axially in a narrow tube. The wire is heated electrically and assumes a temperature which depends upon the properties of the gas passing over it. When the composition of the gas changes the wire temperature and hence its resistance change. If the wire forms one arm of a Wheatstone bridge this change in resistance is converted into a small e.m.f. which can readily be recorded.

The best katharometers now available can detect changes in composition of a gas such as hydrogen or nitrogen of the order of 1 part per million. Sensitivity of this order demands extraordinarily high thermal and electrical stability and it is somewhat surprising that this stability can be achieved in a relatively simple piece of apparatus.

The modern katharometer consists of two identical thermal conductivity gauges built into the same massive brass block. One serves as a reference gauge and is placed in the pure carrier gas stream while the other is placed in the gas emerging from the column. The effects of minor fluctuations in the flow rate, ambient temperature and pressure are then greatly reduced. For high stability it is important that the two balanced gauges are as exact replicas of each other as possible. The wires must have exactly the same resistance (within 0·1 per cent) and they must be mounted congruently in their respective channels.

In developing the theory of the katharometer we suppose that the two gauges are mounted in a Wheatstone bridge as shown in Figure 4.2 and that a voltage E (say, 4–12 volts) is applied across the gauges in series. The gauges each have a resistance R and the balancing arms resistances R'. The additional resistance R'' is required in practice to compensate for small differences between the other resistances. It is variable and of much higher resistance than R'.

It can readily be shown that if E remains constant the power given out by any gauge also remains constant to a first approximation for small changes in its resistance. We can therefore carry out operations such as differentiation at constant power dissipation.

Heat is lost from the wires both by conduction and by forced convection. If we assume that the gas leaving the gauge has attained thermal equilibrium we can write[7]

$$\begin{aligned} \text{Power dissipated} &= i^2 R = E^2/4R \\ &= (2\pi\lambda L + fC)\, a . \Delta T \qquad 4.1 \end{aligned}$$

where i = current through wires; λ = thermal conductivity of gas; L = wire length; f = flow rate in moles per unit time; C = molar specific heat of gas at constant pressure; ΔT = difference between temperature of wire and block, and a = a geometrical constant given by

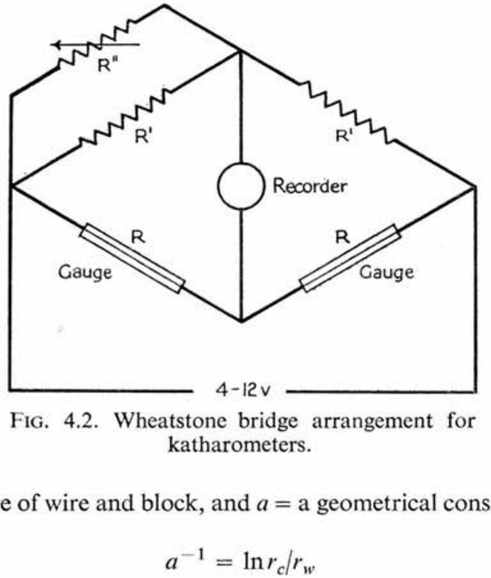

FIG. 4.2. Wheatstone bridge arrangement for katharometers.

$$a^{-1} = \ln r_c/r_w \qquad 4.2$$

where r_c and r_w are the radii of the channel and the wire respectively.

If the composition of the gas changes by an amount dX due to the replacement of a fraction dX of the carrier gas by molecules of some other vapour then the thermal conductivity and specific heat will change by amounts given very roughly by

$$\begin{aligned} d\lambda &= (\lambda_{\text{carrier}} - \lambda_{\text{vapour}})\, dX = \Delta\lambda . dX \\ dC &= (C_{\text{carrier}} - C_{\text{vapour}})\, dX = \Delta C . dX \qquad 4.3 \end{aligned}$$

By differentiating equation 4.1 with power constant we obtain a value for the temperature change of the wire

$$dT = -\left(\frac{2\pi L\Delta\lambda+f\Delta C}{2\pi L\lambda+fC}\right).\Delta T.dX \qquad 4.4$$

The resistance of the wire will then change by an amount

$$dR = \alpha R dT \qquad 4.5$$

where α is the thermal coefficient of resistance. The off balance e.m.f. generated by this change in resistance is

$$dE = -\tfrac{1}{4}E.dR/R = -\tfrac{1}{4}E.\alpha dT \qquad 4.6$$

If dT and ΔT are eliminated between equations 4.6, 4.4 and 4.1 we obtain for the sensitivity of the gauge

$$S = \frac{dE/E}{dX} = \left\{\frac{(2\pi L\Delta\lambda+f\Delta C)}{a(2\pi L\lambda+fC)^2}\right\}\cdot\frac{\alpha E^2}{16R} \qquad 4.7$$

The various factors which affect the sensitivity of the katharometer and its stability may now be considered. In equation 4.7 the electrical terms are grouped in the second factor on the right-hand side while the geometric terms and those relating to the carrier gas are in the first factor.

The sensitivity of the gauge clearly depends upon the square of the bridge voltage and inversely upon the gauge resistance, that is, it increases directly as the power dissipated in the gauge. The actual response dE to a given change in composition will increase as E^3 and thus a small percentage change in bridge voltage will induce three times the percentage change in the off balance e.m.f. of the bridge. Stabilization of the bridge e.m.f. must be carried out with this in mind. Generally it is sufficient to place a small 1 or 2 ohm variable resistance between the batteries and the bridge and to adjust the bridge voltage to a definite value using a voltmeter with a reading accuracy of about 0·1 per cent.

Change of carrier gas affects the sensitivity of the gauge through the thermal conductivity and heat capacity terms. Since $\Delta\lambda$ and ΔC are generally of opposite sign it is important that the two terms in the numerator of equation 4·7 do not exactly cancel out. With most gauges under their normal working conditions the thermal conductivity term is much larger than the heat capacity term but their relative magnitudes will depend upon the nature of the carrier gas, flow rate and length of the wire. This is seen more clearly by reference to Table 4.1 where values of λ and C are tabulated for a number of carrier gases and typical vapours. When the specific heat effect is slight the sensitivity equation takes the form

TABLE 4.1

Thermal conductivities and specific heats

		$10^5 \Delta\lambda$			ΔC
Substance	$10^5\lambda$	H_2	N_2	C	H_2 or N_2
Hydrogen	32·7			6·8	
Helium	33·9			5·0	
Nitrogen	5·2			6·9	
Argon	3·9			5·0	
Methane	6·5	26·2	−1·3	8·5	−1·6
Ethylene	3·9	28·8	1·3	10·1	−3·2
Hexane	3·0	29·7	2·2	35	−28

λ in cal cm^{-1} sec^{-1} deg^{-1}; C in cal deg^{-1} mole^{-1}.

$$S = \frac{dE/E}{dX} = \frac{\Delta\lambda}{2\pi\lambda^2 La}\cdot\frac{\alpha E^2}{16R} \qquad 4.8$$

For heavier vapours (e.g. hexane) the sensitivity is higher with nitrogen than with hydrogen owing to the predominant effect of the λ^2 factor in the denominator. However the specific heat effect will be much more pronounced when using nitrogen as the carrier gas and will result in a marked decrease in sensitivity with a vapour such as hexane. Depending upon the design of the katharometer this may well reduce the sensitivity to that when using hydrogen as the carrier. With hydrogen one also notes that the sensitivity to different vapours varies only slightly while with nitrogen wide variations will occur and the sensitivity will change sign for gases lighter than nitrogen. In certain borderline cases, for example C_2 hydrocarbons, the sensitivity is very low and variable. Hydrogen is therefore superior from this point of view and one can assume that the molar sensitivities for different vapours are roughly equal although for accurate work calibration is still essential.

The specific heat effect introduces a further complication as it can give rise to peak reversal. The specific heats of complex molecules in the vapour phase increase rapidly with temperature as the molecular vibrations contribute more and more to the internal energy of the molecules. The thermal conductivity changes much less rapidly. If the specific heat effect is at all important at low temperatures it will become increasingly so at higher temperatures. It is thus possible for the gauge sensitivity to change with temperature, to become zero and eventually negative at high temperatures. The variations in the effective values of $\Delta\lambda$ and ΔC lead to further complications when peak reversal becomes possible. Owing to non-linear variations of λ and C with mixture composition the inversion temperature depends upon mixture composition and instead of simply obtaining flattened peaks, which one might have expected, *M* and *W* shaped peaks are obtained in the region between positive and negative sensitivity. Under these conditions quantitative measurement is impossible. This effect occurs much more readily with carrier gases like nitrogen than with hydrogen and one must always guard against it. In order to check that one is not close to the peak reversal region it is advisable to carry out a few experiments with the bridge voltage about double the normal value. If peak reversal occurs at the high bridge voltage then the original bridge voltage was still too high. With hydrogen peak reversal does not occur under normal circumstances because of its much higher conductivity than nitrogen.

While the sensitivity of a katharometer is of great importance, the ratio of the sensitivity to the magnitude of the various disturbing factors is more important. It is always possible to amplify an electrical signal and straightforward sensitivity does not really limit katharometer performance. Katharometers like most detectors can suffer from both noise and drift. The term noise is used to refer to random short-term fluctuations of the bridge output. Drift is a slow long-term change in the output.

Noise in katharometers can arise from three sources. Electrical noise arises if the bridge voltage is poorly stabilized. This can occur if a power pack is used to supply the bridge voltage but is unlikely with accumulators in good condition if the contacts are clean. Mechanical noise from filament vibration is most likely to occur with straight wire katharometers used at elevated temperatures, but is less likely with self-sprung coiled filaments. Very low frequency noise results from gauge contamination. This generally arises when a gauge is run at a lower temperature than the column, and when the stationary phase is slightly volatile. It is cured simply by washing out the gauge with a suitable solvent and running it thereafter at a sufficiently high temperature. Noise will increase directly with the power dissipated in the gauge and the sensitivity/noise ratio cannot be improved by using a different bridge voltage.

Fortunately noise is not the main limiting factor when using katharometers. Drift is much more important. It generally results from gradual changes in the flow rates through the two sides of the katharometer or from changes in the ambient temperature.

Drift from flow fluctuations stems from variation in the specific heat term as the flow rate changes. It may be treated quantitatively by considering equation 4.1. At constant power dissipation, with a given carrier gas, the temperature change due to a flow rate change df will be

$$dT = -\frac{C\Delta T}{(2\pi L\lambda + fC)}.df \qquad 4.9$$

Eliminating dT and ΔT as before we obtain the sensitivity to flow fluctuations as

$$D = \frac{dE/E}{df} = \frac{C}{a(2\pi L\lambda + fC)^2}\cdot\frac{\alpha E^2}{16R} \qquad 4.10$$

The stability of any gauge is governed largely by the sensitivity to composition changes divided by the sensitivity to flow changes, that is by the ratio S/D. This may be called the stability factor.

$$\text{Stability factor} = S/D = (2\pi L\Delta\lambda + f\Delta C)/C \qquad 4.11$$

ΔC does not vary much from one carrier gas to another but $\Delta\lambda$ will change at least sixfold in going from a light gas such as hydrogen to a heavier gas such as nitrogen (see Table 4.1). The highest stability will be obtained for the highest value of $\Delta\lambda$, that is by using the lighter carrier gases hydrogen and helium. This is in general borne out by experience.

Drift due to thermal instability is readily corrected by better thermostatting of the katharometer block. In order to make the best use of the high heat capacity of the katharometer block it should be mounted in an air thermostat not in a liquid thermostat. With a well-balanced katharometer quite crude thermostatting should be adequate. A katharometer working at room temperature is best placed in a well-insulated box and protected from draughts.

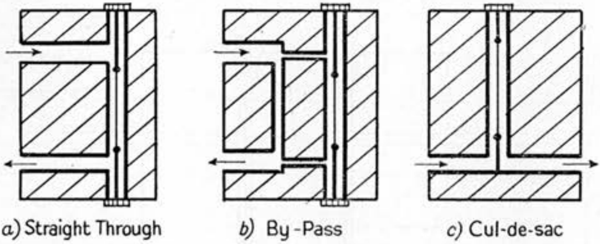

FIG. 4.3. Possible positions of the filament in a katharometer *vis-à-vis* the gas stream.

The geometry of the katharometer can affect both its sensitivity and liability to drift. Both peak inversion effects and drift are reduced by making the thermal conductivity term large in comparison to the specific heat term (equation 4.1). This means that the katharometer wire should be long and the flow rate low. Taken to extremes this would give a gauge of rather low response time and in practice a compromise is accepted. Filaments are usually 1–3 cm in length and flow rates are in the region of 10–100 ml/min.

The positioning of the wire relative to the gas stream strongly influences the stability of a gauge but stability is always bought at the expense of speed of response. Three possible arrangements are shown in Figure 4.3. The 'cul-de-sac' arrangement relies on diffusion and the flow rate past the filament is almost zero. It is therefore very insensitive to variations in the rate of flow of gas from the column but has a response time of about 30 sec. The straight-through arrangement is the most sensitive to flow and has a low response time of about 0·2 sec. The intermediate by-pass arrangement is a compromise with a response time which depends upon the fraction of the gas stream which flows over the filament. It is useful when one is interested only in the analysis of substances with high retention times. However for general use a katharometer of the lowest possible response time is normally chosen.

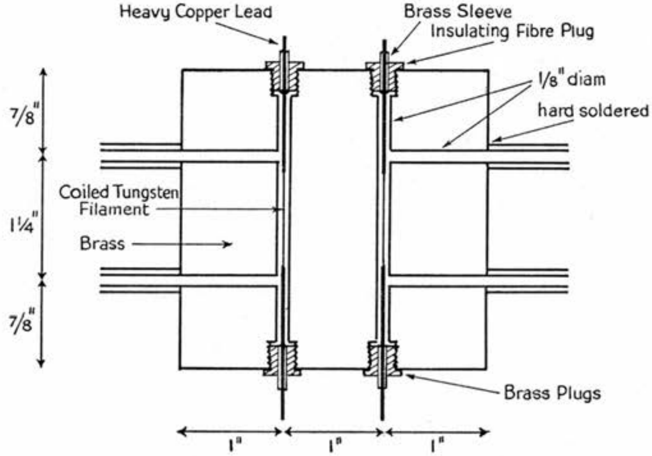

FIG. 4.4. A simple katharometer.

Commercial katharometers are now marketed for about £30 and are highly reliable. Matched sets of replacement filaments may also be obtained. It is therefore generally not worth while to make one's own. However, for those who do, a design which has been widely used in our own laboratories and works well is shown in Figure 4.4. These katharometers are more sensitive to drift than the best commercial models owing to the difficulty of matching the filaments exactly. They must be well thermostatted and the two sides supplied with identical gas streams preferably from two identical columns fed from the same supply of carrier gas.

Thermistors may be used instead of wires, and provided that they are selected to be of similar properties a thermistor katharometer is as satisfactory as a wire katharometer. They are particularly useful when a detector of very small volume is required.

Katharometers are supplied with between 4 and 12 volts as shown in Figure 4.1. The wire resistances may be between 10 and 100 ohms at room temperature while the resistances R' are conveniently made from 100 ohm wire wound radio resistances. The variable resistance R'' can be a 0–11,110 ohm resistance box or a wire wound potentiometer of similar resistance.

An alternative electrical arrangement is to use a low resistance helipot between the two 100 ohm radio resistances for balancing purposes. Standardization of the bridge e.m.f. is necessary only when absolute measurements are made. This is most simply carried out by placing a 1 or 2 ohm slide-wire between the batteries and the bridge. The bridge voltage can then readily be adjusted. The chromatograms obtained using a katharometer as detector are usually recorded on a 1 or 2·5 mV recorder with a response time of 1 or 2·5 sec.

The flame temperature detector

A detector which compares in simplicity and sensitivity with the katharometer is the flame temperature detector illustrated in Figure 4.5. Nitrogen is used as the carrier gas and hydrogen is added at a carefully controlled rate at the outlet of the column. The resulting mixture is burnt at a jet and the flame impinges on a thermocouple mounted 1–2 cm above the flame and encased in a fine quartz tube. The e.m.f. from the thermocouple when only nitrogen and hydrogen are passing is balanced out by a potentiometer. When an organic vapour emerges from the column its heat of combustion is added to that of the hydrogen and the flame temperature is increased. The increase in the temperature of the thermocouple, measured as an off-balance e.m.f., is proportional to the rate of heat liberation in the flame. The response of this detector is quite accurately proportional to the heat of combustion of the vapour eluted and the detector thus becomes progressively more sensitive on a molar basis with increasing molecular weight. It is particularly suitable for the analysis of high boiling substances when it compares in sensitivity with a good katharometer. A valuable feature of the flame detector is that it

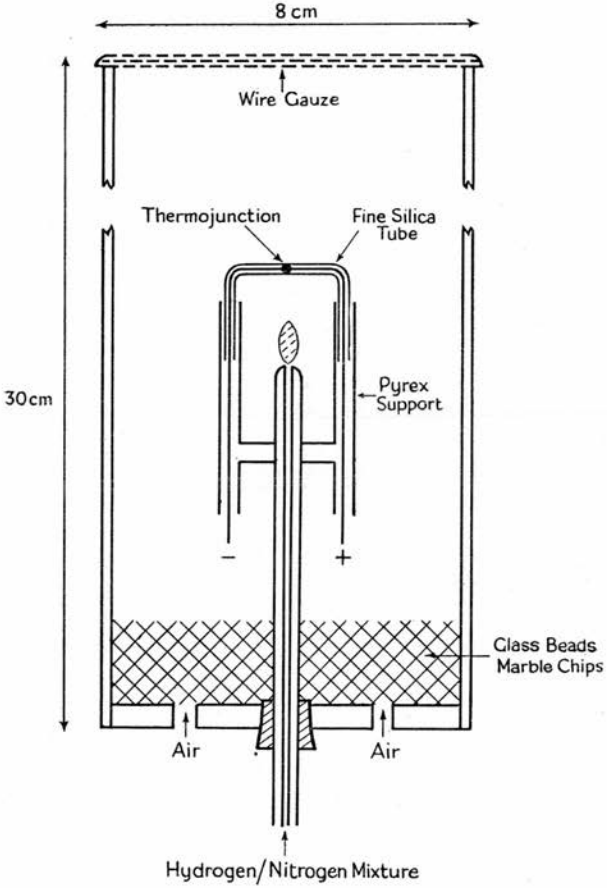

FIG. 4.5. The flame temperature detector.

measures the quantity of eluted material rather than the concentration. Thus doubling the flow of gas through the column will not alter the area of a peak due to a given quantity of any substance. The peak will be half the width but twice the height. For calibration purposes accurate control of flow rate is unnecessary.

The flame detector works best when the nitrogen/hydrogen ratio is about unity and the thermocouple arranged so as to be between 500 and 800°C. The detector is very sensitive to draughts and must be placed in a draught-proof box.

The gas density balance

This detector invented by Martin and James[8] is the only detector which measures an accurately defined property of the eluted vapour. The detector is a somewhat complex arrangement of channels and throttles mounted in a block and it forms a dynamical analogue of the Wheatstone bridge. A difference in density between the effluent from the column and a reference stream of carrier gas results in a proportional flow of gas through a small cross channel in the block. This channel houses an electrical anemometer which gives an electrical signal proportional to the rate of gas flow through the tube. The detector is rather insensitive to flow changes and it has the additional merit that only one calibration is required to define the relationship between anemometer output and density difference. The signal from any eluted vapour is then directly proportional to its concentration and the difference between its molecular weight and that of the carrier gas.

The major drawback to the density balance is difficulty of construction but a number of commercial models are now available. Their sensitivity is comparable with that of a katharometer.

Ionization detectors (general)

The detectors so far discussed, with the exception of the integral detectors, depend upon the measurement of a general property of the components of the column gas – thermal conductivity, heat of combustion, density. With such detectors small changes in the condition of the carrier gas, resulting say from flow rate or temperature fluctuations, can produce signals comparable in size to those from small quantities of eluted vapours. The limit of their sensitivity is set by the stability of the carrier gas stream. The ideal detector for gas chromatography is one which measures a specific property of the eluted vapours and which gives virtually no signal when the carrier gas alone passes through it. All the modern high sensitivity detectors are of this type. They are based upon measurement of the electrical conductivity of gases which have been partially ionized. The conductivity is altered by the appearance of an eluted vapour in the otherwise pure carrier gas.

The most widely used of the ionization detectors are the argon detectors invented by Lovelock[5] and the flame ionization detector invented by McWilliam and Dewar[6]; they are about 10^3 to 10^4 times as sensitive as a good katharometer. However, a number of other ionization devices have been developed as detectors for gas chromatography and their potentialities have recently been reviewed by Lovelock.[9] The use of these other ionization detectors will certainly become wider in the near future and before describing the argon and flame ionization detectors in detail ionization detectors in general will be briefly discussed.

When high energy radiation, for example β radiation from a radioactive source, passes through a gas ion pairs are first formed as the highly energetic electrons lose their energy. The *ionization cross-section detector* uses this phenomenon directly. Long range β radiation from a 10 millicurie Sr^{90} or Pm^{147} source (usually alloyed in silver or gold foil) generates ion pairs at a rate dependent upon the intensity of the source and the ionization cross-section of the gas mixture. If the ionization chamber is small and the absorption of electrons weak the rate of formation of ion pairs is given by

$$i_s = kc \sum (Q_i X_i)$$

were $c =$ gas concentration in molecules per c.c.; $Q_i =$ ionization cross-section of component i, and $X_i =$ the mole fraction of component i in the mixture. k is a constant proportional to the strength of the radioactive source and dependent upon the geometry of the ionization chamber. When an increasing potential is applied between the electrode and the wall of the ionization chamber (see Figure 4.6) the current rises from zero to a steady value i_s when all the ions and electrons produced by the radiation are collected at the electrodes. At very high potentials the current rises above this value due to ion and electron multiplication processes.

This detector is unselective and responds to all gases. It is similar to the katharometer in that the largest part of the signal arises from the carrier gas. It is therefore somewhat insensitive and the limit of detection is about 0·01 per cent of eluted vapour in the carrier gas. It will however give a linear response up to 100 per cent vapour and so has a linear range of about 10^4 which compares favourably with that of a katharometer. Unlike the katharometer the cross-section detector is insensitive to changes in flow rate or temperature since the drift rate of the ions is much higher than the gas velocity through the

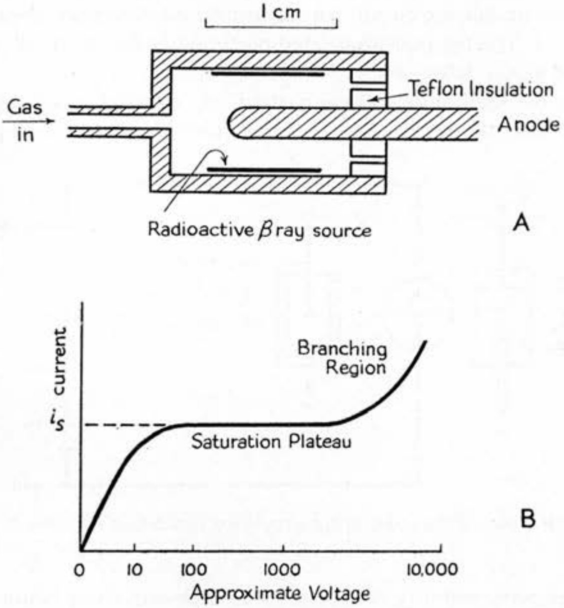

FIG. 4.6. (A) ionization cross-section detector (after Lovelock). (B) Current voltage curve (approximate) for (A).

detector. The background signal from the detector is about 10^{-8} to 10^{-9} amp. This output can only be satisfactorily measured with the help of an electrometer amplifier. With ionization detectors generally background currents are between 10^{-10} and 10^{-8} amp and the amplifier must measure faithfully currents from a lower limit of between 10^{-14} and 10^{-10} amp to an upper limit of about 10^{-6} amp. The basic measuring circuit for all ionization detectors is shown in Figure 4.7. The figure is annotated particularly for the flame ionization and argon detectors.

The cross-section detector is particularly suitable for use in large-scale gas chromatography and in semi-automatic gas chromatography where extreme stability is required and high sensitivity is not necessary.

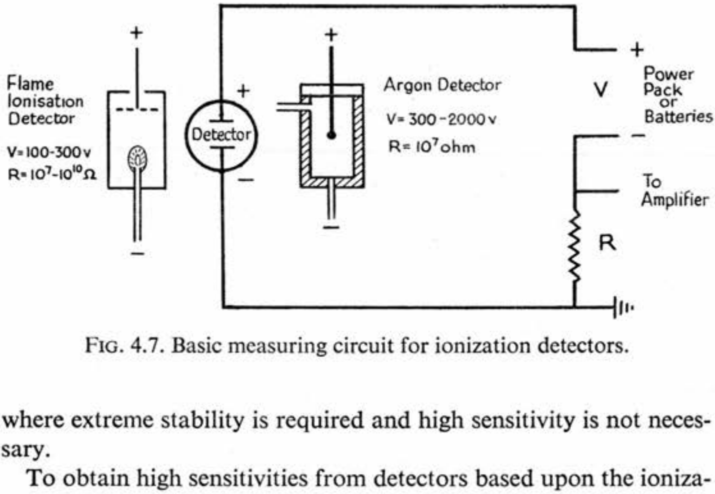

FIG. 4.7. Basic measuring circuit for ionization detectors.

To obtain high sensitivities from detectors based upon the ionization of gases it is necessary to make use of a specific property of the eluted vapours, and one inevitably loses some generality thereby.

In the *flame ionization detector*, described more fully later, a hydrogen/nitrogen mixture is used as the carrier gas and is burnt in the detector at a jet above which a collector electrode is placed (see Figure 4.8). The rate of ion production in the flame is measured by applying a potential of 100–300 volts between the jet and the collector electrode. This is sufficient to give the saturation current. With only hydrogen burning in the flame the ionization efficiency is exceedingly low and only about one hydrogen molecule in 10^{12} produces an ion.

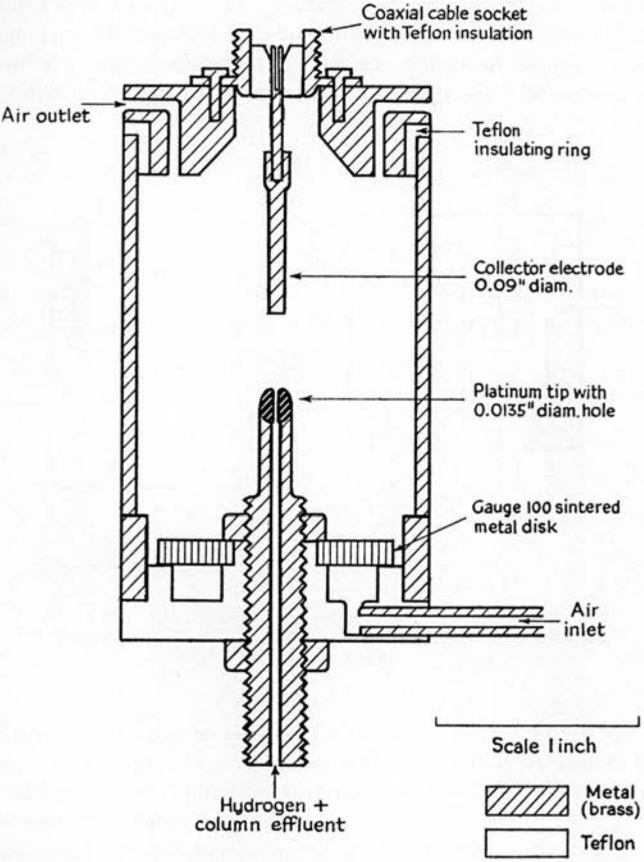

FIG. 4.8. The flame ionization detector (after Desty, Geach and Goldup (1960), *Gas Chromatography, 1960*, p. 46).

On the addition of an organic substance to the flame the ionization increases greatly, the ionization efficiency per carbon atom being about 1 in 10^5. The reason for this great increase in ionization efficiency is not yet fully understood but it cannot be accounted for by differences in the ionization potentials of hydrogen and typical organic molecules. According to one view the ions derive from minute carbon particles formed in the flame, solid carbon having a much lower ionization potential than organic molecules. According to another the ionization results from pooling of energy stored in excited molecules, radicals and free atoms. Both explanations are open to the criticism that the ionization process would not be expected to be first order in the concentration of the organic molecules, and they would not give a detector response proportional to the concentration of the organic vapour in the flame.

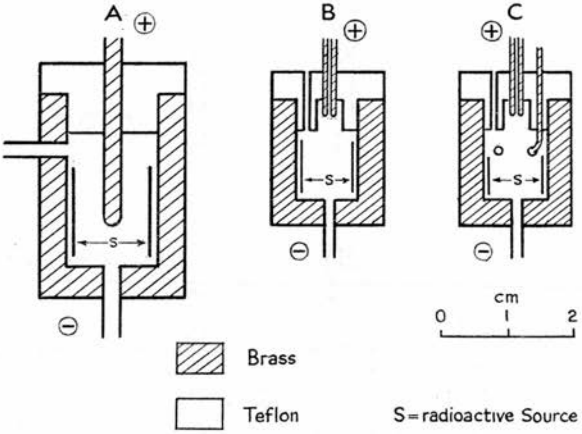

FIG. 4.9. The Argon detectors (*a*) simple, (*b*) small, (*c*) triode (taken from Lovelock (1960) *Gas Chromatography 1960*, p. 16).

The operation of the *argon detectors* (see Figure 4.9) depends upon the fact that argon in common with other noble gases, possesses an electronic state whose excitation energy is well below its first ionization potential but above those of most organic molecules. When argon is irradiated with high-energy radiation both ionization and excitation occur according to reactions (1a) and (1b) below

$$\text{Ionization:} \qquad \mathrm{Ar} \xrightarrow{\alpha,\beta} \mathrm{Ar}^{+} + e \qquad (1a)$$

$$\text{Excitation:} \qquad \mathrm{Ar} \xrightarrow{\alpha,\beta} \mathrm{Ar}^{*} \qquad (1b)$$

when an excited argon atom collides with an organic molecule there is a high probability that the excitation energy will be transferred to the organic molecule bringing about its ionization according to reaction (2)

$$\mathrm{Ar}^{*} + \mathrm{RH} \longrightarrow \mathrm{Ar} + \mathrm{RH}^{+} + e \qquad (2)$$

The electron liberated in this reaction is now accelerated by a powerful electric field (300–2,000 volts across the detector) and can excite, but not ionize, further argon atoms. A potentially branching chain reaction thus results and in the absence of serious ion recombination or the accumulation of space charge the ion current will theoretically become infinite at a finite concentration of the organic vapour which depends only upon the applied field. This does not however occur in practical detectors. Since the electron mobility is very much higher than the ion mobility, the electrons tend to be collected by the anode while the positive ions accumulate in the gas phase. The accumulation of this space charge neutralizes to some extent the applied voltage and by careful design can be used to increase the linear range of the argon detector greatly. Because of this the construction of argon detectors is highly critical.

Selective ionization of eluted vapours may also be achieved by means of high energy photons. The *photo ionization detector* recently described by Lovelock[10] employs this principle. Clean carrier gas (helium, argon, nitrogen or hydrogen) enters the ionization chamber (see Figure 4.10) through a hollow anode at a pressure of about 10 cm Hg. A glow discharge is produced between the anode and a heavy ring cathode by means of a constant current high voltage supply. Photons of high energy are formed in the discharge and those not absorbed by the carrier gas pass down the tube and can ionize any eluted vapour which enters from the column through a hollow electrode at the opposite end of the ionization chamber. The rate of photo ionization is determined by applying a potential of about 100 volts between the inlet tube from the column and a cylindrical anode.

This detector is still in a rudimentary form but it appears to be stable over long periods and to be uninfluenced by contaminants. It is also insensitive to flow rate and operating pressure. The detector is highly sensitive and has a background current of about 10^{-10} amp. In contrast to the flame ionization and argon detectors it can probably be used for permanent gases.

The three high-sensitivity detectors just described depend upon the selective ionization of eluted vapours in a carrier gas which is itself not significantly ionized. With the possible exception of the photo ionization detector, they are insensitive to permanent gases whose ionization potentials are high. Such substances can however be detected which high sensitivity if they have high electron affinities or if they are particularly effective in slowing down fast-moving electrons.

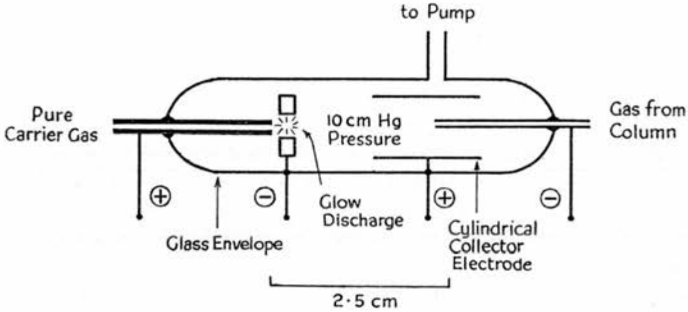

FIG. 4.10. The photo-ionization detector (after Lovelock).

Substances with moderate or high electron affinities can readily be detected by the *electron capture detector* shown in Figure 4.11. This detector depends for its operation upon the fact that the rate constant for the recombination of oppositely charged ions is some 10^6 times greater than that for recombination of a positive ion and an electron. The carrier gas is ionized by a suitable radioactive source and for quantitative analysis a sufficient potential is applied to the two electrodes just to collect all ions and electrons. When an electron capturing substance enters the ionization chamber electron capture occurs to give negative ions which are rapidly removed from the system by recombination. The ion current is thereby reduced. The reduction in current follows a law similar to the Beer law for optical absorption

$$i = i_0 e^{-kxc}$$

where i = current passing in the presence of a concentration 'c' of electron capturing vapour; i_0 = current passing in the absence of any foreign vapour; k = a constant depending upon the field strength and the absorption cross-section of the vapour, and x = a geometrical factor.

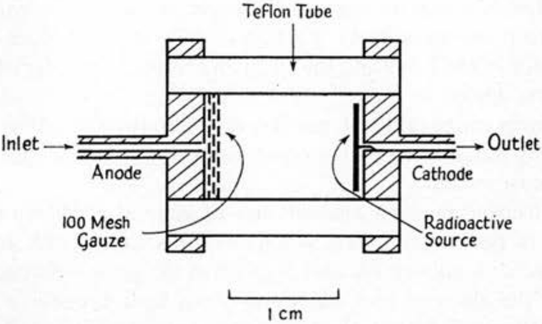

FIG. 4.11. The electron capture detector (after Lovelock).

This detector is exceedingly sensitive to substances containing atoms or groups of atoms of high electron affinity, and it is ideal for the quantitative determination of acids, esters, halogen-containing compounds, carbonyl compounds, nitro compounds, etc. It is less sensitive to ethers and rather insensitive to hydrocarbons other than aromatics. The electron capture detector has the unusual feature that its sensitivity to different chemical types depends upon the average electron energy in the pure carrier gas. Substances of low electron affinity can only be detected when the average electron energy is low; those of high electron affinity can be detected at higher electron energies. By suitable selection of the average electron energy it is thus possible to detect certain chemical types and not others. The electron capture detector thus provides a means of qualitative as well as quantitative analysis and it has great potentialities when used in conjunction with some other detector for identification of eluted bands from capillary columns. The change of electron energy which is required for qualitative analysis can be effected either by changing the potential across the ionization chamber of by changing the carrier gas. When argon is used as the carrier gas the average electron energy is high since the collisions of electrons with argon are in general highly elastic. When nitrogen or hydrogen is used as the carrier gas the electron energy is lower. Carbon dioxide is a still more efficient deactivator of electrons and the electron energy is an order of magnitude lower again.

The linear range of this detector is only about 10^3 but Beer's law is sufficiently well obeyed for the non-linear range to be used for quantitative measurement.

The *electron mobility detectors* are of general application in the analysis of permanent gases. When electrons collide with argon the collisions are highly elastic and because of the great difference in the mass of the electron and the argon atom little transfer of energy occurs. When a field is applied to argon containing free electrons the energy absorbed by the electrons is only very slowly transferred to the argon except in the rare inelastic collisions which produce excited argon atoms, and the average electron energy or the electron temperature is much higher than the average energy or temperature of the argon atoms. When foreign gases are added the collisions with these molecules are less elastic than those with argon and a lowering of the average electron energy results. There are two methods of detecting this change in the energy of the electrons.

In the so-called indirect method use is made of the fact that there will always be an equilibrium concentration of excited argon atoms which is directly related to the average electron energy. The higher the electron energy the higher the chance of an inelastic collision. The concentration of such atoms is readily found by adding a trace of a hydrocarbon (say propane) to the argon and observing the ion current produced. The appearance of a permanent gas as impurity in the argon then lowers the ion current. For this method of detection the normal argon detector is used with a voltage of about 1,000 volts and about two parts of propane in 10^8 added to the argon. Instead of slightly contaminated argon commercial helium may also be used as this contains sufficient in the way of impurities to give a substantial amount of ionization. This detector suffers from the disadvantage that it depends upon the reduction of a large signal obtained from the carrier gas alone. It is therefore of rather low sensitivity and is not significantly better than a good katharometer. It is however insensitive to flow rate changes, and is the most convenient to use when the apparatus normally uses an argon detector.

In the direct method the change in electon temperature is measured by observing the change in electron mobility. As the electron temperature decreases the drift rate or mobility of electrons in an electric field increases. The increase in electron mobility consequent upon the addition of a permanent gas to the argon can be determined by using a pulsed field. The design of the *electron mobility detector* invented by Lovelock is the same as that of the electron capture detector except that the gas flow is reversed and a short range tritium source is used. The potential across the chamber is pulsed in such a way that the with pure argon flowing the duration of the pulse is just too short to allow the electrons generated close to the cathode to reach the anode. When a permanent gas contaminates the argon the electron mobility is increased and a fraction of the electrons can now reach the anode in the time of the pulse. The current flowing under these circumstances then gives a direct measure of the concentration of impurity in the argon. In practice the pulses are half rectified sine waves of a frequency between 0·2 and 1·0 Mc/sec and about 100 volts in amplitude. This detector in its present form is capable of detecting about 1 part of CO_2 in 10^8 of argon.

It is clear that there is a considerable range of ionization devices which can be used as detectors in gas chromatography and those discussed above by no means exhaust the possibilities. They are mostly still in an early stage of development and considerable improvements can be confidently expected. In particular one expects great improvements in the methods of detecting the permanent gases with high sensitivity.

At the present time however only the argon and flame ionization detectors are in general use and these will now be described in somewhat greater detail.

Argon detectors

Three varieties of argon detector designed by Lovelock[11] are shown in Figure 4.9. The detectors are constructed of brass and have teflon or ceramic insulation. The radioactive source, in the form of a piece of thin gold or silver alloy foil, may contain 20–50 microcuries of an α emitter (radium or radium-D) or, more usually, 10–50 millicuries of a β emitter (Pm^{147}, Sr^{90} Kr^{85} or tritium). Whatever the source it must be powerful enough to give a background electron current of about 10^{-8} amp. The casing of the detector is usually earthed and the anode supplied with a voltage of 300–2,000 volts. The e.m.f. developed across a resistance of 10^7–10^8 ohm connected between earth and the low voltage side of the power supply is then measured by an electrometer amplifier. The basic measuring circuit is shown in Figure 4.7.

The 'simple' argon detector is the least satisfactory of the three and has recently been shown to be a particularly inefficient form of argon detector. It has a relatively high noise level and its response falls from linearity at vapour concentrations above about one part in 2,000 of argon. It is also the least sensitive of the argon detectors because of its low ionization efficiency of about 10^{-4}. Furthermore its large volume means that it can only be used with packed columns. The lower limit of detectability is about 2 parts of an organic vapour in 10^8 of argon, giving a linear range of about 2×10^4 which is roughly the same as that of a good katharometer. Even at its highest sensitivity however it is relatively insensitive to changes in flow rate and no special precautions need be taken to ensure high flow stability. It is normally sufficient to supply the whole apparatus with argon at constant pressure or constant flow rate from a two stage reducing valve or needle valve fitted directly to the cylinder.

The 'small' detector was specifically designed for use with capillary columns but it is some thirty times as sensitive as the 'simple' detector and now generally replaces it. The anode is constructed to give a high field strength in its immediate neighbourhood and the ionization efficiency here is high. When the effluent from a capillary column is led through the small hole in the anode the reactions between the argon and the organic vapour occur within a volume of a few cubic millimetres close to the anode tip. However, some reaction can occur outside this region and it is necessary when using capillary columns to purge the detector continuously with a stream of clean argon (about 50 ml/min) entering the detector through a tube opposite to the anode. When the detector is used with a packed column, the column effluent is led into the detector at the scavenger port and part of it passes out through the anode. This detector is some thirty times as efficient as the 'simple' detector and with careful design which utilizes the space charge limitation it can be made linear up to much higher ion currents. The design of the anode is however highly critical. Under the best conditions the detector is linear up to concentrations of about one part of organic vapour in 500 of argon and the linear range is above 10^6. The small argon detector, like the flame detectors, is a quantity not a concentration sensitive detector.

The 'triode' detector has very much the same construction as the 'small' detector but includes a third ring electrode near the anode. The sensitivity is increased a further thirty times and the linear range is about 10^8. The detection limit is about three parts of organic vapour in 10^{11} of argon. The third electrode functions as follows. Electrons from the radioactive source approach the anode in a narrow pencil-shaped beam. The third electrode is a ring placed so as to avoid this stream. It collects a high proportion of the positive ions generated by the argon reaction but none of the primary electrons. The background current is thereby reduced from about 10^{-8} amp to about 10^{-11} amp. The noise level, which is about 3×10^{-10} amp in the diode detector, is now reduced to less than 10^{-13} amp. According to Lovelock the addition of a fourth electrode can increase the sensitivity still further.

Argon detectors can thus be made exceedingly sensitive, but to make use of this sensitivity stringent precautions must be taken to ensure that the gas emerging from the column in the absence of eluted vapours is free from contaminants. Clearly any bleed of stationary phase from the column will result in a positive signal from the detector and instability of the base line. It is therefore essential to use the highest quality liquid phases and it is advisable to run any new column for some time at a considerably higher temperature than is likely to be used later. Water causes severe loss of efficiency because of its high electron affinity which lowers both the concentration and energy of the electrons. The concentration of activated argon atoms is thus greatly reduced in the presence of water vapour and for satisfactory operation of argon detectors its concentration must be below 20 p.p.m. Other gases which are not ionized by collision with excited argon atoms reduce the electron energy and so cause loss of sensitivity. The most likely contaminants of this type and their maximum permissible concentrations are: carbon dioxide (100 p.p.m.), oxygen (300 p.p.m.), hydrogen and nitrogen (1,000 p.p.m.). Cylinder argon is generally sufficiently pure for there to be no trouble except from water vapour. It is always advisable to pass the argon before use through a drying tube. The most efficient is a tube containing about 20 g of granulated molecular sieve at −80°C. However, for most purposes a tube of Celite at −80°C or a tube of molecular sieve at room temperature is adequate.

Loss of sensitivity from air in argon is nearly always the result of diffusion of air through connecting tubing. For this reason it is best to use metal tubing joined by gas unions for all gas lines. If rubber or plastic tubing is used it should be thick walled and as short as possible.

The sensitivity of the argon detectors to different substances varies considerably but for most organic materials with molecular weights above 100 the response is proportional to weight concentration. When analysing substances with molecular weights below 100 calibration is required.

The argon detector as we have already noted is insensitive to most inorganic substances and with the following it gives either no response or negative response: noble gases, hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide (negative), cyanogen, water (strongly negative and deactivating to subsequent components) and fluorocarbons. A number of organic substances give between 1 per cent and 10 per cent of the expected response. Some of these are: methane, ethane, acetonitrile and propionitrile. The last named for this reason is useful in making up dilute solutions to be analysed in apparatus with argon detectors. Some inorganic substances and organic substances which one might expect to give poor response behave normally. Amongst them are: hydrogen sulphide, carbonyl sulphide, carbon disulphide, oxides of nitrogen, ammonia, phosphine, boron trifluoride, acetylene and ethylene. The argon detectors must be used with care when analysing halogen containing compounds as the halogen atoms have a high electron affinity and tend to absorb free electrons. One normally has to use rather high detector voltages and to check that the response is linear within the concentration range required. For such substances the 'small' detector is considerably better than the 'simple' detector.

The flame ionization detector

The flame ionization detector devised by McWilliam and Dewar[6] is the simplest of the high-sensitivity detectors yet devised and it has been the subject of considerable research. Both the theory and properties of this detector have been investigated in detail by Ongkiehong.[12] One version of the detector is shown in Figure 4.8. Carrier gas from the column is mixed with hydrogen or a hydrogen/nitrogen mixture and burnt at a jet above which is placed a cylindrical metal electrode. The composition of the mixture is not critical but it usually contains about 50 per cent hydrogen. The total flow rate should be between 20 and 200 ml/min, and the detector body should be purged with clean air at a rate of 400 to 2,000 ml/min. The flame ionization detector can be used with both packed and capillary columns. With the latter the hydrogen/nitrogen mixture is added at the outlet end of the column and a ten to hundredfold dilution of the column gas is inevitable. However, the sensitivity of the detector is so high that this is not a serious disadvantage.

The rate of ion formation in the flame is determined by applying a potential of 100–300 volts between the jet and cylindrical collector electrode. This is sufficient to give the saturation current (see Figure 4.6) so that all ions and electrons produced in the flame are collected. The flame ionization detector thus differs from the argon detectors in that its response cannot be increased by increasing the voltage across the electrodes. Sensitivity changes are effected by changing the series resistance shown in Figure 4.7 from 10^7–10^{10} ohm. In the circuit shown the jet is earthed and the power supply is floating. This presents no difficulties if the high voltage is supplied from high-tension batteries. They are mounted in a metal sheath connected to the resistance side of the batteries and each battery is placed in a polythene bag to prevent electrical leakage. Hearing-aid batteries are ideal for the purpose. When the high voltage is supplied by a power pack it is simpler to earth the low voltage side of the power pack and leave the detector electrodes floating. Both the jet and the collector must then be insulated from the body of the detector.

The detector has an effective reaction volume of only a few cubic millimetres and it is highly suitable for use with capillary columns. The background current is about 10^{-12} amp and the noise level about 2×10^{-14} amp. The minimum detectable concentration of organic material is about 1 part in 10^9 of hydrogen and the detector is linear up to a concentration of about 0·5 per cent. The linear range is thus about 10^7. Since the ionization efficiency with this detector is only about 10^{-5} as compared to 10^{-2} in the small argon detector one requires a rather better amplifier for a flame ionization detector than for an argon detector of the same sensitivity.

In operating the flame ionization detector the hydrogen and air supplies must be clean and free from dust, and neither the collector electrode nor the platinum jet must become so hot that thermionic emission occurs. If this happens severe instability and a high background signal will result. For this reason the collector electrode should be at least 1 cm above the visible top of the flame.

The flame detector like the argon detectors is insensitive to inorganic compounds except those containing elements in groups I and II of the periodic table. It responds to all organic substances except formic acid. The flame detector is not affected adversely by water halogens, etc., and therefore has a great advantage over the argon detectors in the analysis of aqueous solutions. The response to organic compounds is roughly proportional to the amount of carbon they contain but this does not hold for oxygenated and nitrogen-containing compounds which give a lower response than expected from their carbon content. Calibration is therefore generally necessary for quantitative results. Unfortunately calibration factors depend upon the design of the detector and upon flow rate. It is therefore necessary to use standard operating conditions.

One great merit of the flame ionization detector is that it is simple to construct and that the dimensions are not critical.

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CHAPTER 5

Ancillary Equipment

The column and detector are the vital parts of any gas chromatography apparatus but they cannot function without cooperation from other essential pieces of equipment, flow meters, injection systems, thermostats, amplifiers, recorders, etc. The design and operation of this ancillary equipment is described in this chapter.

Flow regulators and flow meters

The degree to which the flow of carrier gas must be controlled in any gas chromatography apparatus depends largely upon the detector. A katharometer requires a well-stabilized flow of gas free from both short and long-term fluctuations, but an argon detector only rough control. A rough measure of the short and long-term flow stability required by different detectors is given below.

	Short-term control (per cent)	*Long-term control (per cent)*
Katharometers and flame temperature	0·01	1
Density balance flame ionization	0·1	1
Argon detectors	1	1

Flow controls adequate for the strictest requirements are marketed but are somewhat expensive (about £20). They combine the functions of a pressure reducing valve and a high-grade needle valve. For use in many laboratories the simpler and cheaper arrangement shown in Figure 5.1 is quite satisfactory. Gas from a cylinder is metered out roughly by means of a cylinder needle valve or by a two-stage reducing valve equipped with a constriction such as a piece of fine capillary tubing or a simple needle valve. It is led via a T-piece to a blow-off from which gas will escape to the atmosphere when a critical pressure is reached. In order to obtain regular bubbling it is necessary to grind the outlet end of the delivery tube at an angle of about 45° and to place a plug of cotton wool or some such material near the bottom of the tube. The blow-off or bubbler can contain water when low

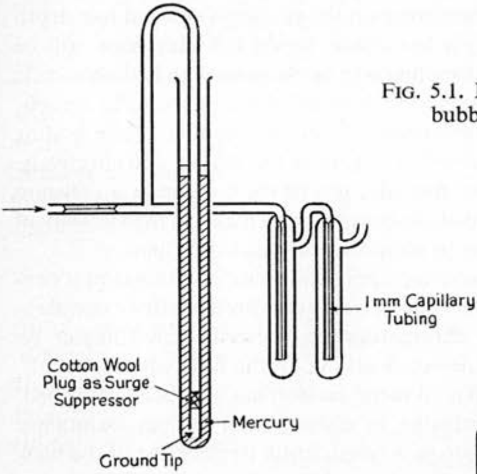

FIG. 5.1. Flow control by means of bubbler and buffer vessels.

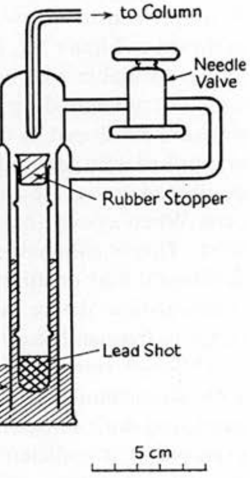

FIG. 5.2. A glass constant flow regulator.

pressures are required or mercury for higher pressures. With mercury suck-back can be simply prevented by extending the delivery tube at least 76 cm above the mercury surface. Unfortunately the formation of bubbles is always accompanied by pressure pulses. These are somewhat reduced when using mercury if the surface is covered to a depth of a few centimetres by a less dense liquid but they must still be smoothed out if a stable base line is to be obtained with katharometers or other flow sensitive detectors. A series of five or six buffer vessels, each consisting of a 10 cm length of 1 mm bore capillary tube leading into a volume of about 20 ml, will achieve this simply and effectively. Since the bubbler system provides gas to the column at a constant pressure the temperature of the column (which affects the viscosity of the carrier gas) must also be constant and free from ripple.

Sometimes it is desirable to supply the column with gas at a constant mass flow rate rather than at a constant pressure (for example in temperature rising gas chromatography described in Chapter 6). A simple constant flow device, working on the float valve principle, is shown in Figure 5.2. An all metal version has also been described[1] and is available commercially. In essence both devices maintain a constant pressure drop across a constriction irrespective of the back pressure developed by the flow through the column. The float version is supplied with gas at about twice the maximum pressure likely to be developed across the column. It gives a flow constant to about 1 per cent. When a newly-made regulator is first used the float may tend to hunt. This is eliminated by grinding the jet at a slight angle to the horizontal and dusting the top of the rubber stopper with talc. A constant-flow device is often useful when it is desired to switch columns frequently as when split or multiple columns are used.

Although somewhat elaborate flow control devices are required with katharometers much simpler means of flow control can be employed with ionization detectors. With the argon detectors, for example, it is sufficient to use either a cylinder needle valve or a normal two-stage reducing valve depending upon whether one requires a constant flow or a constant pressure head across the column. When using only a needle valve on the cylinder it is advisable to fit a manometer before the column so that excessive pressures are not developed inadvertantly.

Flow rates can be measured in several ways. Three simple flow meters are shown in Figure 5.3. Float meters, which cost between £5 and £10, give a simple and continuous measure of flow rate accurate to about 1 per cent. The small float moves in a vertical conical tube and assumes a steady position when its weight is just balanced by the upthrust of the moving gas. The position of the float gives the flow rate directly. A calibration graph will normally be supplied by the manufacturers for any particular gas. The capillary flow meter, unlike the float meter, can readily be constructed in the laboratory. It is of slightly higher accuracy. The gas passes through the capillary and the pressure developed is measured by the manometer. The flow rate is directly proportional to the pressure difference. Capillary flow meters must be calibrated for each gas used. The soap bubble flow meter, which can be made from a 50 ml graduated tube, is the simplest absolute flow meter and is capable of an accuracy of about 0·1 per cent if allowance is made for water vapour pressure. Soap bubbles are generated by pressing the rubber bulb at the bottom of the graduated

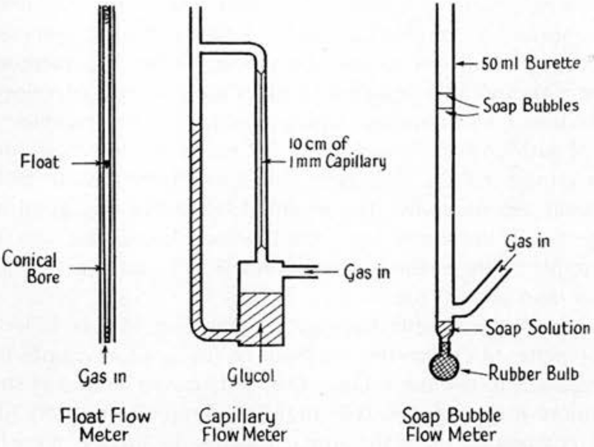

FIG. 5.3. Three simple flow meters.

tube so that the soap solution momentarily covers the inlet tube. The bubbles are timed between convenient graduations.

Injection systems

The important requirements of any injection system are that its volume should be small when compared with that of the column, and that it should enable injection to be effected almost instantaneously.

The injection of liquids in quantities of the order of 0·1–5 mg presents no special problems other than that of reproducibility of sample size, which is often unimportant. One of the simplest methods of injecting liquids is to use the syringe/serum cap method (see Figure 5.4). Specially designed syringes are available (developed by the Beckman Corporation) which enable 1–5 mg samples to be injected with an accuracy of about 0·2 per cent. Other less complex microsyringes on the market enable small injections to be made somewhat less precisely. The essential feature of any good microsyringe is that the needle has a small volume compared with that of the sample. This method of injection is not suitable for samples smaller than about 1 mg.

An alternative simple method for injecting liquids is to use a micropipette. Micropipettes are made by fusing short lengths of very fine capillary into wider tubing. They may have volumes as small as 0·01 micro litres (approx. 0·01 mg) The sample completely fills the capillary when the tip of the pipette touches the surface of the liquid. Different types of micropipette and their operation are shown in Figure 5.4. Injection by micropipette is accurate to about 2 per cent but care must be taken that the sample does not partly evaporate before being introduced into the column.

In order to achieve nearly instantaneous injection rapid vaporization of the sample is required. Mixtures containing high boiling components must therefore be injected either directly on to the hot column packing or preferably into a preheated tube before the column. When a preheater is used it should be between 50 and 100 degrees hotter than the column itself.

Injection of liquid samples may also be carried out by breaking sealed ampoules or capillary tubes.

Gaseous samples can, like liquids, be injected by syringes of 0·1–5

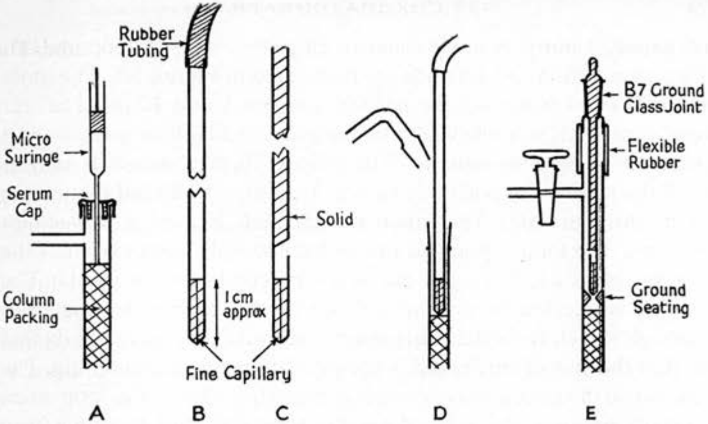

FIG. 5.4. Liquid injection. (A) syringe and serum cap; (B) simple micropipette; (C) positive action micropipette; (D) use of B. The rubber tubing is stroked to drive the sample out of the pipette; (E) use of C. The flexible rubber connection is momentarily compressed so as to bring the two ground-glass surfaces into contact and thereby drive the liquid out of the pipette.

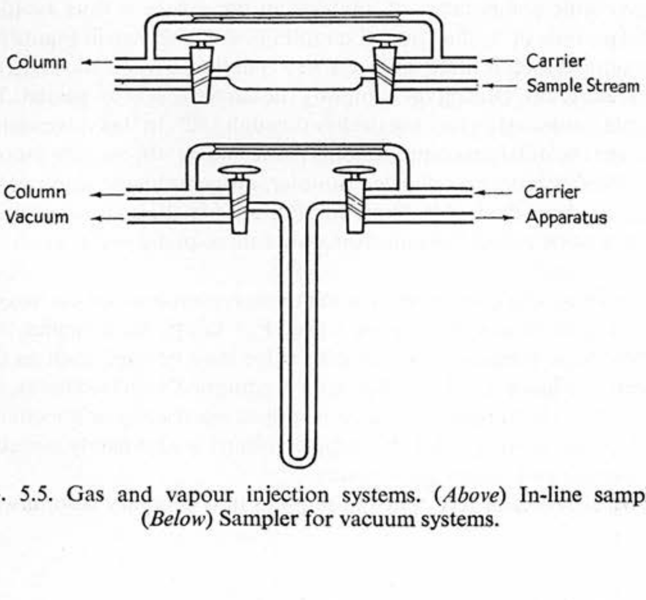

FIG. 5.5. Gas and vapour injection systems. (*Above*) In-line sampler. (*Below*) Sampler for vacuum systems.

ml capacity but it is more usual to employ a by-pass loop system. Two straightforward versions are illustrated in Figure 5.5. The most suitable size for the sample loop is between 1 and 10 ml. The 'in-line' sampler is suitable when the sample is available in quantity at a pressure above atmospheric. The loop is flushed out with sample with the taps in the positions shown. Injection is effected by turning them through 180°. The other arrangement is used with vacuum systems. The loop is pumped out and the sample measured in at the desired pressure. It may if necessary be condensed in the U. The sample is injected by turning the taps so that the carrier gas flows through the U. In both arrangements a capillary by-pass is provided so that the flow of carrier gas is not interrupted during sampling. The resistance of the capillary is much greater than that of the loop when the taps are open. When it is desired to condense a small sample from a large excess of some uncondensable gas it is best to use a 'W'-shaped tube filled with glass beads or helices in order to assist trapping.

Metal sampling valves with plastic moving surfaces are now beginning to replace glass systems. They have the merit that no lubricant is required. Irreproducibility and 'memory' due to solution of involatile components of mixtures in tap grease is thus avoided. A simple type of 'in-line' metal sampling valve is shown in Figure 5.6. The sample loop is filled when the key is in the position shown in the upper diagram. During the sampling the carrier gas is by-passed. The sample is injected by turning the key through 180°. In this valve sealing between the different compartments is effected by silicone or neoprene 'O' rings. A more complicated sampler, also employing slanting 'O' rings, has been devised by Pratt and Purnell.[2] It allows for the sample volume to be evacuated and works on a three-phase cycle: evacuate, sample, inject.

Repetitive injection which is sometimes required is best carried out with a greaseless metal/plastic valve. For sampling at higher than atmospheric pressure a simple gate valve may be used such as that shown in Figure 5.7. The teflon gate is equipped with two holes, one of which is the sample volume. It is moved electrically or pneumatically up and down so that the sample volume is alternately placed in the sample and carrier gas streams.

The injection of reproducible samples into capillary columns is a problem which has not been altogether satisfactorily solved. There is as yet no direct method of introducing an accurately measured sample of about 10^{-6} g into a gas stream. At present it is usual to inject a much larger sample into a gas stream of which approximately 1 per cent enters the capillary column, the rest being rejected. This is achieved, as shown in Figure 5.8, by placing a T-junction immediately after the sampler. The capillary column is attached to one arm and a needle valve or more simply a short length of capillary to the other.

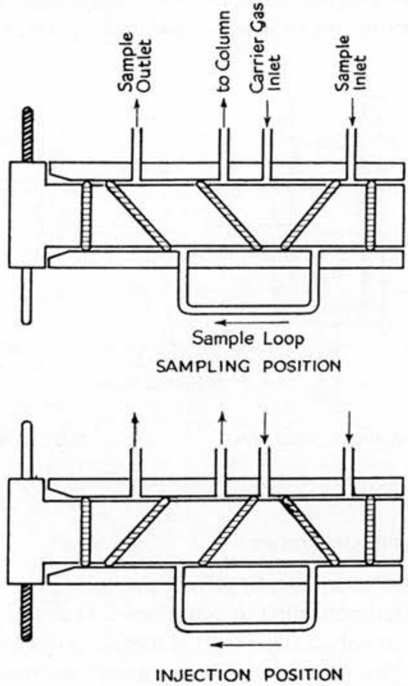

FIG. 5.6. Metal sampling valve employing slanting 'O' rings.

The second alternative is attractive since the rejection ratio is immediately obtained from the lengths of the two pieces of capillary tubing. In constructing the T-junction it is essential that the column enters directly into the gas stream so that there is no dead space at the start of the column. It is equally important to avoid dead space at the detector end of the column and details of the attachments to a flame ionization detector and an argon detector are also shown in Figure 5.8.

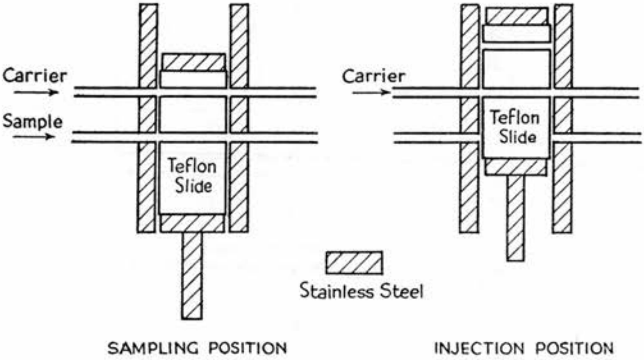

FIG. 5.7. Repetitive injector (based upon an I.C.I. design).

Control of column temperature

The temperature of a column affects the retention volumes of the vapours separated according to equations 2.11 and 2.12, and it may affect the flow rate of carrier gas. It is therefore important to control the temperature to some extent. For accurate measurements of retention volumes carried out for publication purposes it is necessary that the column temperature be uniform and steady to about 0·1 degree. This is best achieved by means of a vapour jacket. Vapour jackets are, however, cumbersome and the interchange of columns and alteration of temperature is complicated. If high precision is not required some form of electrical heating is preferable. For routine analysis a temperature stable to within a degree is desirable. Since the temperature of the column itself must be free from ripple one must use either

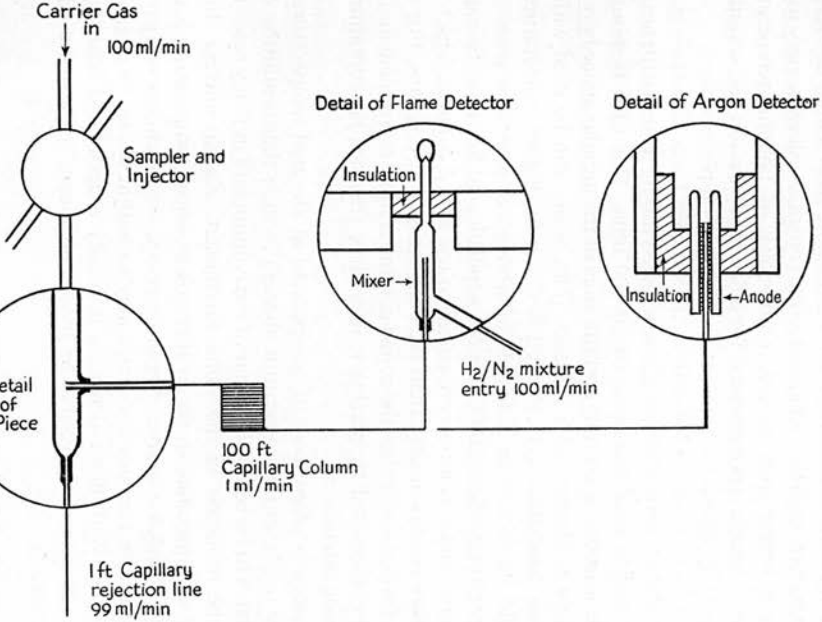

FIG. 5.8. Details of connections for capillary columns.

a proportional temperature controller (which cycles continuously with a variable ratio of on/off times), or one must mount the column itself inside a massive metal billet which can be placed in quite a crude thermostat controlled by a bimetallic strip. Often less refined temperature control is adequate and a constant voltage supply to the column heater may suffice. Uniformity of column temperature along its length is not essential for efficient separation and variations of up to 20 degrees have no noticeable effect on performance.

For U- or multiple U-columns the simplest form of heating jacket is a 100 cm length of 30 mm diameter glass tubing wound with heating tape with a total resistance of 50–100 ohm. This tube is mounted inside a second glass tube and the ends of the annular space between the two is plugged with asbestos. The heater can be used without further insulation up to about 120°C but for higher temperatures it should be placed in a length of fibre-glass pipe insulation. For temperatures above 200°C a more sophisticated heater or furnace is required and it is most convenient to use coiled columns which can be more readily housed than the conventional U-columns. For subzero temperatures also, the coiled column is more convenient and can be thermostatted by placing it in a large thermos jar containing a freezing mixture.

Detectors often have to be operated at elevated temperatures in order to prevent condensation. Generally their thermostatting does not have to be better than that of the column and in many cases they can be mounted in the same thermostat. Katharometers should always be mounted in an air thermostat whose temperature is constant to within a degree. Argon detectors are much less sensitive to temperature changes and constancy to within about 10 degrees is adequate. With flame detectors it is only necessary to heat the jet although it may of course be more convenient to heat the whole detector.

Identification of fractions – traps

One of the major problems in gas chromatography is the identification of the separated components of an unknown mixture which appear as peaks on a chromatogram. Identification can be carried out with moderate confidence by passing known substances through the column and comparing the retention times of the known with those of the unknown peaks. If the thermostatting of the column is poor it is best to add the known components one by one to the unknown mixture and look for coincidence of peaks. Unfortunately any such coincidence is by no means conclusive evidence of identity unless the number of possible components in the original mixture is very small. Confidence can be somewhat increased by repeating the experiment on a column containing a liquid phase of very different polarity.

However, to be really sure identification must be carried out by methods which do not depend upon the measurement of any property remotely connected with retention volume, vapour pressure or boiling point. Such independent methods are infra-red, nuclear magnetic resonance and mass spectroscopy. To use them successfully it is first necessary to collect the unknown substances which emerge from the column.

Efficient trapping is not always easy especially if the concentration of the substance in the carrier gas is low. When a dilute mixture of a condensable vapour in an uncondensable gas is cooled suddenly the vapour will form minute droplets which are carried through any simple trap. For efficient collection it is best to fill traps with glass beads or better coarse Celite (say, 40–60 mesh). Although mass spectrometry and N.M.R. are not sensitive to small traces of contaminants such as water and carbon dioxide these must be rigorously excluded when infra-red is used for identification purposes since both substances have strong absorptions in the 800–3,500 cm^{-1} region used for the identification of organic materials. Traps should then be provided with guard tubes at both sides. Magnesium perchlorate can be used for removing water and a mull of potassium hydroxide in ethylene glycol supported on Celite for removing carbon dioxide. To avoid any unnecessary condensation of contaminants traps should be cooled in the freezing mixture only just before the peak to be collected is due and disconnected immediately after it has passed. Thereafter they should be kept sealed until the fractions can be identified; taps or ground-glass stoppers can be used for the purpose.

All three methods mentioned above are highly sensitive and enable identifications to be carried out on as little as 10^{-7} mole. Details of the application of infra-red spectroscopy are given by Anderson.[3]

Vapour converters

Vapour converters are devices which convert all organic vapours emerging from a gas chromatographic column into a single gas such as hydrogen, carbon dioxide, methane or acetylene. They enable the Janak nitrometer to be used for all organic substances whether gaseous or not. They enable home-made katharometers to be operated at room temperature even when high boiling substances are being analysed and they greatly simplify calibration.

A simple example of a vapour converter is a tube containing copper oxide wire heated to about 800°C which oxidizes any organic material passing through it into water and carbon dioxide. The water can be removed by a drying agent and the carbon dioxide passed to the detector, or the water may be reduced to hydrogen by passage over red hot iron wire and the carbon dioxide absorbed. In either case the yield of carbon dioxide or hydrogen is known from the formula of the eluted substance and only a single calibration for carbon dioxide or hydrogen is required. If the water is passed through a tube containing calcium carbide it is converted into acetylene. One additional merit of vapour converters is that they often increase the sensitivity of detection. They also enable carbon/hydrogen ratios to be obtained and when using the gas density balance even the molecular weight and formula of the eluted vapour.

Vapour converters must obviously be constructed with as small a dead volume as possible and the reactant material must be in a granulated form which presents a large area to the flowing gas yet does not seriously impede its flow. The requirements of a small volume and a reasonable lifetime clearly conflict.

The advantages of vapour converters are unfortunately largely offset by their disadvantages. They increase the dead volume between the injector and the detector and so impair resolution; the reagents require frequent regeneration, and the eluted vapours are destroyed and cannot therefore be identified after detection.

Absorbents

Absorbents for the removal from mixtures of specific components or groups of components are widely used in conventional gas analysis.

They can often be advantageously combined with gas chromatography. This is particularly so when it is desired to analyse a mixture for a number of components present as traces in some major component. Such a situation often arises in the study of reaction kinetics where it is desirable to work to low percentage conversions in order to minimize secondary reactions. Absorbents suitable for use in vacuum systems can be made by dissolving or making a mull of the required reagent in ethylene glycol and supporting the mixture on Celite as is normally done when making up a gas chromatographic packing. Often the absorbent packing can be made up into a precolumn which is placed before the main analytical column.

Some of the absorbents which have been successfully used in our laboratories are the following:

Olefins Mercuric acetate/mercuric nitrate mull in ethylene glycol; bromine on activated charcoal followed by a bromine remover (not suitable for use in vacuum systems).

Acetylenes Saturated silver nitrate in ethylene glycol (requires frequent renewal).

Aldehydes Sodium bisulphite mull in ethylene glycol.

Bromine Diethyl-*p*-toluidine or NN′-tetramethyl-*p*-diaminodiphenyl.

Chlorine Copper bronze.

Hydrogen bromide, etc. Sodium bicarbonate followed if necessary by absorbents for water and carbon dioxide.

Peak recorders and peak integrators

Galvanometers are the simplest recording instruments and they can be used with nearly all detectors but they require someone to record readings against a stop-watch and their use is only justified if capital equipment is very scarce. The great majority of gas chromatographers use some form of strip chart recorder which draws the finished chromatogram on a moving strip of paper.

There are two types of strip chart recorder in general use, galvanometer and potentiometric recorders. Galvanometer recorders are relatively cheap (about £50) but generally require an amplifier since they require a rather larger signal than is supplied by most detectors.

Suitable amplifiers cost about £100. Potentiometric recorders are more expensive but do not always require an amplifier. The cheapest costs about £130. Potentiometric recorders use the off-balance e.m.f. from a bridge to operate a synchronous motor which adjusts a slide wire contact until the bridge is balanced. This contact is attached to a pen which records the position of balance on a moving chart. When balanced such recorders take no current from the input circuit. Because of their mode of operation potentiometric recorders generally have much wider charts than galvanometer recorders and the pen moves in a straight line instead of an arc. Potentiometric recorders can now be obtained to give full-scale deflections for 500 microvolts and with response times of 0·25 sec. but normally one uses a 1 or 2·5 millivolt recorder with a response time of about 1 sec. The more expensive potentiometric recorders cost about £250. As high-speed gas chromatography develops photographic recorders may become popular.

In the quantitative interpretation of chromatograms it is generally necessary to measure peak areas although for some applications peak heights are sufficiently accurate. Peak areas may be measured manually in several ways. If the chromatogram is recorded on squared or lined paper, the area can be obtained by adding up squares or by summing the lengths of trapesia using dividers. A better method is to use a planimeter whose accuracy can be increased by making several circuits round each peak. These methods are rather slow but with care are accurate to about 1 per cent.

Electrical integration is to be preferred to any of the manual methods as it is both quicker and probably more accurate. When an electrical integrator is used the base line of the chromatogram must be extremely steady and with pure carrier gas passing through the detector the integrator must give a zero count. Peak integrators may give a digital output, they may record pips at the edge of the chart or they may draw out the integrated area on a chart. The digital output is basically the most satisfactory but, unless frequent print-out is available, it has the disadvantage that an operator must be present to record areas after the passage of each peak. The digital method can however be refined so that the integrator prints out the integrated area whenever a col is reached between two partly resolved peaks or the base line is regained, but this requires an additional differentiating circuit. The pipping method is more straightforward. The recorder is fitted with an extra pen which marks a pip at the edge of the chart each time a certain unit of area is traversed by the pen (see Figure 1.7). Every tenth pip is larger than the rest to facilitate addition. The third method whereby the integrator draws out the integrated area on the chart has the value of great clarity but it is essential to have the differential chromatogram also recorded in order that the areas of partially resolved peaks may be measured. Two recorders are therefore required and the method is expensive. Of the three methods the pipping method is likely to be the most popular.

Several commercial integrators are now marketed at about £150 each. It is doubtful if integrators can be made in the laboratory for much less than this although many have been described in the literature.[4]

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CHAPTER 6

Additional Gas Chromatographic Methods

In the preceding chapters only analytical applications of isothermal gas chromatography have been considered. In this chapter we consider the application of gas chromatography to the analysis of mixtures of wide boiling-point range (multiple columns and temperature rising columns) and to the purification of substances on a preparative scale.

Multiple columns

There are many quite simple mixtures whose components boil over a wide temperature range which cannot be analysed successfully on a single isothermal gas chromatographic column. In studying the reactions of butyl radicals, for example, a mixture containing C_2–C_4 and C_8 hydrocarbons is obtained. In order to separate the lower hydrocarbons one requires a column from which the C_8's would take a very long time to emerge. Such a mixture can be quickly analysed on two columns in series. The first column, say 2 metres of 10 per cent squalane on Celite, operated at 70°C, is used to separate the C_8 hydrocarbons. The lower hydrocarbons emerge rapidly but unseparated and pass immediately to the second column, say 5 metres of 10 per cent squalane on Celite at 20°C, which separates them satisfactorily. Depending upon the elution times from the two columns two procedures are possible. If the lower hydrocarbons emerge from the second column before the C_8's emerge from the first column, the former are analysed first by passing the gas from the second column to the detector. After the elution of the last C_4 hydrocarbon the second column is disconnected by turning a three-way tap between the two columns and the gas from the first column is passed to the detector. The chromatogram of the lower hydrocarbons separated on the complete column is thus recorded first followed by the chromatogram of the C_8's separated on the first column. If, on the other hand, the lower hydrocarbons do not emerge from the second column before the C_8's start emerging from the first, the former can be 'bottled' in the second column by turning the three-way tap and the elution of the C_8's recorded initially. When this is complete the second part of the column is again connected up to the carrier gas supply and the lower hydrocarbons eluted. There are innumerable permutations of this type of system. Sometimes it is convenient, when using a katharometer, to place one gauge after the first column and the second after the second column. The whole chromatogram can then be recorded without any disturbance of the gas flow. However the high boiling substances then pass on to the second column and will eventually be eluted from it as long flat bands which may disturb subsequent analyses. When using this modification components emerging from the first column will give an opposite signal to those emerging from the second. Care must be taken that the peaks from the two columns do not interfere.

Parallel columns may also prove useful for certain mixtures. Hill,[1] for example, has used two adsorption columns in parallel to analyse anaesthetic mixtures. A column containing Linde molecular sieve is used to determine oxygen and nitrogen, and another containing silica gel for air, carbon dioxide and cyclopropane. The lengths of the columns and their flow rates are so arranged that the peaks from the two columns do not overlap.

Sometimes one is interested only in the low boiling components of a mixture and it is inconvenient to wait for the elution of the higher boiling components before carrying out the next analysis. Much time can be saved if, after the elution of the important low boilers, the flow of carrier gas is reversed and the high boilers eluted from the start of the column. Provided that the volume of gas passed during the period of reversed flow is greater than that passed during the period of forward flow the unwanted high boilers will never pass to the detector.

An ingenious modification of this idea is used by Swoboda[2] for the elimination of water from aqueous solutions. The solution is injected at the top of a short pre-column containing diglycerol on Celite. This retains the water strongly but passes the organic components readily. When these have emerged and passed into the main analysis column the carrier gas inlet is switched to a point between the pre-column and the main column. The flow through the pre-column is thereby reversed and the water eluted to the atmosphere while the rest of the sample is analysed in the normal way on the main column.

Rising temperature columns[3] – temperature programming

When mixtures of wide boiling-point range are analysed on isothermal columns the volatile components give sharp peaks following closely on the 'air peak' while the involatile components give wide flat peaks. Neither the early nor the late peaks are suitably shaped for quantitative measurement. A typical such chromatogram is shown in Figure 6.1. With simple mixtures the split column technique may be used but this is no longer satisfactory when the mixture contains a large number of components whose boiling points are evenly spaced. To obtain a satisfactory chromatogram a rising temperature column must be used. Suppose a mixture to be analysed contains components boiling between 40° and 250°C. The sample is injected when the column is at room temperature. The low boilers are eluted quickly but the remaining components are retained at the beginning of the column. When the temperature is gradually raised, at say 5 degrees per minute, the less volatile components move off successively roughly in order of their boiling points. When it has reached 250° the highest boilers will have emerged. Since each component will emerge from the column at a temperature approaching its boiling point all peaks will be of roughly the same shape and equally sharp. Comparison of the two chromatograms of the same mixture shown in Figure 6.1 illustrates this clearly. With temperature programming the early peaks are spread out and their resolution improved while the later peaks are sharpened. The areas of all peaks can now be measured with comparable accuracy and the time for the analysis is not increased.

Temperature rising columns can, of course, be used for the analysis of simple mixtures which could be adequately dealt with on multiple columns. Tap turning during the analysis with the consequent disturbance of flow rates is avoided but the column must be cooled between analyses. The four chloromethanes for example can be determined on a column whose temperature is raised during the analysis from about −30° to +70°. Four well-separated and evenly spaced peaks are then obtained.

The details of the apparatus required for temperature rising gas

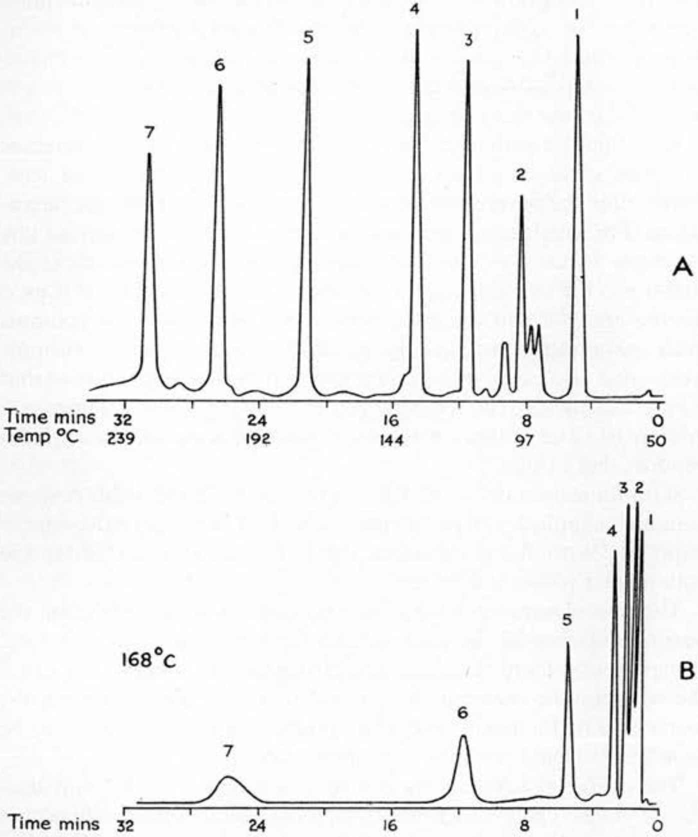


FIG. 6.1. (A) Programmed temperature chromatogram of seven *n*-hydrocarbons: (1) pentane, (2) hexane, (3) heptane, (4) 1-octene, (5) decane, (6) 1-dodecene, (7) 1-tetradecene. (B) constant temperature chromatogram at 168°C of same mixture (taken from Dal Nogare and Bennett (1958) *Anal. Chem.* **30**, 1157).

chromatography depend to a considerable extent upon the detector used and also upon the precision and reproducibility of programming which is required. Since the viscosity of a gas increases with temperature the carrier gas must be supplied to the column at a constant mass flow rate when concentration detectors are used if peak areas are to be proportional to amount. Even with quantity detectors a constant flow rate is advisable in order to minimize base line drift which might occur if the flow rate changed.

Although the katharometer is still the most widely used detector in temperature rising gas chromatography it is one of the least suitable for the purpose because of its sensitivity to flow rate fluctuations. For satisfactory operation of laboratory made apparatus it is necessary to use two identical columns which supply identical gas streams to the two sides of the detector. One of the columns is used for the analysis and the other serves as a 'dummy'. The columns must contain the same packing and must be of identical dimensions. They must also be mounted congruently in the heating jacket so that minor fluctuations in temperature between the two columns are minimized. The katharometer itself must be mounted in an independent thermostat.

With ionization detectors the conditions are less critical. A single column is supplied with carrier gas at constant flow rate or pressure as required. With flame detectors the hydrogen is added after the column at a constant flow rate.

The rate of temperature rise is not critical and depends upon the desired duration of the analysis and the total rise of temperature. It may be anywhere between 1 and 20 degrees per minute. The faster the temperature rises the shorter will be the analysis time but the worse will be the resolution. The optimum rate of heating must be found by trial and error for each application.

The degree of temperature control is also a matter for individual choice. As gas chromatography equipment becomes more refined and less home-made it is becoming the practice to employ linearly programmed heaters, that is heaters with a constant rate of temperature rise. There is, however, no theoretical reason for choosing this particular type of programming. It would be theoretically more satisfactory to employ a uniformly changing reciprocal temperature. For any type of temperature programming the heating system must have a low thermal capacity. The temperature of the system is measured by a thermocouple and potentiometer. A subsidiary e.m.f. which rises say linearly with time is generated and balanced against the thermocouple e.m.f. The off-balance e.m.f. is then used to switch more or less power to the heater. Several designs of heater have been described but the simplest consists of a pair of concentric metal tubes equipped with a powerful heater and fan. The fan circulates air rapidly through the central tube and back along the annular space between the two tubes. The system is rapidly cooled by switching off the heater and opening the system to a cold air supply with the fan running. Very rapid heating can be achieved by wrapping the columns directly with heating tape or by using metal columns as their own heaters. However with the latter systems it is more difficult to ensure controlled and regular temperature rise and care must be taken that the column packing is evenly heated.

For many applications precisely reproducible programming is not required and some irreproducibility of heating rates from one analysis to another can be tolerated. It may often be enough simply to switch power to the heater at predetermined times or better by using a Variac temperature will then rise rapidly at first and more slowly afterwards. One can be slightly more sophisticated by successively switching more power to the heater at predetermined times or better by using a variac transformer fitted with a geared motor to give a regularly increasing voltage to the heater. The last arrangement gives a reasonable compromise between accurate temperature programming and the sudden increase of power to the heater at a certain point in an analysis. With these simpler methods of increasing column temperature the simple tubular heater described in Chapter 5 is satisfactory. It is quickly cooled by compressed air.

The range of liquid phases available for temperature rising gas chromatography is more limited than for isothermal gas chromatography. Only substances with high boiling points and wide liquid ranges can be used. Before carrying out analyses it is necessary to run the column for some time at the highest temperature to be used in order to remove any volatile components in the stationary phase. It is also vital that the carrier gas be free from water and other condensable impurities as these are likely to be retained by the cold column and eluted as flat peaks when it is hot. Carrier gases are most effectively cleaned by passing them through a tube containing a granulated adsorbent such as 60–80 mesh charcoal at −80°C.

Preparative gas chromatography

Gas chromatography can be used not only for analytical purposes but also for the purification of materials on the 0·1 to 100 g scale. The scaling up of the analytical apparatus can surprisingly enough be carried out with only small loss of efficiency if certain precautions are observed.

In order to avoid extreme overloading columns for preparative gas chromatography are between 2 and 20 cm in diameter. Carrier gas flow rates are correspondingly increased and for reasons of expense and safety only nitrogen and air can be used. Detection of eluted vapours is no longer a problem and the katharometer, gas density balance or ionization cross-section detectors are the best.

The main problems to be solved in maintaining the high efficiency of the analytical apparatus when the scale of operations is increased up to 10,000 times are (1) the rapid injection of large samples, (2) the maintenance of the high plate efficiency of the analytical column when its diameter is greatly increased, and (3) the efficient trapping of the separated fractions emergent from the column.

Atkinson and Tuey[4] have examined the problem of injection. To evaporate 1 g of a substance of molecular weight 200 which boils at about 200° some 300–500 cal are required. If this is to be supplied by a block of metal cooling by 30–50 degrees then its mass must be approximately 100 g. The injection system should therefore be made from a massive block of metal whose heat capacity is sufficient to vaporize any reasonable sample. Materials like glass should be avoided as their thermal conductivity is low. However, the sample must not be injected so fast that the rapid vaporization causes a blow back into the carrier gas line. If for example a flow rate of 1,000 ml/min is used the rate of injection of a sample of average molecular weight 200 must be less than 5 g per minute. A typical large scale injection system is shown in Figure 6.2.

The construction of the column itself requires care if its plate efficiency is to be comparable to that of an equivalent analytical column. Hutyen, van Beersum and Rijnders[5] have found that the best method of packing a large diameter column is to pour in the packing at about 20 g/min while the column is continually tapped endwise. Lateral vibration tends to concentrate any finer material at the centre of the tube. Even so under the best conditions the outer parts of the packing are more porous than the inner parts and some loss of efficiency results from this. This loss is reduced if lateral mixing is encouraged by making up columns in several short lengths (say, 50–100 cm) connected by narrow tubing. The shape of the entry and exit sections of each column section is also important and the most satisfactory arrangement seems to be a cone about 80 per cent filled with the packing material.

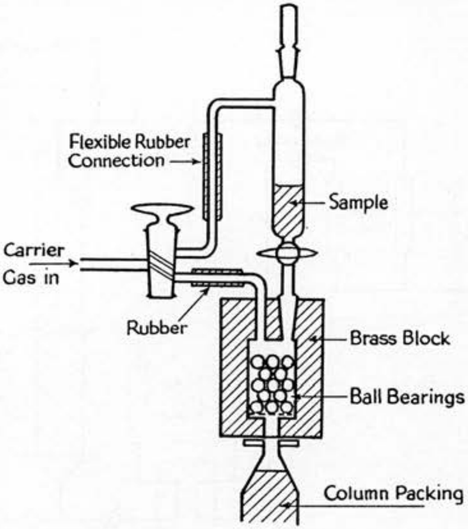


FIG. 6.2. Injection system for large samples.

Using columns prepared in this way and containing 30 per cent by weight of liquid phase plate heights of 2 mm were obtained with a 3 cm diameter column and 2·5 mm with a 25 cm diameter column. One would have expected only slightly better performance from an analytical column containing the same packing.

Detection of components as they emerge from the column presents no special problems and either an ionization cross-section detector or a katharometer is used. It is best to pass only a small fraction of the effluent gas through the detector (say, 1–5 per cent) and it may be advantageous to dilute this stream say 10 times with more carrier gas to avoid overloading. The detector stream is conveniently tapped off from the main stream through a piece of fine capillary tubing. A typical preparative scale apparatus is shown in outline in Figure 6.3.

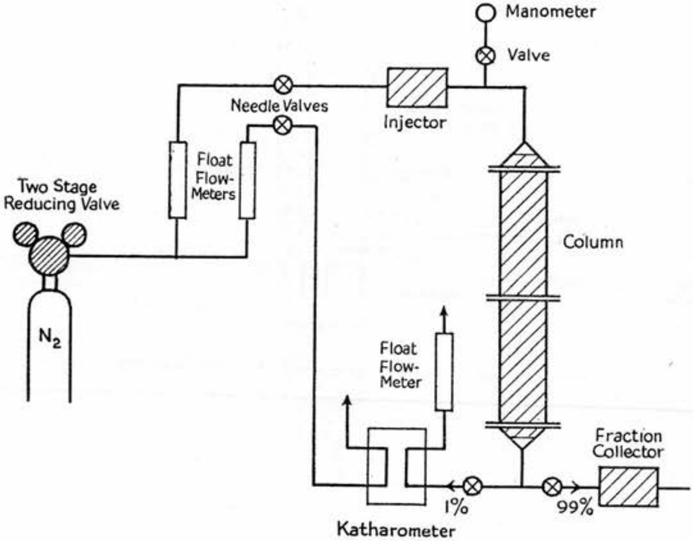
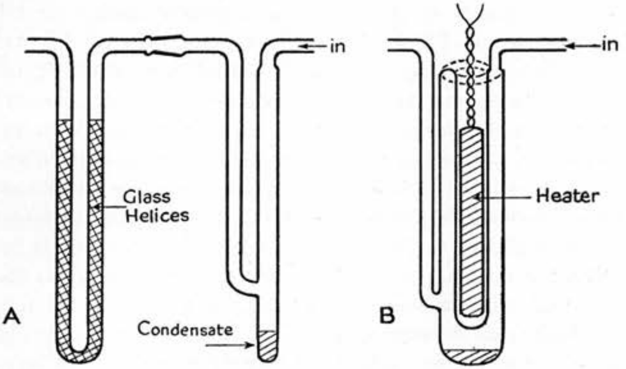


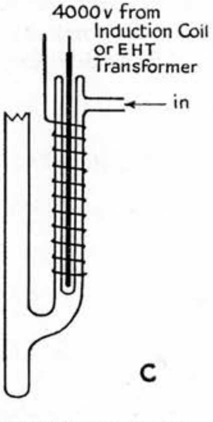
FIG. 6.3. Arrangement for preparative scale gas chromatography.

The effective collection of separated components as they emerge from the column presents two problems. The first is the rapid cooling of a large mass of gas to a low enough temperature for the materials to condense, and the second is the efficient collection of the condensed material which is often in the form of a finely dispersed fog. Effective cooling is best effected by passing the gas through a metal tube whose high thermal conductivity ensures that the heat is rapidly removed



Double "U" Tube Trap

Annular Trap



Electrostatic Precipitator

FIG. 6.4. Traps for use in preparative gas chromatography.

from the gas stream. Collection of the droplets of material formed on cooling is often more difficult. Straightforward traps are not very effective and may collect only 10 per cent of the condensable material in the gas stream. On the other hand, traps filled with glass beads tend to become blocked. A compromise arrangement used in our laboratories is shown in Figure 6.4(*a*). The major part of the material collects in the first empty trap and a good part of the remainder collects in the second trap filled with glass helices. After collection the flow of dry carrier gas is passed in the reverse direction and the second trap is warmed up so that the material in it is carried into the first trap. Finally, the first trap is warmed up and the bottom section which will contain the purified material cut off. Another arrangement is shown in Figure 6.4(*b*), an annular trap whose inside is heated. Droplets are then subject to a temperature gradient across the line of flow and move towards the colder surface under the force of evaporation from the warmer side. The temperature of the cold side of the trap must not be too low. Electrostatic precipitators[6] may also be used, and a simple design is given in Figure 6.4 (*c*). Whichever method is used it is difficult to trap more than about 90 per cent of a vapour when it is diluted with a large amount of uncondensable carrier gas. It is possible that the addition of, say, 10 per cent of carbon dioxide to the carrier gas before condensation might assist trapping. The carbon dioxide would be readily removed by warming the trap to room temperature.

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CHAPTER 7

The Literature of Gas Chromatography

Although gas chromatography was born only a decade ago its literature now comprises over 3,000 papers and is still growing at an increasing pace. Fortunately the number of really important papers is small and many of them are to be found in the proceedings of various symposia.

Vapour Phase Chromatography (Ed. Desty 1957), *Gas Chromatography 1958* (Ed. Desty) and *Gas Chromatography 1960* (Ed. Scott), all published by Butterworths Scientific Publications, give the papers and full discussion of three symposia arranged by the Gas Chromatography Discussion Group of the Hydrocarbon Research Group of the Institute of Petroleum and held in London, Amsterdam and Edinburgh. They contain a wealth of valuable information.

Gas Chromatography (Ed. Coates, Noebels and Fagerson, publ. Academic Press 1958) and *Gas Chromatography* (Ed. Noebels, Wall and Brenner 1961) give the papers and discussions of symposia held under the auspices of the Analysis Instrumentation Division of the Instrument Society of America in 1957 and 1959.

Papers read at various other symposia held in America are to be found in *Analytical Chemistry*, which also contains the bulk of the American literature.

Gas Chromatography, Second Edn., by Keulemans (Ed. Verver, publ. Reinhold Publishing Co. 1959), is still the best text devoted entirely to gas chromatography. The theoretical sections are excellent but many of the practical sections are somewhat out of date. *Gas Chromatography* by D. and B. A. Ambrose (publ. Newnes 1961) gives an up to date account of the practical aspects.

Recently the problem of assimilating the ever-growing literature has been greatly eased by the publication by Butterworths of *Gas Chromatography Abstracts*. This publication is sponsored by the Gas Chromatography Discussion Group for whom the abstractors work. Members of the group receive abstracts quarterly and the complete abstracts for the preceding year are normally published about June. An extremely valuable feature of *Gas Chromatography Abstracts* is the comprehensive subject index which enables one to survey any particular aspect quickly and thoroughly. There is no doubt that this publication has done a great service to gas chromatography and no active worker in the field should be without it.

List of Symbols

a	constant in katharometer theory	*page* 62
a_f a_m, a_g, a_l	cross-sectional areas of fixed, mobile, gas and liquid phases	1, 14
A	parameter in van Deemter equation	28
b	ratio $-\Delta\ H_s/L$	16
B	parameter in van Deemter equation	28
c	concentration	72
c_g, c_l	concentrations in gas and liquid phases	15
C	parameter in van Deemter equation	28
	differential heat capacity at constant pressure	62
d	liquid film thickness	27
D	parameter in theory of gas chromatography	35
	drift parameter (katharometer theory)	66
D_g, D	diffusion coefficients in gas and liquid phases	27
e	porosity of packing	29
E	voltage	61
f	flow rate	62
f_{av}, f_{o}	average and outlet flow rates	12
h	peak height	11, 13
H, H^*	HETP, height equivalent to a theoretical plate, optimum plate height	20, 29
i, i_0, i	current, basic current, saturation current	62, 72, 79
k	constants in theory of ionization detectors	72, 79
K	column capacity coefficient	15
L	molar heat of vaporization	16
	column length	29
	wire length (katharometer theory)	62
m	weight of stationary phase in column	15
M_s	molecular weight of stationary phase	15

N	number of theoretical plates	*page* 20, 23
p_{av}, p_i, p_m, p_o	average, inlet, mean and outlet column pressures	12
p_r	ambient laboratory pressure	12
p, p^0	partial vapour pressures	15
P	parameter in theory of gas chromatography	35
P_r, P_m, P_{tot}	contents of particular plates (theory of gas chromatography)	21
Q	parameter in theory of gas chromatography	35
Q_i	ionization cross-section of *i*th component	72
r, r_m	ordinal number of plates	21
r	particle or capillary radius	27, 33
r_c, r_w	radii of channel and wire (katharometer theory)	62
R	gas constant, 1·986 cal $mole^{-1}$ deg^{-1}	15
	resolution; resistance	24, 61
S	separation number	25
	sensitivity (katharometer theory)	63
t, t_R	elution time, retention time	35, 12
T, T_r	column and ambient laboratory temperatures	12
T_b	boiling point	17
u, u^*	linear gas velocity; optimum gas velocity	2, 27, 29
v_g, v_l	volumes of gas and liquid phases in column	11, 12, 15
V	volume of carrier gas passed	20
V_R	true retention volume	11
V'_R	net retention volume	11, 12
V_{exp}	experimental retention volume	12
V_r^T	specific retention volume	16
w	peak width at base	11, 14
x	distance from centre of peak	13
	geometrical factor for electron capture detector	79
X	mole fraction	15, 62, 72
y	peak ordinate	13
α	solubility	15
	thermal coefficient of resistance	63

α_{12}	solubility ratio α_1/α_2	*page* 25
$\beta_e, \beta_{1/2}$	peak widths at 0·368 and 0·5 of maximum	11, 14
γ	constant in van Deemter equation	27
	activity coefficient	15
$\Delta H_m, \Delta H_s$	partial molar heats of mixing and of solution	16
η	viscosity	29
λ	parameter in plate theory	21
	constant in van Deemter equation	27
	thermal conductivity	62
ρ	density of stationary phase	15
	ratio d/r	35
σ	standard deviation	11, 13, 14
ϕ	parameter in plate theory	23

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[8]

1

THE RATE CONSTANTS OF HALOGEN ATOM REACTORS

G. C. FETTIS AND J. H. KNOX

CONTENTS

I. INTRODUCTION

Halogenation reactions, in particular those of hydrogen, have played a leading part in the development of reaction kinetics. Indeed one can justifiably claim that the modern phase was initiated by the classic work of Bodenstein (1894–9)[1] on the hydrogen/iodine reaction and of Bodenstein and Lind (1907)[2] on the hydrogen/bromine reaction. The rate expression derived for the latter reaction was of a type previously unknown and was much more complex than that for the simple second order hydrogen/iodine reaction. Interpretation of this expression independently by Christiansen,[3] Hertzfeld[4] and Polanyi[5] (1919–20) by the now well known bromine atom scheme introduced physical chemists to the idea that free atoms could take part in chemical reactions as distinct independent species, and provided the basis for the free radical chain mechanisms which were to be extensively developed in the 1930's. Until 1939 the majority of gas kinetic studies were inevitably aimed at the elucidation of the overall rate expressions and reaction mechanisms. As a result of the preoccupation with overall kinetics the study of methods for determining the absolute rate constant of the elementary steps in such reaction schemes was somewhat neglected.

Efforts to determine elementary rate constants were stimulated by the development of the transition state theory in the 1930's, and increasing efforts were made to obtain rate constants of the simpler reactions such as those between an atom and a molecule. Since the war the developments of mass spectroscopy and gas chromatography, and the application of competitive methods to the study of similar reactions have enabled our knowledge of elementary rate constants to be greatly extended. The post-war phase of rapid expansion owed much of its initial impetus to Steacie, and his research school at Ottawa.

In the field of free atom reactions those of the halogens are particularly important since they furnish a more or less continuous series whose activation energies range from zero to over 33 kcal mole^{-1}. The data now available on the absolute parameters of some fifty such reactions should enable transition state models to be extensively tested and there is now some real hope that precise theoretical calculations of A factors and activation energies for atom+molecule reactions may become possible.

In the present review we confine ourselves to the discussion of the rate constants and Arrhenius parameters of gasphase reactions in which a halogen atom, X, abstracts a hydrogen atom or another halogen atom from a suitable donor, RH or RX, or adds to a compound containing a double bond, A. We consider in detail only those experiments which have yielded reliable Arrhenius parameters. Much of the early work on overall reaction rates, work on reactions in solution, and work carried out over a restricted temperature range is therefore omitted. We also omit discussion of halogen atom recombination reactions which are best considered separately.

The reactions which concern us, (2), (2′) and (5), are important steps in the free radical halogenations of organic substances. The generally accepted mechanisms for such processes involve some or all of the following elementary steps:

Initiation	$X_2+M = 2X+M$		(1) thermal	
	$X_2+h\mu = 2X+$		(1) photochemical	
Propagation	$X+RH = XH+R$	(2)	$X+A = AX$	(2′)
	$R+X_2 = RX+X$	(3)	$AX+X_2 = AX_2+X$	(3′)
Inhibition	$R+XH = RH+X$	(4)	$AX = A+X$	(4′)
	$X+RX = X_2+R$	(5)	$X+AX_2 = X_2+AX$	(5′)
Termination	$X+X+M = X_2+M$			(6)
	$X+R = RX$ (or $A+XH$)	(7)	$X+AX = AX_2$ (or $A+X_2$)	(7′)
	$R+R = R_2$ (or $RH+A$)	(8)	$AX+AX = XAAX$ (or $A+AX_2$)	(8′)
Molecular	$RH+X_2 = RX+XH$	(9)	$A+X_2 = AX_2$	(9′)
	$RX+XH = RH+X_2$	(10)		

Since we shall be dealing mostly with reactions (2) and (2′) we shall generally denote their rate constants and Arrhenius parameters simply by k, A and E rather than by k_2, A_2 and E_2. Where it is necessary to specify one or both of the reactants we shall use the notation $k(\mathrm{RH})$, $k(\mathrm{X})$ or $k(\mathrm{X+RH})$.

The Arrhenius parameters given in the tables are those defined by the rate equation

$$k = A.\exp[-E/RT] \tag{1}$$

The units of k and A are mole^{-1} l. sec^{-1} and those of E cal mole^{-1} unless otherwise stated.

Equations other than (1) are sometimes used to express the variation of the rate constants of bimolecular reactions with temperature, the most widely used being (2) which can be derived from collision theory.

$$k = B.T^{1/2}.\ \exp[-E'/RT] \tag{2}$$

Although (2) has some theoretical justification the true exponent of T is unlikely to be exactly 0·5 and may well vary with temperature. Furthermore it is not generally possible from experimental data to determine the exponent to better than ±2. Accordingly we prefer to use the simpler expression A. The parameters defined in equations 1 and 2, when relating to the same data, are connected by the relations

$$A = 1{\cdot}649\ B\,T_m^{1/2} \qquad E = E' + 1/2\ RT_m$$

where T_m is the mean temperature.

The determination of absolute rate constants and Arrhenius parameters of reactions such as 2, 2′ and 5 is generally difficult since a knowledge of the free atom concentration is required, and it is only in a few cases that accurate determination of k over a wide range of temperature has been possible. Fortunately the number of absolute rate constants which must be determined independently is small since it is experimentally simpler and usually more accurate to determine other absolute rate constants from competitive experiments in which substances of unknown rate constants are competed against a substance whose absolute rate constant is established. The independent determination of the absolute rate constants of several similar reactions which can be carried out competitively is only useful as a means of establishing the absolute scale more precisely than would be possible from a single absolute determination.

Since rate constant ratios are simpler to determine than absolute rate constants, and since the results of the competitive experiments prove useful in discussion of the best values for some absolute Arrhenius parameters, we consider the competitive experiments first.

In the tables which follow we list both relative Arrhenius parameters derived from competitive experiments (Tables 1, 3, 4 and 6) and absolute values (Tables 2, 5, 7, 8 and 9). The A factors in every case are those for individual C—H bonds of a given type. Thus the A factor for any molecule as a whole is obtained from the listed values by multiplying by the number of C—H bonds of the appropriate type. For example, the A factor for $Cl + priC_3H_8$ is listed as $1{\cdot}7 \times 10^{10}$. The value for the whole molecule is $6 \times 1{\cdot}7 \times 10^{10} = 10 \times 10^{10}$ since there are 6 primary C—H bonds in propane.

In all the tables the errors quoted are twice the standard deviations and represent the 95 per cent confidence limits assuming that the errors are random. Generally rate constants are known more accurately than Arrhenius parameters and the error limits in A and E must be taken together. Thus when we write

$$k(Cl + H_2) = (8{\cdot}3 \pm 0{\cdot}5) \times 10^{10}.\exp[-5480 \pm 140)/RT]$$

we mean that the extreme limits of the Arrhenius equation are

$$k(Cl + H_2) = 8{\cdot}8 \times 10^{10}\ \exp[-5620/RT]$$

and $$k(Cl + H_2) = 7{\cdot}8 \times 10^{10}\ \exp[-5340/RT]$$

The low value of A does not go with the high value of E.

II. THE DETERMINATION OF RELATIVE RATE CONSTANTS BY COMPETITIVE EXPERIMENTS

In competitive experiments two or more substances are made to react simultaneously with the same reagent. For example if R_aH and R_bH are made to react with halogen atoms X the following reactions will occur:

$$X+R_aH = XH+R_a \tag{2a}$$

$$X+R_bH = XH+R_b \tag{2b}$$

$$R_a+X_2 = R_aX+X \tag{3a}$$

$$R_b+X_2 = R_bX+X \tag{3b}$$

With olefins the analogous reactions would be (2a′), (2b′), (3a′) and (3b′).

In the absence of complicatng features the rates of (2a) and (2b) can be found either by measuring the rates of disappearance of the two H donors, the "consumption method", or by measuring the rates of formation of the two halides, the "product method". The relevant expressions being

$$\frac{k_a}{k_b} = \frac{\mathrm{Log}([R_aH]_i/[R_aH]_f)}{\mathrm{Log}([R_bH]_i/[R_bH]_f)} \tag{3}$$

$$\doteqdot \frac{\Delta[R_aH].[R_bH]_m}{\Delta[R_bH].[R_aH]_m} \quad \text{Consumption method} \tag{4}$$

$$\frac{k_a}{k_b} \doteqdot \frac{[R_aX].[R_bH]_m}{[R_bX].[R_aH]_m} \quad \text{Product method} \tag{5}$$

where $[RH]_i$, $[RH]_f$, $[RH]_m$ are the initial, final and mean H-donor concentrations, $\Delta[RH] = [RH]_i-[RH]_f$, and [RX] is the concentration of halide formed. The approximate forms (4) and (5) are accurate to better than 1 per cent if the consumption of either H donor is less than 30 per cent. With olefins the expressions are similar, RH and RX being replaced respectively by A and AX_2.

Since the free atom concentration does not enter into the expressions for k_a/k_b its actual value is unimportant. The reactions may thus be initiated either thermally or photochemically and the nature of the chain terminating steps is irrelevant provided that they do not remove or produce significant amounts of the H donors. Extreme purity of the reactants is not essential provided that the impurities do not react with a significant fraction of the radicals R formed in reactions 2a or 2b.

The occurrence of either 4 or 5 may lead to errors if not allowed for. Reaction 4 competes with 3 for R and becomes significant when it is exothermic and of low activation energy. For Cl or F, 4 is endothermic or thermoneutral and is unimportant except possibly for $Cl+H_2$. With bromine it is exothermic with hydrogen, methane and most C—H bonds other than possibly tertiary C—H.

With hydrogen and methane (the most exothermic pair) k_4 is about 1/10th of k_3[6,7]. With iodine 4 will be exothermic for all hydrocarbons and for hydrogen its rate constant is again about 1/10th that of 3.[8] Even in the most unfavourable cases reaction 4 is unlikely to be important unless an excess of HX over X_2 is present. In systems where no HX is present initially its effect will be negligible. The measurement of the consumption of the two H donors should therefore give an accurate rate constant ratio unless the reactants are produced from a completely different source not considered in the mechanism.

Unfortunately the consumption method, attractive in principle, suffers from two serious disadvantages. Firstly it requires the measurement of differences between initial and final concentrations and even for moderately accurate work at least 10 per cent of the less reactive component must be consumed. When the rate constant ratio is close to unity both competitors are consumed in roughly the same proportion and the method is capable of high accuracy, but when k_a/k_b differs markedly from unity accuracy falls. For example when $k_a/k_b = 10$ reasonably accurate results could be obtained if about 20 per cent of R_bH and 90 per cent of R_aH were consumed, but when the ratio is 100 only 1 per cent of R_aH would remain when 5 per cent of R_bH had disappeared. The consumption method is thus limited in practice to competitions where the reactivities of the competitors differ by factors of less than about 50.

The second and in principle more serious disadvantage of the consumption method is that it cannot distinguish between different types of H-atoms in the same molecule, for example the primary and secondary H-atoms in propane.

For these reasons the product method is more satisfactory in practice but the reaction mechanism must be more carefully checked. It is obviously essential that a very high proportion of the radicals R formed in 2 react by 3 and that the halides formed should not decompose or be formed by any reaction other than 3. The effects of reaction 4 have already been shown to be normally unimportant. Reaction 5 is always endothermic but only for F and Cl is it more endothermic than 2. For Br both 5 and 2 have roughly the same endothermicity; for I reaction 5 is less endothermic than 2 and the overall reactions $I_2+RH = RI+HI$ are strongly reversed. However even with I atoms the only effect of 5 *initially* is to increase the concentrations of R; the initial rate of formation of RX is not affected. Although competitive iodination experiments will be difficult because of their reversibility, the rapidity of 5 in comparison to 2 provides a method of studying the competitive reactions of I atoms with iodides (*see* section 3F).

Pyrolysis or isomerization of R will lead to inaccurate results if not allowed for. Pyrolysis of unsubstituted, alkyl radicals normally requires over 25 kcal mole^{-1} activation energy[9] and will only become important above 300°C. With increasing substitution however the activation energy for decomposition falls and for C_2Cl_5 is only 17 kcal[10] while that of its competitor 3 increases. Decomposition of R may then become important above 150°C. Isomerization, decomposition, recombination and disproportionation can all in principle be detected by carrying out experiments at different halogen concentrations, and should they prove to be significant their effect can be allowed for by making an extrapolation to infinite halogen concentration, or by making more complete analysis of the products.

Secondary halogenation of the initial reaction products will occur especially when the initial products are more reactive than the original reactants. It can be allowed for by more complete analysis except where two secondary products are the same or where one of them is the same as one of the initial reactants (for example in the chlorination of methane/methylene chloride mixtures). Although it is always best to avoid secondary halogenation by working to low conversion of the reactants this may not always be possible if k_a/k_b differs markedly from unity.

Decomposition of the halide products may occur and in principle can be allowed for by more detailed analysis, but the systems then become increasingly complicated. Decomposition is likely to occur with iodides, secondary and tertiary bromides and tertiary chlorides.

With olefins the position regarding halogenations generally is unsatisfactory and to date only chlorinations have been successfully studied. Reaction 4′ is now unimolecular and under normal working conditions is some 10^5 faster than an equivalent bimolecular reaction 4 with the same activation energy. Thus in the chlorination of C_2Cl_4 the decomposition of the C_2Cl_5 radical is important at 150°C and becomes rapidly more important above this temperature.[10] There is thus a sharp cut off at a temperature above which it is experimentally impossible to allow for the decomposition of AX by working at high halogen pressures.

Since the chloroalkyl radicals $C_nH_{2n}Cl$ decompose with higher activation energies than C_2Cl_5 one might expect that the direct and competitive chlorination of unsubstituted or slightly substituted olefins would be more straightforward. This is not so. Experiments by Dainton and co-workers[11–14] on chloroethylenes have shown that it is highly probable that the initial adduct, ACl*, of Cl to an olefin, which must initially contain the activation energy E_2 plus the heat of dissociation of A—Cl, is capable of several reactions[6]

$$A+Cl = ACl^* \tag{2'}$$

$$A\ Cl^* = A+Cl \tag{α}$$

$$ACl^*+Cl_2 = A+Cl+Cl_2 \tag{β}$$

$$ACl^*+Cl_2 = A\ Cl+Cl_2 \tag{γ}$$

$$ACl+Cl_2 = ACl_2+Cl \tag{3'}$$

It is only with C_2Cl_4 that the reactions α and β appear to be unimportant and that all the initially formed activated ACl* reacts to form the product ACl_2.

When reactions α, β and γ are important it is possible to determine k_2', only if k_α, k_β and k_γ are also known. In general it is possible to separate k_α from $(k_\beta+k_\gamma)$ by carrying out experiments at different chlorine pressures, but it is not generally possible to separate k_β and k_γ. This can only be done if reaction β can be made to produce a product distinguishable from the original A. One method would be to use isotopic exchange of radio-chlorine. Ayscough, Cocker and Dainton[11] used the catalysed isomerization of *cis* and *trans* dichloroethylene. The species ACl* formed from either of these olefins is the same and on reaction by α and β will produce a mixture of *cis* and *trans* olefins. Thus measurement of the rate of isomerization relative to chlorination of the pure *cis* and pure *trans* olefins enables the three rates to be separated, and k_2, to be found.

A. *Competitive Fluorinations*

The reactions of fluorine atoms are difficult to study because they are extremely fast and exothermic. With few exceptions fluorine atoms appear to abstract hydrogen atoms from organic compounds with zero activation energy. Since the A factors of other halogen atom reactions are close to the collision numbers, F-atoms probably react with H donors at nearly every collision. If reliable rate data are to be obtained care must obviously be taken to ensure that the F-atoms are thermally equilibrated before they react and do not possess excess kinetic energy from their formation. Since F-atoms generated by reaction 3 carry a large excess of energy it is therefore essential that the H-donor mixture be diluted with a large excess of inert gas so that the great majority of F-atoms will react only after a number of deactivating collisions. Apart from this the fluorination mechanisms should be simple since 4 and 5 are very endothermic.

In the past the study of F-atom reactions has been made difficult by the necessity of producing rather large amounts of products, with the attendant difficulties of maintaining isothermal conditions and preventing secondary fluorination. These difficulties can be overcome by using gas chromatography for analysis. The quantities of products required are small and consequently it is possible to work with low conversions of RH in the presence of a large excess of inert gas.

Anson, Fredricks and Tedder[15,16] were the first to apply gas chromatography to fluorination studies. They examined the fluorination in the gas phase of n- and iso-butanes and of some monohalogenated butanes. Mercer and Pritchard[17] studied the competitive fluorination of methane and hydrogen using the consumption method. Later Fettis, Knox and Trotman-Dickenson[18] studied the competitive fluorination of a number of hydrocarbon mixtures using the product method and gas chromatography for analysis. The results obtained in these competitive experiments are given in Table 1. The agreement between the results of Anson, Fredricks and Tedder and of Fettis, Knox and Trotman-Dickenson is satisfactory. Since the former experiments were carried out in a flow system and the latter in a static system the agreement is good evidence that the rate constant ratios are true values for thermal F-atoms.

For only three pairs of H-donors has any activation energy difference been obtained: $E(H_2)-E(CH_4) = 500$ $E(CH_4)-E(C_2H_6) = 930$ and $E(C_2H_6)-$

E(priC_3H_8) = 280 cal mole^{-1}. These activation energy differences are considerably lower than those found for the corresponding Cl-atom reactions, and it seems likely that the activation energies for all hydrocarbons higher than ethane are close to zero (with Cl they are between zero and 1000 cal mole^{-1}). There is unfortunately no known absolute rate constant for any F-atom reaction and in drawing up Table 2 we have assumed that $E(C_2H_6)$ = 280 cal mole–^{1} and *E* for all higher hydrocarbons is zero.

TABLE 1. COMPETITIVE FLUORINATIONS

Competitors a	b	A_b/A_a per H-atom of given type	E_b-E_a cal mole^{-1}	Ref.
CH_4	H_2	2·0 (0·8–2·5)	500 ± 200	17
C_2H_6	CH_4	3·9 ± 0·7	930 ± 80	18
priC_3H_8	C_2H_6	1·84 ± 0·10	280 ± 25	18
secC_3H_8	priC_3H_8	0·83 ± 0·05	0 ± 40	18
pri-n-C_4H_{10}	priC_3H_8	1·11 ± 0·12	0 ± 50	18
pri-n-C_4H_{10}	pri-iso-C_4H_{10}	1·05 ± 0·08	0 ± 40	18
sec-n-C_4H_{10}	pri-n-C_4H_{10}	0·87 ± 0·12	0 ± 80	18
		0·83 ± 0·15		15
tert-iso-C_4H_{10}	pri-iso-C_4H_{10}	0·71 ± 0·08	0 ± 70	18
		0·80 ± 0·12		15
cycloC_3H_6	pri-n-C_4H_{10}	1·02 ± 0·12	0 ± 60	18
cycloC_3H_6	pri C_3H_8	1·13 ± 0·30	0 ± 130	18
pri-iso-C_4H_{10}	neo C_5H_{12}	0·18 ± 0·05	0 ± 30	18

Error limits are twice the standard deviation.

The *A* factors listed in Table 2 are also assumed values. Calculations of *A* factors referred to later (section 4A) show that even with a relatively crude model it is possible to calculate *A* factors which differ by factors of less than two from the experimental values for Cl and Br atom reactions. It is therefore probable that the calculations can be extended with reasonable confidence to the F-atom reactions. Accordingly in Table 2 we have assumed that the *A* factor for F+C_2H_6 is equal to the calculated value of $1{\cdot}00 \times 10^{10}$ mole^{-1} litre sec^{-1} per C—H bond, i.e. $6{\cdot}0 \times 10^{10}$ mole^{-1} litre sec^{-1} for the whole molecule.

B. *Competitive Chlorinations*

The competitive reactions of chlorine atoms have been more extensively studied than those of any other halogen. This is chiefly because Cl is a more convenient reagent for such studies than F, Br or I, although Br is more convenient for the determination of absolute rate constants.

The earliest competitive experiments with Cl were those of Farkas and Farkas[19] on H_2+HD mixtures (1934) and those of Rollefson (1934) on H_2 and

TABLE 2. ABSOLUTE ARRHENIUS PARAMETERS FOR FLUORINATIONS

Standard reaction: $F+C_2H_6 = HF+C_2H_5$ Assumed $E = 280$ cal mole^{-1} $A = 1{\cdot}00\times10^{10}$ mole^{-1} l. sec^{-1}

Compound	Competitors	10^{-10} A mole^{-1} l. sec^{-1} per H-atom	E cal mole^{-1}	Ref.
H_2	CH_4, C_2H_6	5·9 (3·8–8·8)	1710 ± 220	17, 18
CH_4	C_2H_6	3·05 ± 0·5	1210 ± 80	18
Primary C—H bonds				
C_2H_6	Standard	1·00	280	Assumed values
C_3H_8	C_2H_6	0·55 ± 0·04	0 ± 25	18
nC_4H_{10}	C_3H_8, C_2H_6	0·48 ± 0·07	0 ± 70	18
isoC_4H_{19}	nC_4H_{10}, C_3H_8, C_2H_6	0·50 ± 0·07	0 ± 70	18
neoC_5H_{12}	isoC_4H_{10}, nC_4H_{10}, C_3H_8, C_2H_6	0·47 ± 0·07	0 ± 80	18
Secondary C—H bonds				
C_3H_8	C_2H_6	0·63 ± 0·04	0 ± 25	
nC_4H_{10}	C_3H_8, C_2H_6	0·59 ± 0·07	0 ± 65	18, 15
cycloC_3H_6	C_3H_8, C_3H_6	0·48 ± 0·11	0 ± 100	18
Tertiary C—H bonds				
isoC_4H_{10}	nC_4H_{10}, C_3H_8, C_2H_6	0·70 ± 0·12	0 ± 80	18, 15

D_2+CO mixtures.[20] The chlorination of other isotopic hydrogen mixtures has been carried out more recently. $HT+H_2$ mixtures were investigated very carefully by Jones[21] and $HD+H_2$ mixtures by Bigeleisen, Klein, Weston and Wolfsberg.[22] The only other study of the chlorination of isotopic mixtures was that of Newton and Rollefson[23] on $CHCl_3+CDCl_3$ mixtures.

The competitive chlorination of hydrocarbon mixtures or of different positions in the same molecule was first studied by Hass, McBee and Weber[24] (1935) using a flow system. They measured the relative rates of formation of the isomeric chlorides from propane and isobutane using distillation to separate the products. Their results differ from those obtained in later work and cannot now be regarded as reliable. More recently Pritchard, Pyke and Trotman-Dickenson,[25] Knox,[26] Knox and Nelson,[27] and Anson, Fredricks and Tedder[15] have investigated the competitive chlorination of a range of hydrocarbons. Competitive chlorination of halogenated hydrocarbons has been studied by Fredericks and Tedder[16], Knox[28] and Goldfinger, Huybrechts and Martens.[29]

The data on the competitive chlorination of isotopic species are summarized in Table 3. Rollefson[20] in his study of the chlorination of mixtures of H_2 and D_2+CO obtained relative rate constants which he believed to be those of reactions 11 and 12 in the general scheme

$$Cl_3+H_2 = HCl+Cl_2+H \tag{11}$$

$$Cl_3+CO = COCl+Cl_2 \tag{12}$$

$$COCl+Cl_2 = COCl_2+Cl \tag{3'}$$

which gives

$$\Delta[H_2]/\Delta[CO] = (k_{11}/k_{12})([H_2]/[CO]) \tag{6}$$

The aim of Rollefson's experiments was to prove that his scheme was superior to that of Bodenstein who proposed that the reaction forming COCl was reversible. For the competitive system the relevant reactions according to the Bodenstein scheme would be

$$Cl+H_2 = HCl+H \tag{2}$$

$$Cl+CO \rightleftharpoons COCl \qquad (2') \rightharpoonup (4') \leftharpoondown$$

$$COCl+Cl_2 = COCl_2+Cl \tag{3'}$$

which leads to

$$\Delta[H_2]/\Delta[CO] = (k_2k_4'/k_3'k_2')([H_2]/[CO][Cl_2]) \tag{7}$$

Rollefson plotted the left hand side of equation 6 (or 7) against $[H_2]/[CO]$. The points show a rather wide scatter although they are distributed randomly about a straight line. Rollefson states that this plot is better than that of the same function against $[H_2]/[CO][Cl_2]$ (equation 7). However replotting the data shows that the evidence is not convincing and that the spread of points is similar for both plots. In view of the recent work of Burns and Dainton[31] on the phosgene reaction it is clear that Rollefson's results should be interpreted in terms of the Bodenstein mechanism involving the COCl equilibrium. Nevertheless his rate constant ratios for H_2 versus D_2 should not be seriously in error although the estimate of ±10 per cent is probably optimistic. They are in good agreement with a single value obtained by Bigeleisen, Klein, Weston and Wolfsberg (BKWW)[22] but are not sufficiently accurate to enable an activation energy difference to be determined. The accurate data of Jones[21] and of BKWW[22] on other hydrogen isotopes show however that the *A* factor ratios for such reactions agree excellently with those predicted either by collision theory or transition state theory, both of which give the same expression

TABLE 3. COMPETITIVE CHLORINATION OF ISOTOPIC MIXTURES

Competitors a	Competitors b	A_b/A_a expl.	Calc.	E_b-E_a cal mole^{-1}	E_0^0 (a)–E_0^0 (b) cal mole^{-1}	Ref.
H_2	HD	0·81 ±0·04	0·83	490 ± 12	808	22
H_2	HT	0·74 ±0·05	0·73	560 ± 20	1105	21
H_2	D_2	(0·73)	0·73	(1220)	1770	20, 22
$CHCl_3$	$CDCl_3$	0·7 ±0·3	1·00	700 ± 200	1080	23

$$A_a/A_b = \{(M_b M_a^*)/(M_a M_b^*)\}^{\frac{1}{2}} \tag{8}$$

where M_a and M_b are the molecular weights of the two hydrogen isotopes and M_a^*, M_b^* are the molecular weights of the transition state complexes, H_2Cl, etc. It is therefore reasonable to assume that accurate experiments on the H_2/D_2 system would likewise give the *A* factor ratio predicted by theory. Assuming this to be true we arrive at an activation energy difference of 1220 cal mole^{-1} for D_2 and H_2 on the basis of Rollefson's results. In Table 3 we list the available data on the Arrhenius parameters of isotopic competition reactions and in the last column we record the difference in zero point energies which may be compared with the activation energy differences.

The theoretical calculations of BKWW[22] were not able to accommodate all the rate constant data for hydrogen isotopes although several models were considered, but until more accurate data on the H_2/D_2 system is available it is not possible to tell whether the discrepancy is real or simply the result of experimental error.

In the experiments of Newton and Rollefson[23] on the $CHCl_3/CDCl_3$ mixtures relative rates were found by analysis for the HCl and DCl formed, the hydrogen deuterium chlorides having been reduced to H_2 and D_2 and the composition determined by thermal conductivity.

The first reliable study of the competitive chlorination of hydrocarbon mixtures was that of Pritchard, Pyke and Trotman-Dickenson.[25] Hydrocarbon +chlorine mixtures were sealed in glass ampoules, brought up to reaction temperature and irradiated. The amounts of the two hydrocarbons were determined before and after the reaction. The experiments were carried out over a temperature range of 300–500°K. While they were able to obtain reasonably accurate values for rate constant ratios when both competitors were consumed at comparable rates, they experienced difficulty with H_2/CH_4 and CH_4/C_2H_6 mixtures where the reactivities differed markedly. The results are given in Table 4 along with 95 per cent probability errors estimated from the scatter of the experimental points. The errors in E's are generally of the order of a few hundred cal mole^{-1}.

With the application of gas chromatography by Knox,[26] by Anson Fredricks and Tedder[15,16] and by Knox and Nelson[27] it became possible to obtain accurate relative rates by analysing the reaction products. This method is particularly useful when the two competitors differ greatly in reactivity. It also enables relative rates of attack of Cl at different points in the same molecule to be determined. The temperature range covered in the experiments of Knox and Nelson was 200–600°K. Comparison of the results of Pritchard, Pyke and Trotman-Dickenson, of Knox and Nelson and of Anson, Fredricks and Tedder show excellent agreement where they overlap and provide good evidence that the product method is reliable for hydrocarbons. The values of Knox and Nelson are generally the most accurate and have been used for the calculation of the majority of absolute values given in Table 5.

The results of Knox[28] on the competitive chlorination of chloromethanes against methane and propane are also given in Table 4. Combining these results with those of Knox and Nelson two closed circuits can be completed in which every adjacent pair of compounds have been chlorinated in competition:

(i) methane, ethane, propane, methylene chloride, methane,
(ii) methane, ethane, propane, methyl chloride, chloroform, methane.

The agreement within the two series is excellent and argues strongly for the reliability of the derived Arrhenius parameters.

The competitive chlorination of the chloromethanes against tetrachloroethylene has been investigated by Goldfinger, Huybrechts and Martens.[29] A careful study of the chlorination of both tetrachloroethylene and pentachloroethane by Goldfinger and co-workers[10] had resulted in the determination of several elementary rate constants and rate constant ratios, but since the chain termination reactions were predominantly 8 and 8′ no absolute rate constants for 2 and 2′ could be obtained. However using the absolute Arrhenius parameter determined by Knox for the chloromethanes the absolute Arrhenius parameters for the reactions of Cl with C_2Cl_4 and C_2HCl_5 were found. The values obtained in this way are given in Table 5. It is of particular interest that $E(C_2Cl_5)$ is zero as this provides support for the accuracy of the Arrhenius parameters for the reaction of Cl with hydrogen. It may also be noted that $E(C_2HCl_5)$ is close to that for chloroform.

Ayscough, Cocker, Dainton and Hirst[14] have carried out competitive experiments with mixtures of vinyl chloride + *cis*-dichloroethylene and trichloroethylene + *cis*-dichloroethylene. These experiments do not however give unambiguous values for k_2, and their discussion is left till section 3B.

TABLE 4. COMPETITIVE CHLORINATIONS

Competitors a	 b	A_b/A_a per H-atom of any type	$E_b - E_a$ cal mole^{-1}	Ref.
Hydrocarbons				
CH_4	H_2	6·6 ±1·5	1650 ± 180	27
C_2H_6	CH_4	0·39 ± 0·08	2810 ± 130	26
priC_3H_8	C_2H_6	0·90 ± 0·06	40 ± 30	27
secC_3H_8	C_2H_6	0·43 ± 0·03	360 ± 30	27
pri-n-C_4H_{10}	C_2H_6	1·13 ± 0·18	250 ± 90	27
sec-n-C_4H_{10}	C_2H_6	0·71 ± 0·12	770 ± 100	27
sec-n-C_4H_{10}	pri-n-C_4H_{10}	0·63 ± 0·10	520 ± 90	27
		0·52 ± 0·15	410 ± 50	15
pri-isoC_4H_{10}	C_2H_6	1·15 ± 0·16	220 ± 75	27
tert-isoC_4H_{10}	C_2H_6	0·62 ± 0·17	1020 ± 130	27
tert-isoC_4H_{10}	pri-isoC_4H_{10}	0·54 ± 0·16	800 ± 130	27
		0·50 ± 0·10	570 ± 100	15
neo C_5H_{12}	C_2H_6	1·22 ± 0·10	80 ± 60	27
C_2H_6	cycloC_3H_6	0·56 ± 0·06	3100 ± 90	27
cycloC_4H_8	priC_3H_8	0·40 ± 0·08	175 ± 120	27
CH_4	H_2	6·2 ±2·0	1650 ± 300	25
C_2H_6	CH_4	0·32 ± 0·13	2850 ± 500	25
C_3H_8	C_2H_6	0·90 (0·5–1·6)	330 ± 400	25
isoC_4H_{10}	C_2H_6	1·02 ± 0·20	140 ± 200	25
neoC_5H_{12}	C_2H_6	1·97 ± 0·30	300 ± 150	25
cycloC_5H_{10}	C_2H_6	0·67 ± 0·10	420 ± 150	25
Chlorinated hydrocarbons				
CH_3Cl	CH_4	0·34 ± 0·13	490 ± 300	25
C_2H_6	C_2H_5Cl	0·46 ± 0·15	490 ± 200	25
priC_3H_8	CH_3Cl	0·78 ± 0·16	2400 ± 100	28
pri-n-C_3H_8	CH_2Cl_2	0·96 ± 0·18	2025 ± 180	28
CH_2Cl_2	CH_4	0·50 ± 0·05	875 ± 80	28
$CHCl_3$	CH_4	0·88 ± 0·07	575 ± 70	28
CH_3Cl	$CHCl_3$	0·78 ± 0·06	265 ± 40	28

Halogenated n-butanes

(1) (2) (3) (4)	A_4/A_3	A_4/A_2	A_4/A_1	E_4-E_3	E_4-E_2	E_4-E_1	Ref.
CH_3–CH_2–CH_2–CH_3	0·52 ± 0·15	0·52 ± 0·15	unity	400 ± 50	400 ± 50	zero	15
CH_2F–CH_2–CH_2–CH_3	0·53 ± 0·25	0·75 ± 0·3	1·1 ± 0·4	400 ± 100	150 ± 150	0 ± 100	16
CH_2Cl–CH_2–CH_2–CH_2	0·59 ± 0·2	1·25	1·2	550 ± 100	500 ± 400	0 ± 200	16

TABLE 5. ABSOLUTE ARRHENIUS PARAMETERS FOR CHLORINATIONS

Standard reaction: $Cl+H_2 = HCl+H$ $E = 5480 \pm 140$ cal mole^{-1}
$A = (4{\cdot}1 \pm 0{\cdot}3).10^{10}$ mole^{-1} l. sec^{-1}
Secondary standard: $Cl+CH_4 = HCl+CH_3$ $E = 3830 \pm 250$ cal mole^{-1}
$A = (0{\cdot}6 \pm 0{\cdot}3).10^{10}$ mole^{-1} l. sec^{-1}

Compound	Competitors	10^{-10} A mole^{-1} l. sec^{-1} per H atom.	E cal mole^{-1}	Ref.
H_2	Standard	4·1	5480	*See* text
HD	H_2	3·3 ±0·2	5970 ± 20	22
HT	H_2	3·0 ±0·2	6040 ± 20	21
D_2	H_2	3·0 ±1·0	6600 ± 150	20
CH_4	H_2	0·6 ±0·2	3830 ± 180	25, 27
Primary C—H bonds				
CH_4	Secondary standard	0·6	3830	
C_2H_6	CH_4	1·5 ±0·3	1020 ± 130	25, 26
C_3H_8	C_2H_6, CH_4	1·7 ±0·3	980 ± 130	27
nC_4H_{10}	C_2H_6, CH_4	1·4 ±0·3	770 ± 140	27
isoC_4H_{10}	C_2H_6, CH_4	1·3 ±0·3	800 ± 140	27
neo C_5H_{12}	C_3H_8, C_2H_6, CH_4	1·4 ±0·3	900 ± 140	27
Secondary C—H bonds				
C_3H_8	C_2H_6, CH_4	3·6 ±0·7	660 ± 130	27
nC_4H_{10}	C_2H_6, CH_4; priC_4H_{10}*	2·4 ±0·5	300 ± 140	15, 27
cycloC_3H_6	C_2H_6, CH_4	0·9 ±0·2	4120 ± 140	27
cycloC_4H_8	C_3H_8, C_2H_6, CH_4	3·2 ±0·7	800 ± 150	27
Tertiary C—H bond				
isoC_4H_{10}	C_2H_6, CH_4; pri-isoC_4H_{10}	2·1 ±0·5	100 ± 160	15, 27
Chlorinated methanes and ethanes				
CH_3Cl	$CHCl_3$, CH_4; C_3H_8, C_2H_6, CH_4	1·1 ±0·3	3280 ± 200	25, 28
CH_2Cl_2	C_3H_8, C_2H_6, CH_4; CH_4	1·3 ±0·2	2960 ± 100	28
$CHCl_3$	CH_4	0·69 ±0·06	3320 ± 90	28
$CDCl_3$	$CHCl_3$, CH_4	0·5 ±0·2	4000 ± 200	28, 23
C_2H_5Cl	C_2H_6, CH_4	0·7 ±0·25	1500 ± 250	25, 27
C_2HCl_5	C_2Cl_4, chloromethanes	0·5 ±0·15	3400 ± 200	28, 29
Addition reactions				
CH_2CHCl	Direct	0·32	1000	13
cis $C_2H_2Cl_2$	Direct	0·25	950	13
C_2HCl_3	Direct	0·40	700	13
C_2Cl_4	Chloromethanes, CH_4	0·16 ±0·05	0 ± 200	28, 29
NO	Direct via $CO+Cl_2$	1·09 (0·6-2·0)	1060 ± 300	31

* Commas are placed between competitors in a series, semicolons between different series of competitors.

TABLE 5 (*Cont.*)

Halogenated butanes

(1) (2) (3) (4)	E_1	E_2	E_3	E_4
$CH_3–CH_2–CH_2–CH_3$	770 (std.)	300 ± 50	300 ± 50	770 (std.)
$CH_2F–CH_2–CH_2–CH_3$	770 ± 100	620 ± 150	370 ± 100	770 (assd.)
$CH_2Cl–CH_2–CH_2–CH_3$	770 ± 200	300 ± 400	220 ± 100	770 (assd.)

(1) (2) (3) (4)	A_1	A_2	A_3	A_4	
$CH_3–CH–_2CH_2–CH_3$	1·4 (std.)	2·4 ± 0·3	2·4 ± 0·3	1·4 (std.)	16
$CH_2F–CH_2–CH_2–CH_3$	1·3 ± 0·5	1·9 ± 0·8	2·6 ± 0·9	1·4 (assd.)	16
$CH_2Cl–CH_2–CH_2–CH_3$	1·2 ± 0·4	1·1 ± 0·4	2·4 ± 0·9	1·4 (assd.)	16

C. *Competitive Brominations*

Apart from the work of Anson, Fredricks and Tedder[15] on relative bromination rates at a single temperature the only competitive bromination studies are those of Fettis, Knox and Trotman-Dickenson.[32] The reason for the neglect of competitive brominations is partly that Br is a less convenient reagent than Cl and partly because it is more easy to obtain absolute rate constants for Br atom reactions than for any other halogen. This is because the thermodynamic concentration of Br atoms can more readily be set up under accessible experimental conditions than that of Cl or F[33]. However there is a definite disadvantage in carrying out a number of absolute measurements on reactions which can be studied competitively since the errors in any derived rate constant ratios are likely to be large.

Absolute rate constants and Arrhenius parameters are known for the reactions of Br with H_2,[2,6] D_2,[6] CH_4[7] and CH_3Br[7] although the accuracy is not as high as that for $Cl+H_2$. Any of these substances would have served as the standard competitor for a series of competitive brominations but methyl bromide was chosen by Fettis, Knox and Trotman-Dickenson as having the highest reactivity. The absolute rate constants for the bromination reactions could however be placed on a firmer foundation if competitive experiments were carried out to tie together the reactions of Br with H_2, D_2, CH_4 and CH_3Br.

The results of the competitive experiments are given in Table 6. The absolute values calculated from them along with all other known absolute values are given in Table 7. It is interesting to note that the activation energy found independently by direct bromination of ethane by Anderson and van Artsdalen[34] ($13{,}500 \pm 500$ cal mole^{-1}) is in excellent agreement with the value of $13{,}400 \pm 270$ determined from the competitive experiments.

D. *Competitive Iodinations*

The only iodine atom reaction of type 2 whose rate constant is known is that with hydrogen.[8] No competitive studies have been carried out and any attempt is likely to be fraught with difficulties. The activation energies of most I-atom reactions are high and high temperatures will be required to obtain reasonable rates of reaction. Furthermore all iodination reactions proceed to equilibrium which is often far on the side of $RH+I_2$. The reaction of I_2 with H_2 is largely molecular and it would be necessary in any study of the reactions of iodine with hydrocarbons to check carefully for molecular reaction.

TABLE 6. COMPETITIVE BROMINATIONS

Competitors a	b	A_b/A_a per H atom	E_b-E_a cal mole^{-1}	Ref.
CH_3Cl	CH_4	3·8 (1·9-7·6)	4400 ± 700	32(a)
C_2H_6	CH_3Cl	1·06 ± 0·16	1050 ± 200	32
C_2H_6	CH_3Br	1·36 ± 0·35	2650 ± 270	32
secC_3H_8	C_2H_6	0·51 ± 0·19	3250 ± 150	32
C_2H_6	neoC_5H_{12}	1·24 ± 0·12	890 ± 100	32
tert-isoC_4H_{10}	secC_3H_8	1·28 ± 0·44	2640 ± 200	32
tert-isoC_4H_{10}	sec-nC_4H_{10}	2·1 ± 0·4	2720 ± 100	32

(a) Fettis (Thesis, Edinburgh 1960).

The fact that iodination reactions are highly reversed may provide a means of studying the competitive abstraction of I-atoms from iodides. Recently Sullivan[35] and Benson and O'Neill[36] have independently reinterpreted the results of Ogg[37] on the HI catalysed pyrolysis of iodides and shown that they proceed essentially by reactions 4 and 5. It is possible that a competition between the reactions 5a and 5b could be studied in a system containing a trace of I_2 and a large excess of HI. Reactions 5a and 5b would then more or less inevitably be followed by reactions 4a and 4b.

$$I+R_aI = R_a+I_2 \tag{5a}$$

$$I+R_bI = R_b+I_2 \tag{5b}$$

$$R_a+HI = R_aH+I \tag{4a}$$

$$R_b+HI = R_bH+I \tag{4b}$$

The competing reaction 2 would be unimportant because it is more endothermic than 5, and 3 would be unimportant in the presence of a large excess of HI over I_2.

III. THE DETERMINATION OF ABSOLUTE RATE CONSTANTS

The major difficulty in the determination of the absolute rate constant of a reaction such as (2) is measuring the atom concentration. It is relatively easy to measure the rate of the reaction. Five general methods have been used.

(1) Halogen atoms may be generated thermally under conditions where the thermodynamic equilibrium concentrations is established between X and X_2. This method is the basis of the absolute determination of the rate constants of bromine atom reactions by Bodenstein and Lind,[2] Bach Bonhoeffer and Moelwyn-Hughes[6] and of Kistiakowsky and van Artsdalen.[7] The conditions under which the thermodynamic concentration is effectively set up have not however always been appreciated and have recently been discussed in detail by Benson and Buss.[33]

TABLE 7. ABSOLUTE ARRHENIUS PARAMETERS FOR BROMINATIONS

Standard reaction $CH_3Br + Br = HBr + CH_2Br$ $E = 15{\cdot}850 \pm 600$ cal mole^{-1}
$A = 1{\cdot}67\ (0{\cdot}8\text{-}3{\cdot}2).10^{10}$ mole^{-1} l. sec^{-1}

Compound	Competitors or method	$10^{-10} A$ mole^{-1} l. sec^{-1} per H atom	E cal mole^{-1}	Ref.
H_2	Direct thermal	14 ± 4	19,700 ± 400	*See* text
D_2	Direct thermal	10 ± 3	21,400 ± 400	*See* text
CH_4	Thermal + photochemical	1·5 ± 0·5	18,180 ± 500	7
	CH_3Cl, C_2H_6, CH_3Br	5 (2·6-10)	18,650 ± 800	32
CH_3Cl	C_2H_6, CH_3Br	1·30 ± 0·4	14,250 ± 350	32
CH_3Br	Standard	1·67	15,850	7
C_2H_6	CH_3Br	1·23 ± 0·20	13,200 ± 270	32
	Photochemical		13,500 ± 500	34
secC_3H_8	C_2H_6, CH_3Br	2·5 ± 0·7	9,950 ± 350	32
sec-nC_4H_{10}	t-isoC_4H_{10}, secC_3H_8, C_2H_6, CH_3Br	4·1(2·5-7)	10,030 ± 400	32
tert-isoC_4H_{10}	secC_3H_8, C_2H_6, CH_3Br	1·95 (1·2-3·5)	7,510 ± 400	32
neoC_5H_{12}	C_2H_6, CH_3Br	1·53 ± 0·44	14,090 ± 260	32
$CHCl_3$	Direct thermal	0·23 (0·11-0·45)	9,300 ± 600	55
CCl_3Br*	Direct thermal	7·9 (3-20)	10,310 ± 800	55

* The reaction in question is $CCl_3Br + Br = CCl_3 + Br_2$.

In the thermal method the overall activation energy of the reaction is $E_2 + \frac{1}{2}D(X_2)$ where $DX(_2)$ is the heat of dissociation of the halogen. The overall activation energies are therefore considerably higher than E_2 and the temperature range over which experiments can be carried out is more limited than if the overall activation energy were E_2. This means that the accuracy of E_2 and A_2 are likely to be rather low. Somewhat higher accuracy can be obtained by carrying out concurrent photochemical experiments where the overall activation energy will be $E_2 - \frac{1}{2}E_b$. However there is some uncertainty about the values of E_6. Although E_6 is generally assumed to be zero it is probably slightly negative. The A factor cannot however be obtained in the photochemical experiments and it is necessary to determine at least one absolute rate constant by the thermal method (*see* ref. 7).

(2) Where the chains in the photochemical halogenation are terminated entirely by removal of halogen atoms, and to a large extent by reaction 6, the rotating sector method may be applied. This method yields the mean lifetime of the reaction chains and from this the rate constants k_2 and k_6 may be determined. It is applicable at lower temperatures than the thermal method but is somewhat less accurate and is limited by the necessity of choosing reaction conditions where termination is entirely due to removal of halogen atoms. With chlorine where the thermal method is not applicable the rotating sector method has been applied successfully by Ayscough, Cocker, Dainton and Hirst[12] in the determination of k_2 for dichloroethylene.

(3) In a photochemical system where halogen atoms are generated at a precisely known rate the concentration of X can be found if k_6 is known and if 6 is the only reaction which ultimately removes halogen atoms from the system. Although the method is of general applicability it is only for iodine atoms that the rate constant of 6 is known with any precision for different third bodies.[38] It might be possible to determine some iodine atom rate constants in this way.

(4) Halogen atoms may be generated in a silent electric discharge and their concentration measured directly by a Wrede–Harteck diffusion gauge. This method was used by Rodebush and Klingelhoefer[39] to determine $k(\mathrm{Cl}+\mathrm{H_2})$.

(5) In the few cases where accurate thermodynamic data are available it may be possible to determine k_2 by measurement of k_4 making use of the calculated equilibrium constant of the reaction. Sufficiently accurate data are available only for RH = hydrogen. This method has been used by Steiner and Rideal[40,41] to determine $k(\mathrm{Cl}+\mathrm{H_2})$ and $k(\mathrm{Br}+\mathrm{H_2})$.

A. *The Rate Constant for* $\mathrm{Cl}+\mathrm{H_2} = \mathrm{HCl}+\mathrm{H}$

This reaction is one of the two chain propagating steps in the chlorination of hydrogen. It is theoretically possible to measure its rate by producing Cl atoms in thermodynamic equilibrium with $\mathrm{Cl_2}$ and then measuring the rate of reaction. However Benson and Buss[33] have shown that this is not possible in practice because of the extreme chain lengths and the difficulty that a high proportion of the hydrogen would be consumed before the equilibrium concentration of Cl could be attained. When the initiation is photochemical the difficulty is less serious and it is possible to measure a meaningful overall activation energy, but an absolute rate constant cannot then be obtained. The photochemical activation energy will be the difference between the activation energy of propagation and of termination: $E_p - E_t$ if the termination reaction is first order in the radical concentration of $E_p - \frac{1}{2}E_t$ if second order. Since E_t is likely to be close to zero the overall activation energy is approximately equal to E_p. The propagation reaction in question will be (2) only if the termination reaction involves Cl atoms exclusively. This is the case in the chlorination of hydrogen where the activation energy of (3) is lower than that of (2) and all three termination reactions are third order. However with methane reactions 7 and 8 are second order while 6 is still third order.

Furthermore reactions 2 and 3 probably have comparable activation energies. Thus with methane and all other hydrocarbons the photochemical activation energy even if it could be measured would be E_3 rather than E_2 except under extreme conditions of composition. This has been proved experimentally for the chlorination of C_2HCl_5,[10] C_2Cl_4[10] and C_2HCl_3,[43,44] $C_2H_2Cl_2$.[12]

Two determinations of the overall activation energy of the photochemical combination of hydrogen and chlorine have been made, one by Hertel[42] and the other by Potts and Rollefson.[45] Under their conditions the kinetics indicated that the termination was entirely by Cl atoms although the order of the termination reaction appeared to change with temperature. Assuming $E_t = 0$, Potts and Rollefson obtained $E_2 = 4500 \pm 1000$ cal mole^{-1} below 170°K and 5800 ± 1000 above 200°K. Hertel obtained 5800 ± 1000 cal mole^{-1} at about room temperature. It is therefore reasonably certain that E_2 lies between 5000 and 6500 cal mole^{-1}.

The presently accepted values for the Arrhenius parameters of the reaction $Cl + H_2 = HCl + H$ depend upon three sets of independent experiments carried out at widely different temperatures. Rodebush and Klingelhoefer[39] generated Cl atoms in an electrodeless discharge through Cl_2 at a total pressure of the order of 1mm Hg. The Cl atom pressure was measured directly by a Wrede–Harteck diffusion gauge. A stream of hydrogen was added to the $Cl + Cl_2$ mixture and passed at about room temperature through a 10 ml reaction vessel which terminated in a silver gauze catalyst. This brought about recombination of all unreacted Cl atoms. By measuring the HCl produced, the flow rate and the fraction of Cl_2 dissociated they were able to determine the rate constant directly. The estimated error in their value was 10 per cent but this seems a little optimistic. Their values are listed in Table 8.

TABLE 8. RATE CONSTANTS FOR $Cl + H_2 = HCl + H$

Temperature °K	k mole^{-1} l. sec^{-1} per molecule	Ref.
1071	$7{\cdot}0 \times 10^9 \pm 10\%$	40
1013	$5{\cdot}2 \times 10^9 \pm 10\%$	40
960	$4{\cdot}6 \times 10^9 \pm 10\%$	40
901	$3{\cdot}6 \times 10^9 \pm 10\%$	40
523	$4{\cdot}8 \times 10^8 \pm 8\%$	46
298	$8{\cdot}2 \times 10^6 \pm 15\%$	38
273	$3{\cdot}3 \times 10^6 \pm 15\%$	38

Steiner and Rideal[40] measured the rate of the reaction $H + HCl = H_2 + Cl$ (4) by determining the rate of the HCl catalysed conversion of *ortho* to *para* hydrogen between 900 and 1070°K. It was assumed that a thermodynamic concentration of H atoms was established. This assumption would be untenable if the generation of H atoms was by homogeneous dissociation of H_2 only, but it is almost certain that the equilibrium is quickly set up by heterogeneous processes. The equilibrium constant for the reactions 2 and 4 was calculated from thermodynamic data, and the rate constant of 2 determined from that of 4. Values recalculated using modern thermodynamic data are given in Table 8. Ashmore and Chanmugam[46] obtained the value of k_2 for hydrogen at an intermediate temperature by studying the chlorination of H_2 in the presence of Cl_2 and NOCl. Under their conditions the concentration of Cl atoms is only slightly different from the thermodynamic equilibrium concentration for the reaction

$$\mathrm{NO}+\mathrm{Cl}_2 = \mathrm{NOCl}+\mathrm{Cl}$$

This equilibrium constant is known.[47] In this system there is no question of a slow attainment of equilibrium since the activation energies of both forward and back reactions are quite low. The value of k_2 obtained by the three sets of workers fall on an exceptionally good Arrhenius plot. A least squares treatment of the results yields

$$k(\mathrm{Cl}+\mathrm{H}_2) = (8{\cdot}3\pm0{\cdot}6).10^{10}.\exp[(-5480\pm140)/RT]$$

The Arrhenius plot is shown in Fig. 1.

The value for E_2 is supported by two additional pieces of evidence. Firstly the photochemical activation energy already referred to agrees well, and secondly the activation energies for abstraction of H from isobutane and addition to Cl to tetrachloroethylene are both close to zero if we take $E_2(\mathrm{Cl}+\mathrm{H}_2) = 5480$. Since these activation energies, obtained by competitive experiments, cannot be negative the value of 5480 must be a minimum. E and A for this reaction therefore appear to be highly reliable and are probably amongst the most accurately known Arrhenius parameters for a free radical or free atom reaction.

B. *Rate Constants of other Reactions of* Cl *Atoms*

Burns and Dainton[48] obtained the rate constant k_{11} for

$$\mathrm{Cl}+\mathrm{NOCl} = \mathrm{Cl}_2+\mathrm{NO} \qquad (11)$$

by a study of the NOCl inhibited chlorination of CO. A careful study of the chlorination of CO using the rotating sector technique[31] had yielded the rate constants k_3' and k_7' and the equilibrium constant k_4'/k_2' for the reaction CO+Cl= COCl. In the chlorination of CO this equilibrium is not significantly disturbed by reaction 3′. When NOCl is added to the system the normal termination step 7′ is replaced by 11. In the photochemical reaction the rate of 11 was then equal to the rate of initiation of the reaction which was found by making careful measurements of the light absorbed. By measuring the rate of formation of $COCl_2$ and using the known rate constant k_3' and the ratio k_4'/k_2' the Cl-atom concentration was obtained and hence the rate constant of 11.

The Arrhenius equation for reaction 11 is

$$\text{Log } k_{11} = 10{\cdot}06 \pm 0{\cdot}2 - (1060 \pm 300)/4{\cdot}576T$$

The results obtained by Burns and Dainton[31] for CO provide a means of checking other absolute rate constant values derived by competition experiments which ultimately depend on comparison with hydrogen. If a hydrocarbon RH and CO are chlorinated simultaneously the following reactions will occur

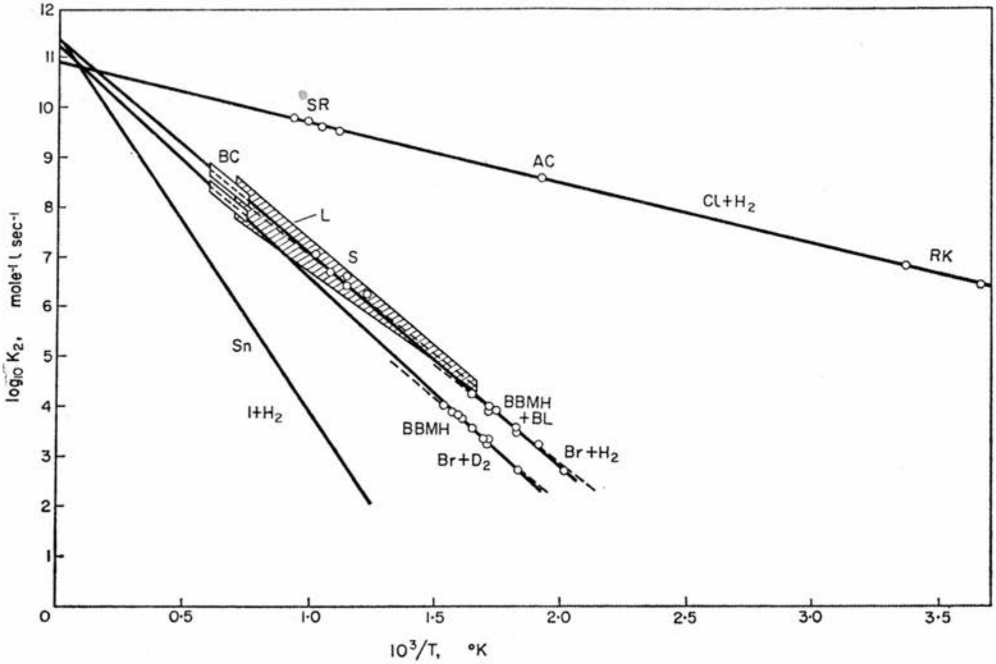

FIG. 1. Arrhenius plots for the reactions of Cl, Br and I with hydrogen and deuterium. SR = Steiner and Rideal;[40] AC = Ashmore and Chanmugam;[46,47] RK = Rodebush and Klingelhoefer;[39] BC = Britton and Cole;[51] L = Levy;[50] S = Steiner;[41] BBMH = Bach Bonhoeffer and Moelwyn-Hughes;[6] BL = Bodenstein and Lind;[2] Sn = Sullivan.[8]

$$\text{RH} + \text{Cl} = \text{R} + \text{HCl} \tag{2}$$

$$\text{R} + \text{Cl}_2 = \text{RCl} + \text{Cl} \tag{3}$$

$$\left.\begin{aligned}\text{CO} + \text{Cl} &= \text{COCl} \quad (2')\\ \text{COCl} &= \text{CO} + \text{Cl} \quad (4')\end{aligned}\right\}\text{in equilibrium}$$

$$\text{COCl} + \text{Cl}_2 = \text{COCl}_2 + \text{Cl} \tag{3'}$$

Reactions 2′ and 4′ are in equilibrium and the relative rates of formation of RCl and COCl_2 are given by

$$\frac{R_{COCl_2}/[CO]}{R_{RCl}/[RH]} = \frac{k_3'k_2'}{k_2k_4'}[Cl_2] \qquad (9)$$

All the primed rate constants or their ratios are known so k_2 can be found. An experiment of this type was performed by Rollefson[20] and has already been referred to. Rollefson completed hydrogen and deuterium against CO and although the interpretation of his results is questionable one can nevertheless derive a value for the complex rate constant in equation 9 from his results. Using Burns and Dainton's rate constant data along with the accepted value of k_2 for hydrogen we find that $k_3'k_2'/k_2k_4'$ should be about 500 l. mole^{-1} at 0°C and 100 l. mole^{-1} at 32°C. The experimental values calculated from Rollefson's data are respectively 100 and 30 l. mole^{-1}. The two sets of values are of the same order of magnitude but the discrepancy is more than can be accounted for by experimental error and suggests that the competitive experiment would be worth repeating. In the light of our present knowledge of elementary rate constants the most suitable compound to compete with CO would be methane. In the presence of 100 mm of Cl_2 these two substances should chlorinate at roughly the same fractional rate at room temperature.

Dainton and co-workers have also studied the photochlorination of ethylene,[13] vinyl chloride,[13,14] *cis*- and *trans*-dichloroethylene[11,12,14] and trichloroethylene[14,43]. This with the work of Goldfinger and co-workers on the chlorination of trichloroethylene[44] and tetrachloroethylene[10] gives a complete coverage of the chloroethylenes.

With all these substances apart from tetrachloroethylene the photochemical mechanism appears to be complicated by the fact that the initially formed adduct ACl* which contains excess energy, $E_2' + D(\text{A—Cl})$, can react in several ways (*see* section 2). Only when a catalysed *cis*- *trans*-isomerization occurs[11] can the relative rates of α, β and γ be separately determined. Thus it is only with *cis*- and *trans*-dichloroethylene in this series that it is possible to obtain k_2', the rate constant for the formation of ACl*. Generally at moderate pressures (say more than 20 mm Hg) the termination of the reaction chains is by reaction 8 and use of the rotating sector method will yield the rate constants k_3 and k_8. However at very low pressures of dichloroethylene and high pressures of chlorine chain termination becomes due predominantly to removal of Cl atoms from the system. Unfortunately removal is both by reaction 6 and by diffusion of the walls of the reaction vessel and under the conditions used by Ayscough, Cocker, Dainton and Hirst[12] about 50 per cent wall termination took place. Allowance was made for this in the application of the rotating sector technique and the following values of k_2' were obtained for *cis*-dichloroethylene

at 39·5°C $\quad k_2' = (2{\cdot}73 \pm 0{\cdot}1) \times 10^9$ l. mole^{-1} sec^{-1}

62·1°C $\quad k_2' = (3{\cdot}11 \pm 0{\cdot}1) \times 10^9$ l. mole^{-1} sec^{-1}

giving $E_2' = 1{\cdot}2 \pm 0{\cdot}7$ kcal mole^{-1} and $\text{Log}_{10}A_2' = 10{\cdot}3 \pm 0{\cdot}4$. The rate constant ratio k_β/k_γ was found to be 0·42 and 0·48 at the two temperatures. Competitive experiments were carried out with C_2H_3Cl and C_2HCl_3[14] against $C_2H_2Cl_2$ and assuming that k_β/k_γ had the same values as for dichloroethylene absolute Arrhenius parameters for the two other chloroethylenes were obtained. It was found that all three reactions had very similar rate constants and it was considered that within experimental error all could be represented by the same Arrhenius parameters $E_2' = 1{\cdot}5 \pm 1{\cdot}0$ kcal mole^{-1} Log $A_2' = 10{\cdot}3 \pm 0{\cdot}6$.

Although the Arrhenius parameters for these reactions are not known as accurately as those of the reaction of Cl with H_2 the rate constants at particular temperatures are known reasonably precisely. It would be of considerable value to carry out competitive experiments with mixtures of *cis* and *trans* dichloroethylene with propane (say) whose Arrhenius parameters are known on the hydrogen scale. This would enable the mechanism of formation of the activated ACl* radicals to be substantiated; it would provide a good way of independently checking the value for the rate constant of the reaction with hydrogen; and it would enable the Arrhenius parameters for the addition of Cl to olefins to be more accurately established.

C. *The Rare Constant of* $Br + H_2 = HBr + H$

The reaction between hydrogen and bromine has been extensively studied between 300 and 1400°K. The classic studies on the low temperature thermal and photochemical reaction, carried out by Bodenstein and Lind,[2] by Bodenstein and Lutkemeyer[49] and by Bach, Bonhoeffer and Moelwyn-Hughes[6] had a profound influence on gas reaction kinetics and led to the first accurate determination of the rate constant of a free atom reaction. Bach, Bonhoeffer and Moelwyn-Hughes (BBMH) studied the thermal bromination of both hydrogen and deuterium. They assumed that a thermal concentration of bromine atoms was established and so calculated the rate constant of reaction 2. Using modern thermodynamic data to recalculate their results and incorporating those of Bodenstein and Lind we obtain

$$\text{Log } k(\text{Br}+\text{H}_2) = 10{\cdot}67 \pm 0{\cdot}50 - (17{,}800 \pm 1400)/4{\cdot}576T$$

$$\text{Log } k(\text{Br}+\text{D}_2) = 10{\cdot}88 \pm 0{\cdot}28 - (20{,}300 \pm 800)/4{\cdot}576T$$

In the light of the competitive experiments on the reactions of Cl with hydrogen isotopes[22] the A factors here appear to be in the wrong order. Log $A(D_2)$ should be about 0·146 units below that for H_2, not 0·21 units above. Furthermore the difference in activation energies, $E(D_2) - E(H_2) = 2500$ cal mole^{-1}, is greater than the difference in the zero point energies of H_2 and D_2 (1770 cal mole^{-1}). This is theoretically impossible, and one or both of the sets of Arrhenius parameters must be in error. Bodenstein and Lutkemeyer[49] obtained values of 17,700 cal mole^{-1} for the overall activation energy of the photochemical reaction and this has often been taken as good evidence for the correctness of the value obtained by BBMH. However a re-examination of their results shows that the probable error is large. Bodenstein and Lutkemeyer's results fall into two groups. Fiften experiments were carried out at 491°K to establish the mechanism of the reaction and a further ten experiments to establish the temperature dependence. These were divided as folows 491 (15); 467 (3); 456 (4); 447 (2) and 433 (1). The agreement between the two groups is poor. A least squares treatment of all the results gives $E = 16{,}000 \pm 1200$ cal mole^{-1} but a similar treatment of only the last ten gives $E = 20{,}500 \pm 1700$ cal mole^{-1}, where the error limits are the 95 per cent confidence limits. The complete Arrhenius plot shows considerable curvature and it is clear that there must have been a systematic error in some of the results. The photochemical results thus add little to our knowledge of $E(\mathrm{Br}+\mathrm{H}_2)$.

If we assume that $A(\mathrm{H}_2)/A(\mathrm{D}_2) = 1{\cdot}40$ as predicted by theory, a series of least squares analyses can be carried out with various values of $E(\mathrm{D}_2)-E(\mathrm{H}_2)$. The best fit overall is obtained with the following Arrhenius equations.

$$\mathrm{Log}\ k(\mathrm{Br}+\mathrm{H}_2) = 10{\cdot}82 \pm 0{\cdot}22 - (18180 \pm 500)/4{\cdot}576T$$

$$\mathrm{Log}\ k(\mathrm{Br}+\mathrm{D}_2) = 10{\cdot}67_5 \pm 0{\cdot}22 - (19730 \pm 500)/4{\cdot}576T$$

$$\text{and } E(\mathrm{D}_2) - E(\mathrm{H}_2) = 1550 \text{ cal mole}^{-1}$$

These equations, plotted as broken lines on Fig. 1, fall within one standard deviation of those obtained when the results of BBMH on the two isotopes are taken separately.

Unfortunately this modification does not bring the thermal bromination results of BBMH into agreement with those obtained by other workers at higher temperatures. Steiner,[41] using essentially the same technique as Steiner and Rideal for the $\mathrm{Cl}+\mathrm{H}_2$ reaction,[40] determined the absolute rate constant for $\mathrm{Br}+\mathrm{H}_2$ between 820 and 980°K. His results shown in Fig. 1 lie considerably above those of BBMH. The results obtained by Levy[50] from flame velocity measurements are also high and although the spread is considerable (shaded area in Fig. 1) the centre of gravity of the points lies well above the BBMH line but close to that through the results of both BBMH and Steiner. Finally Britton and Cole[51] have obtained rather more accurate results at even higher temperatures (1000–1300°C) by shock tube experiments using both H_2 and D_2. The relative rate constants are in good agreement with theoretical expectation and the absolute rate constants agree well with Steiner's values at 625–800°C. We therefore believe that the true Arrhenius parameters for the reactions of Br with the hydrogen isotopes are considerably higher than those generally accepted.

If Steiner's results are taken to have the same weight as those of BBMH and if we again make the condition that the A factor ratio for hydrogen to deuterium should agree with theory we obtain the following best Arrhenius equations.

$$\text{Log } k(\text{Br}+\text{H}_2) = 11{\cdot}43\pm0{\cdot}14-(19700\pm380)/4{\cdot}576.T$$

$$\text{Log } k(\text{Br}+\text{D}_2) = 11{\cdot}29\pm0{\cdot}14-(21400\pm380)/4{\cdot}576.T$$

These lines, plotted in Fig. 1, pass exactly through the results of Britton and Cole for both H_2 and D_2.

The Arrhenius parameters now derived are considerably higher than would be likely from the individual thermal results alone, but they form a more consistent picture when considered in relation to the Arrhenius parameters of other halogen atom reactions. For Cl atoms we can place a high degree of confidence in the activation energy differences obtained by competitive experiments and it is therefore reasonable to plot $E(\text{Br}+\text{RH})$ against $E(\text{Cl}+\text{RH})$ expecting that the true values of $E(\text{Br}+\text{RH})$ would give a smooth curve. The appropriate plot, shown in Fig. 2, suggests that the higher values for $E(\text{Br}+\text{H}_2)$ and $E(\text{Br}+\text{D}_2)$ are to be preferred. We are of course assuming that the activation energies of $\text{Br}+\text{CH}_4$ and $\text{Br}+\text{CH}_3\text{Br}$ (CH_3Br being the standard substance used in the competitive bromination experiment) are correct. It is more correct to conclude from Fig. 2 that the activation energy for $\text{Br}+\text{H}_2$ is about 1500 cal mole^{-1} above that for $\text{Br}+\text{CH}_4$.

Examination of the A factors for the reactions of the three halogens with hydrogen also supports the higher values for the Arrhenius parameters of $\text{Br}+\text{H}_2$. The A factors for $\text{Cl}+\text{H}_2$ and $\text{I}+\text{H}_2$ (*see* section 3E) are

$$\text{Log } A(\text{Cl}+\text{H}_2) = 10{\cdot}92\pm0{\cdot}04, \text{ and Log } A(\text{I}+\text{H}_2) = 11{\cdot}38\pm0{\cdot}22$$

We might therefore expect Log $A(\text{Br}+\text{H}_2)$ to be intermediate between these two with a value in the range $11{\cdot}15\pm0{\cdot}25$. The value of Log $A(\text{Br}\pm\text{H}_2) = 11{\cdot}43\pm0{\cdot}14$ is slightly higher than predicted from this argument but it is in considerably better agreement than the original value of $10{\cdot}67\pm0{\cdot}50$.

D. *The Rate Constants of other Reactions of* Br *Atoms*

Kistiakowsky and van Artsdalen studied the bromination of methane and methyl bromide[7] and carried out a few experiments on the bromination of hydrogen in order to check the reliability of their reaction system. Their method was to obtain overall activation energies for the photochemical brominations by carrying out experiments at 483, 453 and 423°K and to obtain a single absolute rate constant for the reaction of Br with RH by carrying out a few thermal brominations at 570°K.

The experimental activation energy of the photochemical reaction is

$$E_{\text{photochem}} = E_2+\frac{1}{2}(E_{1a}-E_6)$$

The activation energy associated with the photochemical dissociation of bromine, E_{1a}, is determined by the change in the extinction coefficient with temperature. The change is negligible and E_{1a} = zero. The activation energy for the

C

recombination of Br atoms, E_6, will certainly be small. According to simple collision theory it should be RT, that is about 900 cal mole^{-1} at the temperatures used. However studies of iodine atom recombination in the presence of various third bodies show that the reaction probably proceeds through the formation of an intermediate charge transfer complex IM[38] and that the apparent activation energies are slightly negative. The activation energies for the recombination of bromine atoms have been much less investigated but are probably also slightly negative (1–2 kcal mole^{-1}). E_6 is thus uncertain but is probably in the range $E_6 = -1000 \pm 1000$ cal mole^{-1}. The values of E_2 deduced on the assumption that $E_6 = 0$ should be regarded as maximum values which may be up to 1000 cal mole^{-1} too large. The advantage of the photochemical method is that the overall activation energy can be determined more accurately than that of the thermal reaction because of the greater temperature range accessible to experiment. However this is offset by the uncertainty attaching to the value of E_6 and the derived value of E_2.

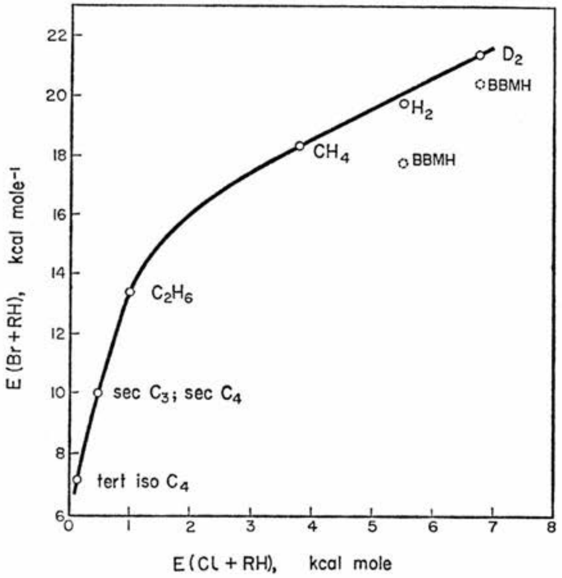

FIG. 2. Correlation of $E(\mathrm{Br+RH})$ and $E(\mathrm{Cl+RH})$ BBMH = ref. 6.

A least squares treatment of the results for methane and methyl bromide assuming $E_6 = 0$ gives

$$\mathrm{Log}\ k_2(\mathrm{Br+CH_4}) = 10{\cdot}78 \pm 0{\cdot}26 - (18180 \pm 550)/4{\cdot}576T$$

$$\mathrm{Log}\ k_2(\mathrm{Br+CH_3Br}) = 10{\cdot}70 \pm 0{\cdot}30 - (15850 \pm 600)/4{\cdot}576T$$

In order to check the reliability of these results and those of the reaction with hydrogen it is desirable that a series of competitive experiments should be carried out between hydrogen, deuterium, methane and methyl bromide.

Van Artsdalen and co-workers also studied the bromination of isobutane,[52] neopentane[53] and toluene[54] by similar methods but in spite of the care with which the experiments were conducted the results are now considered to be unreliable since it is unlikely that a stationary concentration of bromine atoms was achieved during the part of the experiment when the rate of reaction was being measured.[33] The effect of such an error would be to make the observed Arrhenius parameters high as in fact they appear to be.

Recently Sullivan and Davidson[55] carried out a careful investigation of the bromination of chloroform and the exchange reaction of radiobromine with CCl_3Br. They were thereby able to determine the rate constants of both reactions 2 and 5. The activation energy for $Br+CHCl_3$ is much lower than that for $Br+CH_3Cl$ in contrast to those for the corresponding Cl atom reactions which differ very little.[28,29]

E. *The Rate Constant of* $I+H_2 \rightleftharpoons HI+H$

Until recently the iodination of hydrogen was thought to be entirely bimolecular as suggested originally by Bodenstein.[1] However a very careful study of the reaction by Sullivan[8] in the temperature range 623–723°K revealed that 10 to 20 per cent of the reaction proceeds by an atomic mechanism similar to that operative in the bromination of hydrogen. Using a computer to obtain the best fit between the experimental data and expressions derived from the proposed mechanism, Sullivan derived the following Arrhenius equations for the reaction of iodine atoms and iodine molecules with hydrogen.

$$\text{Log } k_2(I+H_2)/T^{\frac{1}{2}} = 9{\cdot}75 \pm 0{\cdot}22 - (33{,}440 \pm 700)/4{\cdot}576T$$

$$\text{or} \quad \text{Log } k_2(I+H_2) = 11{\cdot}38 \pm 0{\cdot}22 - (34110 \pm 700)/4{\cdot}576T$$

$$\text{and Log } k_9(I_2H_2)/T^{\frac{1}{2}} = 9{\cdot}78 \pm 0{\cdot}14 - (40740 \pm 480)/4{\cdot}576T$$

$$\text{or} \quad \text{Log } k_9(I_2+H_2) = 11{\cdot}41 \pm 0{\cdot}14 - (41410 \pm 480)/4{\cdot}576T$$

The *A* factor for reaction 2 is of the expected order of magnitude being slightly greater than for $Cl+H_2$ and is about half of the collision number. The collision theory activation energy, 33,440 cal $mole^{-1}$ is within experimental error equal to the endothermicity of the reaction ($\Delta H = 32{,}960$ cal $mole^{-1}$), showing that the back reaction proceeds with a very small if not zero activation energy. An extrapolation of the Arrhenius plot for the iodine atom reaction is given in Fig. 1.

F. *The Rate Constants of* $I+RI = I_2+R$

Independently and almost simultaneously two papers, by Sullivan[35] and by Benson and O'Neill,[36] appeared in which the results of Ogg[37] on the hydrogen iodide catalysed decomposition of alkyl iodides (CH_3I, C_2H_5I and n-C_3H_7I) were reinterpreted. Ogg had suggested the reactions occurred by the following mechanism

$$HI+RI = RH+I_2 \qquad (10)$$

$$RI = R+I \qquad (12)$$

$$R+I_2 = RI+I \qquad (3)$$

$$R+HI = RH+I \qquad (4)$$

$$M+I_2 = I+I+M \qquad (1)\rightarrow \quad (6)\leftarrow$$

This mechanism is now suspect for two reasons. Firstly, in order to agree with the experimental results it had to be assumed that $k_3 = k_4$. Work by Sullvan[8] shows that for $RH = H_2$, k_4 is about a tenth of k_3. For hydrocarbons the difference is likely to be larger. Similar ratios of k_4/k_3 are obtained in bromination studies.[6,7] Secondly the values of E_{12} derived using Ogg's mechanism are some 10 kcal mole^{-1} less than the now accepted values for the heat of dissociation of RI. Sullivan and Benson both showed that the results could be more satisfactorily explained on the basis of the mechanism

$$RI = R+I \qquad (12)$$

$$I+RI = I_2+R \qquad (5)$$

$$R+HI = RH+I \qquad (4)$$

$$R+I_2 = RI+I \qquad (3)$$

$$R+RI = R'I+RH \qquad \text{(isomerization)} \qquad (13)$$

$$M+I_2 \rightleftarrows I+I+M \qquad (1)\rightarrow \qquad (6)\leftarrow$$

The experimental activation energy now agreed with that predicted from thermochemistry, and the values of $D(R-I)$ were within 1 kcal mole^{-1} of the accepted values. The Arrhenius parameters derived by Sullivan for the iodine abstraction reactions, 5, are given in Table 9.

IV. THEORETICAL INTERPRETATION OF ARRHENIUS PARAMETERS

So far little detailed work has been published on the theoretical interpretation of the Arrhenius parameters of halogen atom reactions, apart from the work of Bigeleisen, Klein, Weston and Wolfsberg[22] on the reactions of Cl with hydrogen isotopes. However it is understood at the time of writing that a detailed analysis of the available data is being carried out by Professor H. S. Johnston.

A. *The A Factors of Halogen Atom Reactions*

The *A* factors of halogen atom reactions have been considered by Pitzer,[56] Wilson and Johnston,[57] Knox and Trotman-Dickenson,[58] Knox and Nelson,[27] Fettis, Knox and Trotman-Dickenson[18,32] and by Goldfinger and Martens.[59] According to transition state theory the A factor for a bimolecular reaction is given by

$$A = \kappa(e^2kT/h).\exp[(\Delta S^*_{\text{tr}}+\Delta S^*_{\text{rot}} \quad +\Delta S^*_{\text{vib}})/R]$$

where κ is the transmission coefficient, generally assumed unity and the ΔS^*'s are the translational, rotational and vibrational entropies of activation. ΔS^*_{tr} can be evaluated with complete certainty from the molecular weights of the reactants and of the complexes. ΔS^*_{rot} can be evaluated with reasonable accuracy on the basis of models of RH and RHX. Knox and Trotman-Dickenson[58] worked out rotational entropies of activation from scale models of the hydrogen donor molecules RH and the complexes RHX, by evaluating graphically the moment of inertia products *ABC* and *A*B*C**. Goldfinger and Martens[59] assumed that the chlorinated methanes and their complexes with Cl could be approximately represented by the linear structures Y—C—H and Y—C—H—Cl. This procedure will lead to less accurate results than that used by Knox and Trotman-Dickenson and appears to give slightly high values of the rotational entropy of activation. The procedure of Knox and Trotman-Dickenson is highly accurate when the complexes have only one possible structure, for example with the chloromethanes, tertiary isobutane, etc., but when there are several structures possible as for example with X—H—$CH_2CH_2CH_2CH_3$ where free rotation is possible the calculations will be only approximate. Accuracy could be improved by evaluating the most probable configuration of the complexes using a computer.

TABLE 9. ABSOLUTE ARRHENIUS PARAMETERS OFR I ATOM REACTIONS

Reaction	Type	$10^{-10} \times A$ mole^{-1} l. sec^{-1} per molecule	*E*	Ref.
$I+H_2$	2	24	34,110 ± 700	8
$I+CH_3I$	5	20	19,800*	35, 37
$I+C_2H_5I$	5	42	16,700*	35, 37
$I+C_3H_7I$	5	11	18,000–19,300	36, 37

* Errors estimated to be about 500 cal mole^{-1}.

The evaluation of vibrational entropies of activation presents a much more difficult problem. Since there is no simple way of determining the vibration frequencies in activated complexes far reaching assumptions nearly always have to be made. Pitzer[56] evaluated reasonable frequencies for the vibrations of the

H—H—Cl complex by making use of the known *A* factor for the $Cl+H_2$ reaction and adjusting the frequencies of the symmetrical stretching and bending of the complex so as to give agreement between the calculated and experimental values of *A*. He then calculated an *A* factor for the reaction of Cl with CH_4 by assuming that the force constants for the vibrations in the CH_4Cl complex were the same as those for the HHCl complex. A simplified form of this procedure was used by Knox and Nelson[27] in calculating the vibrational entropies of activation for chlorine atom reations with hydrocarbons. This procedure was extended to fluorine and bromine atom reactions by Fettis, Knox and Trotman-Dickenson.[18,32] The assumption that only the three vibrational modes involved in the HHCl complex (stretching and doubly degenerate bending) are relevant to the R—H—X complexes is not strictly correct. When the molecule R—H is converted into R—H—X the stretching of the R—H bond becomes the reaction coordinate. The symmetrical stretching and doubly degenerate bending modes of the R—H—X bond considered by Knox and Nelson are the three new vibrational modes introduced into RH by the addition of the X atom. However in addition to these the frequency of rocking of the H atom against the radical group R will be greatly reduced by the addition of the heavy X atom and also by the fact that the bond attaching the H atom to R thereby becomes a half bond of greatly reduced strength. While the entropy of vibration of the doubly degenerate rocking mode of H against R in RH will be small that of the corresponding mode in RHX may well be large and at least comparable with that of the bending modes of R—H—X. The proper evaluation of the vibrational entropy of activation will therefore require consideration of at least five modes of vibration. Only Wilson and Johnston[57] have attempted to allow for all of them but their calculations were limited to a small number of reactions.

The assumptions made by Knox and Nelson are clearly too sweeping and the chief virtue of the calculations is that they provide a rough yardstick against which to measure deviations from a specified behaviour.

The calculated values of the various contributions to the entropies of activation for the F, Cl and Br series are given in Table 9 along with the calculated and experimental *A* factors. The experimental and calculated *A* factors are in unexpectedly good agreement and depend little upon the size or structure of the hydrocarbons, being usually close to the collision frequencies.

The good agreement depends largely upon the fact that the decrease in $\Delta S^*_{tr}+\Delta S^*_{rot}$ as RH increases in size is almost exactly compensated for by the increase in ΔS^*_{vib}. This compensation is to some extent fortuitous since the vibrational entropies of activation depend rather strongly on temperature. While the calculations were carried out for 298°K which is not far from the mean temperatures of the experiments rather different results would have been obtained had the calculations been carried out for higher temperatures. The general effect would have been to have increased the vibrational entropies of activation and hence the *A* factors for the larger RH's.

The general agreement which we have obtained suggests that more far-reaching calculations of *A* factors in which all vibrations were allowed for would be worth while.

B. *Activation Energies and Bond Strengths*

The activation energies in each halogen atom series fall regularly with the accepted order of bond strength when RH is a hydrocarbon, and one is therefore tempted to try to use the activation energies of the halogen atom series to obtain more accurate bond strength data. The only R—H bond strengths which are precisely known are those of the hydrogen isotopes. In Fig. 3 we have accordingly plotted initially the activation energies for the halogen atom reactions with hydrogen isotopes against the endothermicity of the reactions at absolute zero (ΔH_0^0). Using the high value for the activation energies of the Br atom reactions with H_2 and D_2 it is found that all the available data fall on a good straight line except that for the highly exothermic F-atom reaction. The line may be expressed by an Evans–Polanyi[60] type equation:

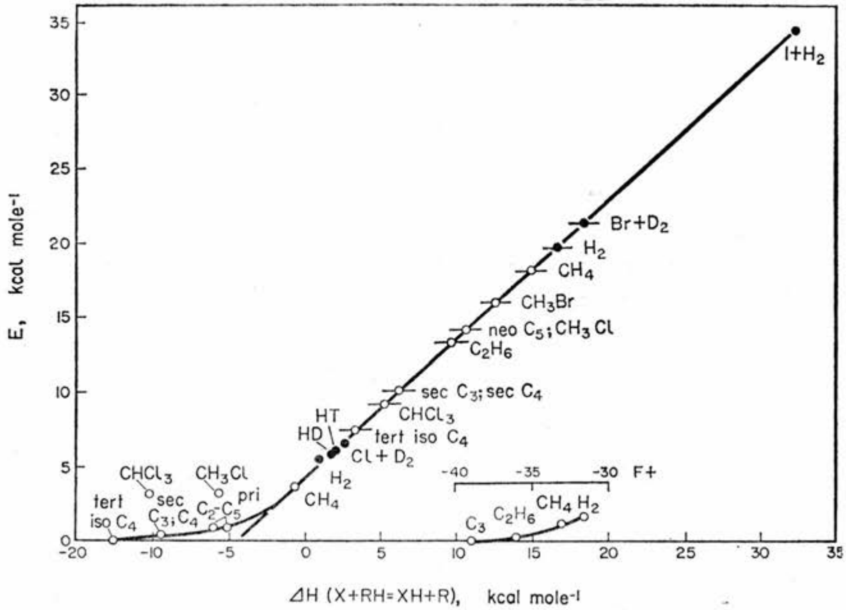

FIG. 3. Plot of $E(X+RH)$ against $\Delta H_0^0(X+RH = XH+R)$.
● points for which ΔH_0^0 is known exactly.
○ points obtained by interpolation of known activation energies.

$$E = a\Delta H_0^0 + c$$

where $a = 0{\cdot}91$ and $c = 4{,}300$ cal mole^{-1}. The gradient 0·91 is close to the gradient of the line through the two points for the brominations and the four points for the chlorination reactions. Such a gradient is about what might be expected for a series of rather endothermic free radical reactions where the activation energies of the exothermic back reactions would be expected to be low. A high α for the forward reactions and a low α for the back reactions is supported by the observations on inhibition of halogenation reactions and by the more direct work on reaction 4 by Fettis and Trotman-Dickenson.[61] One is therefore tempted to extend the relationship to the hydrocarbons and by interpolation of the known activation energies to calculate the endothermicities of the reactions and hence the R—H bond strengths in the hydrocarbons. Since hydrogen and the hydrocarbons do not form a true homologous series this procedure is open to criticism and it is not proven that a plot of the activation energies of the bromination reactions for hydrocarbons will have a gradient of 0·91 although it is unlikely that the true gradient would differ greatly from this value. With these reservations we have added the open points to the figure and derived the bond strengths given in Table 10, from the experimental *E*'s of the

TABLE 10. CALCULATED AND EXPERIMENTAL A FACTORS

Fluorine atoms RH	ΔS^*_{tr} $+28{\cdot}48$(a)	ΔS^*_{rot}	ΔS^*_{vib}	ΔS^*_{tot} $+28{\cdot}48$	10^{-10}x A_{calc} per H atom	A_{exp}	A_{exp}/A_{calc}
H_2	6·99	5·85	0·8	12·7	2·7	5·9	2·2
CH_4	2·31	5·51	5·2	13·0	1·95	3·0	1·55
C_2H_6	1·46	3·73	6·5	11·7	1·00	1·00	1·00(b)
pri C_3H_8	1·07	2·66	7·0	10·7	0·60	0·55	0·90
sec C_3H_8	1·07	2·88	7·0	10·8	0·68	0·63	0·93
pri-nC_4H_{10}	0·84	2·33	7·3	10·5	0·51	0·48	0·93
sec-nC_4H_{10}	0·84	2·33	7·1	10·3	0·48	0·59	1·20
pri-isoC_4H_{10}	0·84	2·05	7·3	10·2	0·46	0·50	1·10
tert-isoC_4H_{10}	0·84	1·99	7·5	10·3	0·48	0·70	1·42
neo C_5H_{12}	0·68	1·70	7·5	9·8	0·41	0·47	1·15
cyclo C_3H_6	1·11	3·13	6·8	11·1	0·71	0·48	0·68
cyclo C_4H_8	0·87	2·50	7·3	10·7	0·59	—	—
C_∞	0·00	0·00	8·4	8·4	0·18	—	—
Cl atoms							
	$+30{\cdot}33$(c)			$+30{\cdot}33$			
H_2	8·73	6·53	1·0	16·3	3·9	4·1	1·05
CH_4	3·48	6·48 [9·79](d)	6·4	16·4	4·0	0·6	0·15

Notes

(a) 28·48 = translational entropy of F at 1 mole l^{-1} and 298°K.

(b) Since no experimental value is available for the *A* factor of any F-atom reaction it has been assumed that the experimental and calculated values are the same for ethane.

(c) 30·33 = translational entropy of Cl at 1 mole l^{-1} and 298°K.

(d) Values thus [ ] are calculated by Goldfinger and Martens.[59]

TABLE 10. (*Cont.*)

Fluorine atoms RH	ΔS^*_{tr} $+28{\cdot}48$[a]	ΔS^*_{rot}	ΔS^*_{vib}	ΔS^*_{tot} $+28{\cdot}48$	$10^{-10}\times$ A_{calc}	per H atom A_{exp}	A_{exp}/A_{calc}
C_2H_6	2·32	4·96	8·0	15·3	2·5	1·5	0·6
pri C_3H_8	1·77	3·45	8·7	13·9	1·23	1·7	1·4
sec C_3H_8	1·77	3·70	8·7	14·2	1·41	3·6	2·6
pri-nC_4H_{10}	1·42	3·15	9·2	13·8	1·15	1·4	1·2
sec-nC_4H_{10}	1·42	2·74	9·1	13·3	0·89	2·4	2·7
pri-isoC_4H_{10}	1·42	2·77	9·2	13·4	0·96	1·3	1·35
tert-isoC_4H_{10}	1·42	2·67	9·1	13·2	0·85	2·1	2·5
neo C_5H_{12}	1·19	2·63	9·5	13·3	0·89	1·4	1·6
cyclo C_3H_6	1·83	4·05	8·6	14·5	1·66	0·9	0·55
cyclo C_4H_8	1·45	3·36	9·0	13·8	1·15	3·2	2·8
CH_3Cl	1·58	5·67	8·9	16·1	3·6	1·1	0·30
CH_2Cl_2	1·04	3·78	9·6	14·4	1·48	1·3	0·9
$CHCl_3$	0·78	2·10	10·4	13·2	0·81	0·69	0·85
		[4·40]					
C_∞	0·00	0·00	11·5	11·5	0·36	—	—
Bromine atoms							
	+32·75(e)			+32·75			
H_2	11·05	6·85	1·1	19·0	4·6	14·4	3·1
CH_4	5·34	7·06	7·2	19·5	5·9	2·0	0·34
C_2H_6	3·86	5·50	9·0	18·4	3·4	1·23	0·39
priC_3H_8	3·08	4·30	10·0	17·4	2·0	—	—
sec C_3H_8	3·08	4·90	9·0	17·0	1·65	2·5	1·5
pri-nC_4H_{10}	2·58	4·1	10·7	17·4	2·0	—	—
sec-nC_4H_{10}	2·58	4·05	10·5	17·2	1·85	4·1	2·2
pri-isoC_4H_{10}	2·58	3·7	10·7	17·0	1·65	—	—
tert-isoC_4H_{10}	2·58	3·66	10·5	16·7	1·45	1·9	1·3
neo C_5H_{12}	2·22	3·34	11·3	16·9	1·6	1·5	0·9
CH_3Cl	2·83	6·61	10·3	19·7	6·5	1·3	0·20
$CHCl_3$	1·67	3·05	11·6	16·3	1·2	0·23	0·20
CH_3Br	1·85	6·90	11·6	20·3	8·7	1·67	0·19
C_∞	0·00	0·00	13·7	13·7	2·5	—	—
Iodine atoms							
	+34·13(f)			+34·13			
H_2	12·38	7·10	1·1	20·6	5·0	12	2·4

(e) 32·75 = translational entropy of Br at 1 mole l^{-1} and 298°K.
(f) 34·13 = translational entropy of I at 1 mole l^{-1} and 298°K.

Br atom reactions. It is clear that they compare favourably with those generally accepted and are in rough agreement with those recently calculated by Pedley.[62] The bond strengths determined by electron impact methods are generally accurate to about ±2 kcal and it may well be that bromination studies can provide a more accurate method for their determination.

Using the bond strengths determined from the bromination results we have plotted the appropriate points for the chlorine atom reactions. For the hydrocarbons these fall on a smooth curve of rapidly decreasing gradient as soon as the reactions become exothermic. Although the point for methane falls well on the line through the bromination points. The points for the fluorination reactions which are extremely exothermic fall on a completely different curve. Also the points for the chlorination of the chloromethanes fall well above the line for the hydrocarbons, and it seems likely that the Polanyi relation if it holds at all is only accurate for reactions of type 2 which are endothermic. In order to examine the relationship more fully more activation energy data for iodine atom reactions is desirable and in particular values for such compounds as isobutane and propane. Another most useful series would be the exchange reactions of the type

TABLE 11. BOND STRENGTHS IN RH

Compound	Halogenation	D_0^0(R—H) kcal mole^{-1} other methods	Pedley[66] calc.
D_2		104·9 *S*	
H_2		103·2 *S*	
CH_4	101·5	102 ± 1 *EI*	101
C_2H_6	96·4	96 ± 2 *EI, P*	96
neoC_5H_{12}	97·3	(95) *HA*	
secC_3H_8, sec-nC_4H_{10}	92·8	94 ± 2 *EI, P*	90
tert-isoC_4H_{10}	89·8	89 ± 2 *EI, P*	86
CH_3Br	99·2		
CH_3Cl	97·3		
$CHCl_3$	91·8	90 ± 2 *EI*	

S = spectroscopic; *EI* = electron impact; *P* = pyrolysis.

Data on *S*, *EI* and *P* are taken from Cottrell, *Strengths of Chemical Bonds*. Second edition, Butterworths Scientific Publications, London (1958).

HA = Hormats and van Artsdalen[53] data from independent bromination work which may not be reliable.

$$X + HX^* = XH + X^*$$

which are of course all thermoneutral. Unfortunately these reactions are largely heterogeneous under the conditions where they have so far been studied.[63,64]

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GENERAL AND PHYSICAL CHEMISTRY

GAS PHASE OXIDATION

By J. H. KNOX

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3. GAS-PHASE OXIDATION

GAS-PHASE oxidation has been covered from time to time in *Annual Reports* [1] but the most recent reviews have been brief. The subject has now been comprehensively treated by Minkoff and Tipper in their book " Chemistry of Combustion Reactions " [2] which covers the literature to the end of 1961. However, a number of projects which were then at intermediate stages have since been materially advanced and merit more detailed treatment.

The highlights of recent developments, in the Reporter's opinion, are (1) the shock-tube experiments of Kistiakowsky and his co-workers on the oxidation of methane and acetylene, (2) the detailed work of Baldwin and his co-workers on the hydrogen–oxygen reaction, (3) the establishment, in considerable detail, of the mechanism of oxidation of methane and (4) the full confirmation of the thermochemistry of the HO_2 radical by Foner and Hudson. The oxidation of alkanes, olefins, and oxygenated compounds is

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[1] *Annual Reports*, 1950, **47**, 39; 1954, **51**, 83; 1955, **52**, 13; 1957, **54**, 41.

[2] G. J. Minkoff and C. F. H. Tipper, " Chemistry of Combustion Reactions," Butterworths Scientific Publns., London 1962.

now, at last, yielding to sustained pressure and there is an increasing amount of more fundamental work being carried out on the rates of elementary reactions of simple radicals such as O, OH, H, CH_3, etc. Experiments on the oxidation of alkyl radicals, produced other than by oxidising alkanes, are still in the early stages.

Shock Tubes and Flames.—Somewhat unexpectedly the chemical reactions occurring in shock waves and flames are often simpler than those occurring at lower temperatures although the techniques for studying them are more difficult. This is because the reactions are very fast; only bimolecular reactions are important and slow degenerate branching reactions do not occur.

Schott and Kinsey,[3] and Skinner and Ruherwein [4] carried out the first successful oxidations in shock tubes with hydrogen and methane, respectively. The former authors observed the ultraviolet emission of OH from the shocked gas and determined the temperature-dependence of the induction period t_i.

$$\log [O_2]t_i \text{ (mole cm.}^{-3}\text{ sec.)} = -13{\cdot}65 + 17{,}100/4{\cdot}576T.$$

Since t_i is inversely proportional to the rate constant of the branching reaction they deduced that this could only be $H + O_2 = OH + O$. This result has been confirmed by Suzuki and Fujimoto [5] although, for some unexplained reason, their induction periods are some five times greater.

Kistiakowsky and his co-workers [6] have extended the technique by using several different methods for following the oxidation of methane and acetylene in a shock tube.

Gardiner [7] has determined the induction period for the oxidation of acetylene between 1600° and 2020° K by measurement of the change in absorption of soft X-rays. His induction periods, for ignition of mixtures of 1·35% of acetylene and 2·04% of oxygen in xenon, are in precise agreement with those of Schott and Kinsey [3] for the hydrogen–oxygen reaction. Bradley and Kistiakowsky [8] have determined the mechanism of the reaction between 950° and 1090° K by use of a time-of-flight mass spectrometer attached to the shock tube. The induction periods observed agree with other determinations and these results, combined with those of Gardiner,[7] suggest very strongly that the branching reaction is again $H + O_2 = OH + O$. The observation of diacetylene in the products suggests that the other important reactions are

$$O + C_2H_2 = OH + C_2H$$
$$C_2H + C_2H_2 = C_4H_2 + H$$
$$OH + C_2H_2 = H_2O + C_2H.$$

Kistiakowsky and Richards [9] have measured the vacuum ultraviolet

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[3] G. L. Schott and J. L. Kinsey, *J. Chem. Phys.*, 1958, **29,** 1177.

[4] G. B. Skinner and R. A. Ruherwein, *J. Phys. Chem.*, 1959, **63,** 1736.

[5] M. Suzuki and S. Fujimoto, 9th Internat. Symposium on Combustion, 1962, preprints.

[6] G. B. Kistiakowsky, *Proc. Chem. Soc.*, 1962, 289. [*Centenary Lecture.*]

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emission from shocked acetylene–oxygen–argon mixtures, containing 85—99% of argon, between 1400° and 2500° K. The induction periods again agree with those of Schott and Kinsey.[3] The time constant for the acceleration of the reaction, τ, was also determined. For the branching reaction $H + O_2 = OH + O$, the rate constant and time constant are related by $[O_2] \times \tau = 1/k$. The calculated value of k agrees precisely with that determined by Fenimore and Jones [10] for $H + O_2 = OH + O$, from hydrogen-flame studies. From the ratio of t_i/τ it is deduced that the reaction increases in rate by a factor of 10^4 during the induction period.

Hand and Kistiakowsky [11] have studied the ionisation accompanying the combustion, which closely parallels the light emission. They conclude, in the light of Hand's earlier experiments [12] on the light emission from acetylene–oxygen flames, that both light emission and ionisation arise from similar sources, namely reactions of CH with O:

$$\begin{aligned} CH + O &= CHO^+ + e^- \\ CH + O &= CO^* + H \\ &= CO + H + h\nu. \end{aligned}$$

Although CH is not included in Bradley and Kistiakowsky's mechanism [8] it probably arises from $C_2H + O_2 = CH + CO_2$ or $C_2H + O = CH + CO$. Its presence in the detonation of acetylene–oxygen mixtures at 2080° K,[13] and in flash-initiated explosions,[14] is well established. The ionisation reaction is supported by Green and Sugden,[15] who find that CHO^+ is by far the most important primary ion in hydrocarbon flames.

The shock-tube oxidation of methane has been studied by Bradley and Kistiakowsky,[8] Hand and Kistiakowsky [11] and by Asaba *et al.*[16] While the different results are in good agreement, they are not as simply explained as are those from acetylene. The time constant of the acceleration is the same as that for acetylene–oxygen ignitions, but the induction periods are much longer and have a higher activation energy. Kistiakowsky *et al.*[8, 11] obtained 33 kcal., and Asaba *et al.* 53 kcal. for rich mixtures, and 20 kcal. for weak mixtures.[16] Kistiakowsky *et al.*[8, 11] conclude that the reaction in the induction period must be a straight-chain, forming a C_2 hydrocarbon. When this has accumulated the oxidation is effectively that of acetylene. The first part of this conclusion is confirmed by flame studies but the formation of a C_2 hydrocarbon does not seem necessary to account for branching by the reaction $H + O_2 = OH + O$.

Fristom and his co-workers [17] have studied the methane–oxygen flame at 1/10th and 1/20th atmosphere pressure, using mass-spectrometer probing

[10] C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, 1958, **62**, 693.

[11] C. W. Hand and G. B. Kistiakowsky, *J. Chem. Phys.*, 1962, **37**, 1239.

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for analysis. They show that all important reactions are bimolecular. The reaction is at first a straight chain, but later branches through formation of H atoms. These appear to arise from the reaction $CO + OH = CO_2 + H$, whose rate constant is well known.[18] Once H atoms are formed the reaction $H + O_2 = OH + O$ can occur. The basic correctness of this mechanism is confirmed by comparison of the calculated value of the rate constant of $CO + OH = CO_2 + H$ at 1950° K with the accepted value. Fristom has also carried out a study with a spherical flame [19] at reduced pressure and confirmed earlier findings. The more recent study indicates, in more detail, the reactions involving H, O, CH_3, and OH.

The methane–oxygen–argon flame (5·5% methane) has been studied by Levy *et al.*[20] The results agree with those of Fristom.[19] In the presence of 0 36% of hydrogen bromide the time scale of the reaction up to the complete consumption of methane is doubled, and thereafter hydrogen bromide has no effect. The authors suggest that chain branching occurs by the reaction $CH_3 + O_2 = CHO + OH + H$ and that hydrogen bromide reacts mainly with OH.[20] It seems more likely, however, that branching is due to $H + O_2 = OH + O$ and that the hydrogen bromide intercepts H atoms by $H + HBr = H_2 + Br$. The bromine atoms regenerate hydrogen bromide by reacting with methane, but as soon as the methane is exhausted the hydrogen bromide is quickly converted into Br_2, and the rate of consumption of the residual carbon monoxide is then the same as in the absence of hydrogen bromide.

Fenimore and Jones [21] have shown that the ethane and ethylene flames are similar to that of methane. Both flames commence with a zone of straight-chain reaction. The main reaction, removing ethylene, is

$$O + C_2H_4 = (C_2H_4O)^* = CH_3 + CHO.$$

This decomposition of the activated ethylene oxide molecule is confirmed by the high yield of methane (up to 20% of ethylene consumed) obtained in the presence of a large excess of hydrogen. The rate constant derived for addition of oxygen atoms to ethylene agrees well with values derived from low-temperature work.[22]

With ethane, the main attacking species are H and OH but the fate of the ethyl radical is uncertain.

The main conclusion from the flame and shock-tube studies is that hydrocarbon flames (apart from acetylene) are essentially hydrogen carbon monoxide oxygen flames fed by the decomposition products of a straight chain, oxygen-catalysed, pyrolysis of the hydrocarbons. This conclusion casts doubt on the interpretation advanced by Falconer and van Tiggeln [23]

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[18] L. I. Avramenko and R. V. Lorentso, *Zhur. fiz. Khim.*, 1950, **24,** 207; C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, 1958, **62,** 1578.

[19] R. M. Fristom, 9th Internat. Symposium on Combustion, 1962, preprints.

[20] A. Levy, J. W. Droege, J. J. Tighe, and J. F. Foster, 8th Internat. Symposium on Combustion, Williams and Wilkens, Baltimore, Md., 1962, 524.

[21] C. P. Fenimore and G. W. Jones, 9th Internat. Symposium on Combustion, 1962, preprints.

[22] (*a*) R. J. Cvetanovic, *J. Chem. Phys.*, 1960, **33,** 1063; (*b*) L. Elias and H. I. Schiff, *Canad. J. Chem.*, 1960, **38,** 1657.

[23] W. E. Falconer and A. van Tiggeln, 9th Internat. Symposium on Combustion, 1962, preprints.

for their flame speed measurements on higher hydrocarbons. They have calculated overall activation energies of 30—40 kcal. and mean molecular weights of chain carriers of 23—28, for the flames of the butanes and neopentane. The results are interpreted in terms of mechanisms similar to those proposed for low-temperature slow oxidations. The validity of the extrapolation is certainly doubtful when it is remembered that even at 500° c pyrolysis reactions are becoming dominant in hydrocarbon combustion.[24]

Hydrogen–Oxygen Reaction. Our present understanding of this reaction owes much to the work of Baldwin and his co-workers.[25, 26] It is now well established that in an aged reactor coated with boric acid, which preserves HO_2 and H_2O_2, the main elementary reactions occurring just above the second limit are

$$OH + H_2 = H_2O + H \tag{1}$$

$$H + O_2 = OH + O \tag{2}$$

$$O + H_2 = OH + H \tag{3}$$

$$H + O_2 + M = HO_2 + M \tag{4}$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \tag{10}$$

$$H_2O_2 + M' = 2OH + M' \tag{7}$$

(the numbering of equations in this section is that of Baldwin). The sequence (1), (4), (10), (7) constitutes a straight-chain, and reactions (2) and (3) are responsible for chain branching. Chain termination probably occurs by

$$H + H_2O_2 = H_2O + OH \tag{14}$$

$$OH + H_2O_2 = H_2O + HO_2 \tag{15}$$

since H_2O_2, by virtue of reaction (7), can be regarded as equivalent to two free radicals. This mechanism, with minor modifications, predicts with high precision the kinetics of the slow reaction outside the second limit. The rate of oxidation is only slightly greater than the rate of decomposition of the hydrogen peroxide present. Various rate-constant ratios can be obtained by comparison of predicted and experimental rates. For example, the ratio k_{15}/k_1 is found to be 7·1 at 500° c. A value of 6 has been obtained by Baldwin and Bratten [27] from a study of the decomposition of hydrogen peroxide, in the presence of hydrogen, in a flow system. This study has firmly established that the reaction is unimolecular in its second-order region. The rate constant, with nitrogen as activating gas, is

$$k_7 = 1{\cdot}7 \times 10^{17} \exp\ (-46{,}000/1{\cdot}987T)\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}$$

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[24] V. Ya. Shtern and N. Ya. Chernyak, *Doklady Akad. Nauk S.S.S.R.*, 1951, **78,** 91; J. W. Falconer and J. H. Knox, *Proc. Roy. Soc.*, 1959, *A*, **250,** 493.

[25] R. R. Baldwin and L. Mayor, *Trans. Faraday Soc.*, 1960, **56,** 80, 103; R. R. Baldwin, P. Doran, and L. Mayor, *ibid.*, p. 93.

[26] R. R. Baldwin, P. Doran, and L. Mayor, 8th Internat. Symposium on Combustion, Williams and Wilkins, Baltimore, Md., 1962, p. 103.

[27] R. R. Baldwin and D. Bratten, 8th Internat. Symposium on Combustion, Williams and Wilkins, Baltimore, Md., 1962, p. 110.

in full accord with all reliable previous work.[28] The study [27] also established that the reaction between H and H_2O_2 must be (14) not (14a),

$$H + H_2O_2 = H_2 + HO_2 \tag{14a}$$

since hydrogen accelerates the decomposition. If reaction (14a) occurs, hydrogen should have no effect on the rate since the sequence

$$H_2O_2 \xrightarrow{(7)} 2OH \xrightarrow[+2_2H_2O_2]{(15)} 2HO_2 \xrightarrow{(10)} H_2O_2$$

is simply replaced by

$$H_2O_2 \xrightarrow{(7)} 2OH \xrightarrow[+2H_2]{(1)} 2H \xrightarrow[+2H_2O_2]{(14a)} 2HO_2 \xrightarrow{(10)} H_2O_2$$

which is kinetically equivalent. If reaction (14) occurs we have

$$H_2O_2 \xrightarrow{(7)} 2OH \xrightarrow[+2H_2]{(1)} 2H \xrightarrow[2H_2O_2]{(14)} 2OH.$$

This is now a chain reaction. The work also establishes that reaction (6) is inadmissible since it would require

$$HO_2 + H_2O_2 = H_2O + O_2 + OH, \tag{6}$$

the decomposition of H_2O_2 in inert gases, to be a chain reaction.

The earlier work of Baldwin *et al.*[25] showed that as the second limit is approached the quadratic branching reaction (8)

$$HO_2 + H = 2OH \tag{8}$$

becomes important. The overall reaction should still be entirely homogeneous and the nature of the surface should have no effect on the explosion limit. This is not strictly true and, in newly coated vessels, the limit was somewhat raised, indicating some surface initiation at the limit.[29]

In the slow oxidation the hydrogen peroxide concentration builds up to a maximum at the maximum rate of reaction. Since the position of the second limit is generally found by the withdrawal method, there is some doubt as to whether the peroxide reaches a stationary concentration before the mixture explodes. Baldwin and Doran [29] have investigated the effect of withdrawal rate, and of arrest of the withdrawal, and find that both have a considerable effect on the limit. They conclude that at 500° c the stationary concentration of hydrogen peroxide is reached before ignition, but at lower temperatures the build-up is slow since the limit at first increases as the withdrawal rate is reduced, although further reduction lowers the limit again. The latter effect is attributed to the effect of accumulated water which, because of its high third body efficiency, increases the rate of reaction (4) to the detriment of (2). A more extensive study at 500° c has confirmed this,[30] and predicted that water should be about five times as efficient as hydrogen in reaction (4).

This explanation has been substantiated by the direct experiments of

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[28] P. A. Giguere and I. D. Liu, *Canad. J. Chem.*, 1957, **35**, 283; D. E. Hoare, J. B. Protheroe, and A. D. Walsh, *Trans. Faraday Soc.*, 1959, **55**, 548; C. K. McLane, *J. Chem. Phys.*, 1949, **17**, 379; C. N. Satterfield and T. W. Stein, *J. Phys. Chem.*, 1957, **61**, 537.

[29] R. R. Baldwin and P. Doran, *Trans. Faraday Soc.*, 1961, **57**, 1578.

[30] R. R. Baldwin, P. Doran, and L. Mayor, *Trans. Faraday Soc.*, 1962, **58**, 2410.

Baldwin and Brooks [31] on the inhibiting effect of water at the second limit in vessels coated with potassium chloride and boric acid. The efficiency relative to hydrogen is 6·4 and is unaffected by temperature or surface between 460° and 540° C. This value compares well with previous values 5·5 (Nalbandyan [32a]), 5·0 (Voevodskii and Talrose [32b]), 6·5 (Ashmore and Tyler [32c]).

The first limit has been reinvestigated by Ivanov and Nalbandyan [33] with a potassium tetraborate surface. The results confirm Baldwin's earlier conclusion [34] that the predominant termination reaction is removal of hydrogen atoms at the walls. They obtain a termination efficiency of $0{\cdot}5 \times 10^{-4}$ which compares with Baldwin's value, in a vessel freshly coated with potassium chloride, of $6{\cdot}6 \times 10^{-4}$ at 520° C.

Inhibition of the hydrogen–oxygen reaction. Baldwin and Simmons [35] carried out a careful investigation of the inhibition of the hydrogen oxygen reaction by ethane, at the first and the second limit, in a potassium chloride-coated vessel and showed that the effect was due to removal of H atoms by the reaction

$$H + C_2H_6 = H_2 + C_2H_5. \quad (16)$$

The alternative inhibition reaction with OH was unimportant, except at high oxygen mole-fractions. The work showed that the same proportion of ethyl radicals resulted in chain termination, whatever the pressure, and they therefore concluded that the final removal of ethyl was by the reactions (17) and (5).

$$C_2H_5 + O_2 = C_2H_4 + HO_2 \quad (17)$$

$$HO_2 = \text{Wall destruction} \quad (5)$$

The main features of the inhibition by ethane were the linear fall in the second limit with ethane mole fraction, i, and the inverse quadratic relation at the first limit $i = \beta - \alpha/P^2$ (where P = explosion limit pressure). The results with added methane were strikingly different.[36] The second limit was only slightly depressed until a critical concentration of methane was reached, when explosion was suppressed completely. Baldwin, Corney, and Walker [36] had to assume that some product of the reaction was responsible for the suppression of explosion. They also concluded that, at concentrations of methane just insufficient to suppress explosion, the limit was thermal, not isothermal as is usual at the second limit. A significant observation was the high rate of slow reaction when the inhibitor concentration was just sufficient to suppress ignition. It seemed most likely that the inhibition arose from formaldehyde. The course of the reaction was visualised as follows. Initially there is virtually no inhibition since the only likely reaction of CH_3 with oxygen is $CH_3 + O_2 = CH_2O + OH$, which yields

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[31] R. R. Baldwin and C. T. Brooks, *Trans. Faraday Soc.*, 1962, **58**, 1782.

[32] (*a*) A. B. Nalbandyan, *Zhur. fiz. Khim.*, 1945, **19**, 210; (*b*) V. V. Voevodski and V. L. Talrose, *ibid.*, 1948, **22**, 1192; (*c*) P. G. Ashmore and B. J. Tyler, *J. Catalysis*, 1962, **1**, 39.

[33] O. A. Ivanov and A. B. Nalbandyan, *Kinetika i Kataliz*, 1960, **1**, 337 (transl. 311).

[34] R. R. Baldwin, *Trans. Faraday Soc.*, 1956, **52**, 1344.

[35] R. R. Baldwin and R. F. Simmons, *Trans. Faraday Soc.*, 1955, **51**, 680; 1957, **53**, 955, 964.

[36] R. R. Baldwin, N. S. Corney, and R. W. Walker, *Trans. Faraday Soc.*, 1960, **56**, 802.

OH rather than HO_2. The concentration of H therefore increases exponentially. At the same time the concentration of CH_2O increases and begins to inhibit the reaction by virtue of reactions (18) and (19).

$$CH_2O + H = CHO + H_2 \tag{18}$$

$$CHO + O_2 = CO + HO_2. \tag{19}$$

The final stationary concentration of CH_2O may, or may not, be sufficient to suppress ignition completely. The experimental results suggest that the establishment of a critical concentration of formaldehyde, at which the branching coefficient is zero, is not a sufficient condition for suppression of ignition, but rather that the rate of the initial burst of reaction must be below a critical value. The final condition is thus thermal. This is supported by the strong effect of diameter on the critical inhibitor concentration and the slight effect of surface.

The more recent work of Baldwin, Booth, and Walker [37] has confirmed this view. With methane concentrations just sufficient to suppress the limit, they observe a whitish glow when the expected explosion limit is crossed during withdrawal of the mixture. The glow is often accompanied by a small pressure pulse due to self-heating. The thermal nature of the limit is finally established by the effect of inert gases.

Confirmation of the rôle of formaldehyde has been obtained by Baldwin and Cowe [38] who have studied the inhibition of the first and the second limit. The inhibition picture is similar to that of ethane. It requires the removal of CHO radicals by $CHO + O_2 = CO + HO_2$ rather than by $CHO = CO + H$ or $CHO + O_2 = CO_2 + OH$. The rate constant for reaction (18) is

$$k_{18} = 6 \times 10^{11} T^{\frac{1}{2}} \exp(-3000/1{\cdot}987T) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}.$$

The data also enable k_2 to be determined. The value when taken with those obtained by Fenimore and Jones [10] from flame studies gives

$$k_2 = 3{\cdot}3 \times 10^{14} \exp(-17{,}600/1{\cdot}987T) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}.$$

Voevodskii has used the inhibition of the hydrogen–oxygen reaction by hydrocarbons to evaluate other rate constants of hydrogen-atom reactions. The values have recently been listed.[39]

Azatyan, Voevodskii, and Nalbandyan [40] have obtained a value of k_2 by an ingenious and independent method. The first explosion limits of mixtures of carbon monoxide and oxygen, containing 0·7—8% of hydrogen, were determined. When a suitable surface such as magnesium oxide is chosen all termination reactions are diffusion-controlled and the mechanism is rather simple, comprising

$$OH + CO = CO_2 + H \tag{20}$$

$$H + O_2 = OH + O \tag{2}$$

$$O + H_2 = OH + H \tag{3}$$

$$O + \text{Wall} = \text{Destruction} \tag{21}$$

$$H + \text{Wall} = \text{Destruction} \tag{22}$$

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[37] R. R. Baldwin, D. Booth, and R. W. Walker, *Trans. Faraday Soc.*, 1962, **58**, 60.

[38] R. R. Baldwin and D. W. Cowe, *Trans. Faraday Soc.*, 1962, **58**, 1768.

[39] V. V. Voevodskii and V. N. Kondratiev, "Progress in Reaction Kinetics," ed. G. Porter, Pergamon Press, London and New York, 1961, Vol. I, p. 41.

[40] V. V. Azatyan, V. V. Voevodskii, and A. B. Nalbandyan, *Kinetika i Kataliż*, 1961, **2**, 340 (transl. 315).

and the explosion limit is given by

$$[O_2]_{\text{lim.}} = (k_{21}/2k_2)(1 + k_{22}/k_3[H_2]).$$

Since k_{21} and k_{22} can be calculated from diffusion theory, k_2 and k_3 can be determined by measurement of the explosion pressure at different small concentrations of hydrogen. The results give

$$k_2 = 1{\cdot}0 \times 10^{14} \exp\ (-15{,}900/1{\cdot}986T) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

$$k_3 = 6{\cdot}7 \times 10^{13} \exp\ (-11{,}700/1{\cdot}986T) \quad ,, \quad ,, \quad ,,$$

The absolute value of k_2 calculated at 1400° K is half the value obtained by Fenimore and Jones [10] and the value at 800° K is identical with that of Baldwin and Cowe.[38] The enthalpy change in reaction (2) is +16 kcal. and therefore the back reaction probably has zero activation energy.

Oxidation of Carbon Monoxide.—Little advance has been made in this field in the last year or two. Cusin and James have studied the inhibition of the oxidation by cyanogen (C_2N_2) [41] and by ethane.[42] The two systems show similar features. At about 900° C, the ignition of either cyanogen alone or cyanogen–carbon monoxide mixtures takes place only when all the cyanogen has been converted into carbon monoxide. The mechanism of inhibition is probably

$$O + C_2N_2 = CNO + CN$$

in competition with the branching reactions

$$O + CO = CO_2^*$$
$$CO_2^* + O_2 = CO_2 + 2O.$$

The kinetics of the inhibition suggest that the initiation of the oxidation is a first-order activation process rather than the bimolecular reaction $CO + O_2 = CO_2 + O$. At lower temperatures (600—700° C) and low concentrations the inhibitor seems to act by adsorption on sites which can normally initiate the oxidation. At higher pressures it also acted homogeneously, as at high temperatures.

Kondratiev and Ptichkin [43] have studied the oxidation of carbon monoxide by ozone between 25° and 160° C. The reaction is chemiluminescent and the authors propose that the initiation is by decomposition of ozone to give oxygen atoms. They deduce from their results, and assumed mechanism, that $E(O + CO) - E(O + O_3) = 3{\cdot}8$ kcal.

The Slow Oxidation of Formaldehyde and Methane.—The slow oxidation of formaldehyde and methane has received renewed attention from Russian workers.

Formaldehyde. Markevich and Filippova [44] have used Kovalski's differential calorimetric method [45] to show the profound effect of surface on the

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[41] F. Cusin and H. James, *J. Chim. phys.*, 1961, **58**, 162, 730.

[42] F. Cusin and H. James, *J. Chim. phys.*, 1962, **59**, 454.

[43] V. N. Kondratiev and I. I. Ptichkin, *Kinetika i Kataliz*, 1961, **2**, 492 (transl. 449).

[44] A. M. Markevich and L. F. Filippova, *Zhur. fiz. Khim.*, 1959, **33**, 2214 (transl. 358).

[45] A. A. Kovalski and M. L. Bogoyavlenskaya, *Zhur. fiz. Khim.*, 1946, **20**, 1325; see Semenov " Some Problems in Chemical Kinetics " (Transl. Bradley), Pergamon Press, London and New York, 1959, Vol. I, 187.

oxidation and have thereby confirmed previous work carried out in static [46] and flow systems,[47] and partly explained the irreproducibility of much of the earlier work.[48]

With Pyrex reaction vessels coated with potassium tetraborate about 70% of the heat of the reaction is liberated close to the walls of the reaction vessel, yet throughout the reaction the temperature rise at the centre gives an accurate measure of the rate of reaction so that there was no change in the percentage heterogeneity. (See also Vanpee.[48]) In this reaction vessel, the only detectable products are carbon monoxide, dioxide, and water, and the rate of reaction is given accurately by Rate $= k[CH_2O]^2[O_2]^0$. These results combined with those obtained in a flow system [47] give $\log_{10} k = 19{\cdot}1 - 50{,}000/4{\cdot}58T$ (k in mole^{-1} cm.^{3} sec.$^{-1}$) between 380° and 550° c.

With a clean surface the reaction is faster, and in clean silica peroxidic products can be isolated. They appear to arise from hydrogen peroxide initially formed by the reactions

$$CH_2O + HO_2 = CHO + H_2O_2$$
$$CHO + O_2 = CO + HO_2.$$

In the borate surface any hydrogen peroxide would be rapidly destroyed.[49]

Markevich and Filippova [44] find marked activation-energy differences between the borate-coated surface (50 kcal.) and the clean silica surface (26 kcal.). This observation may have some bearing on the activation energy changes observed by Harding and Norrish [50] in the oxidations of formaldehyde and of ethylene (where formaldehyde is probably the branching intermediate) from 21 (26) kcal. at 350° c to 39 (42) kcal. at 460° c and (53) kcal. at 550° c (values in parentheses are for ethylene).

The isolation of considerable amounts of hydrogen peroxide from the oxidations of both formaldehyde and methane raises the question of its role as a possible branching agent in these oxidations. The definitive work of Baldwin and Bratten [27] gives the following lifetimes for hydrogen peroxide in an inert-gas concentration (assumed nitrogen) of 10^{-5} mole cm.$^{-3}$ (*i.e.*, about 0·5 atm. at 340° c).

Temp. (°c)	360	380	400	420	440	460	480	500	520
Lifetime (sec.)	5600	1850	650	230	90	37	16	7·2	3·4

Markevich and Pecherskaya [51] have found that, in a molybdenum-glass

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[46] M. D. Scheer, 5th Internat. Symposium on Combustion, Williams and Wilkins, Baltimore, Md., 1955, 435.

[47] A. A. Anisonyan, S. Ya. Beider, A. M. Markevich, and A. B. Nalbandyan, *Zhur. fiz. Khim.*, 1959, **33**, 1695 (transl. 115).

[48] R. Fort and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1930, *A*, **129**, 284; R. Spence, *J.*, 1936, 649; F. F. Snowdon and D. W. G. Style, *Trans. Faraday Soc.*, 1939, **35**, 426; D. W. E. Axford and R. G. W. Norrish, *Proc. Roy. Soc.*, 1948, *A*, **192**, 518; M. Vanpee, *Bull. Soc. chim. belges*, 1953, **62**, 285; A. M. Markevich and L. F. Filippova, *Zhur. fiz. Khim.*, 1957, **31**, 2649.

[49] D. E. Cheaney, D. A. Davies, A. Davis, D. E. Hoare, J. Protheroe, and A. D. Walsh, 7th Internat. Symposium on Combustion, Butterworths Scientific Publns., London 1959, 183.

[50] A. J. Harding and R. G. W. Norrish, *Nature*, 1949, **163**, 797.

[51] A. M. Markevich and Yu. I. Pecherskaya, *Zhur. fiz. Khim.*, 1961, **35**, 1418 (transl. 697).

reaction vessel, the oxidation at 330°, 390°, and 420° C commences with no pressure change although formaldehyde is consumed, probably by the overall reaction $CH_2O + O_2 = CO + H_2O_2$, and that the reaction is slightly autocatalytic, as previously observed by Vanpee.[48] The addition of up to 10 mm. of hydrogen peroxide to 15 mm. of formaldehyde + 300 mm. of air at 420° C has no lasting catalytic effect, although it removes the slight initial autocatalysis. The results of Baldwin and Bratten [27] show that the pyrolysis of 10 mm. of hydrogen peroxide at 420° C should generate hydroxyl radicals at a rate of 5 mm. $min.^{-1}$. The observed initial rate, in the absence of added peroxide, is 4 mm. $min.^{-1}$ and with 10 mm. of peroxide 12 mm. $min.^{-1}$. Either the chains are exceedingly short or the decomposition of the peroxide is somehow short-circuited and does not give hydroxyl radicals. This problem is general throughout hydrocarbon oxidation where substantial yields of hydrogen peroxide are obtained, but where it has very little catalytic effect. A possible explanation is that activation of the peroxide is short-circuited by the collision of a partially activated molecule with formaldehyde, and the occurrence of the reaction

$$HO{\cdot}OH^* + CH_2O = 2H_2O + CO.$$

In other words, we are dealing with a non-Maxwellian distribution of energy among the peroxide molecules, particularly in the region of 40 kcal. and above. The above reaction is sterically plausible and highly exothermic, and there is some evidence for it in the oxidation of methane.

Methane. An important series of papers on the oxidation of methane has appeared under the names of Karmilova, Enikolopyan, Nalbandyan and Semenov.

The reaction was studied in a static system in a 200 ml. silica reaction vessel washed with hydrofluoric acid, and aged for 12 months. The surface was believed to be one of silicic acid and therefore of type (i) in Walsh's nomenclature.[49] The reaction was studied at 423°,[52a] 472°, 491°, and 513° C.[52b] The reaction is initially autocatalytic and at a small percentage conversion reaches a maximum rate which is maintained, in spite of consumption of the reactants, until nearly the end of the reaction. The major products are carbon monoxide, dioxide, and water, with traces of hydrogen and methanol. Formaldehyde and hydrogen peroxide are intermediate products formed in small yield. The stoicheiometry of the reaction up to the maximum rate is accurately represented by

$$CH_4 + \tfrac{3}{2}O_2 = CO + 2H_2O.$$

Later, carbon monoxide is oxidised to dioxide and the yield of the former sometimes passes through a maximum. The overall activation energy of the reaction is 41·5 kcal. for the stoicheiometric mixture. This agrees with Egerton, Minkoff, and Salooja's value [53] for the same mixture but the latter also obtained lower values (23—41 kcal.) for richer mixtures. Karmilova, Enikolopyan, and Nalbandyan [52] tacitly assume that the activation

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[52] L. V. Karmilova, N. S. Enikolopyan, and A. B. Nalbandyan, (*a*) *Zhur. fiz. Khim.*, 1957, **31,** 851; (*b*) *ibid.*, 1960, **34,** 550 (transl. 261).

[53] Sir A. C. Egerton, G. J. Minkoff, and K. C. Salooja, *Proc. Roy. Soc.*, 1956, *A*, **235,** 158.

energy is independent of the methane : oxygen ratio. The overall order of the reaction is 2·7 and the partial orders 1·62 for methane, 0·96 for oxygen, and 0·10 for total pressure. The low exponent of total pressure contrasts with the value of unity obtained by Norrish and Foord.[54] However, they used a soda-glass reaction vessel [type (ii) or (iii) surface] and their rates were about 20 times smaller. Diffusion-controlled termination might therefore have occurred in their experiments.

Karmilova *et al.*,[55] investigating the rôle of formaldehyde, have shown that it appears somewhat before hydrogen peroxide although both reach maximum pressures at the maximum rate of reaction. From Markevich's results [44] on formaldehyde they conclude that the peroxide arises from the oxidation of formaldehyde and is not the degenerate branching intermediate, as had been suggested by Egerton, Minkoff, and Salooja.[53] The maximum formaldehyde concentration rises, with an activation energy of 7·8 kcal., while that of hydrogen peroxide falls; it increases linearly with methane pressure and is independent of oxygen pressure, above 50 mm. The induction period of the reaction falls, with an activation energy of 36 kcal.

These observations are quantitatively explained by the mechanism advanced by Karmilova, Enikolopyan, Nalbandyan, and Semenov: [56]

$$CH_4 + O_2 = HO_2 + CH_3 \tag{0}$$

$$CH_3 + O_2 = CH_2O + OH \tag{1}$$

$$OH + CH_4 = CH_3 + H_2O \tag{2}$$

$$OH + CH_2O = CHO + H_2O \tag{2'}$$

$$CH_2O + O_2 = CHO + HO_2 \tag{3}$$

$$CHO + O_2 = CO + HO_2 \tag{4}$$

$$HO_2 + CH_4 = CH_3 + H_2O_2 \tag{5}$$

$$HO_2 + CH_2O = CHO + H_2O_2 \tag{5'}$$

$$OH = \text{Wall termination} \tag{6}$$

Denoting the rate of the i'th reaction by r_i it was not difficult to show that, at maximum rate when the chains are long, $r_2 = r_{5'}$; $r_{2'} = r_5$; and $r_1 = r_2 + r_{2'} = r_5 + r_{5'}$. Hence the maximum formaldehyde concentration is given by $F_{\text{max.}} = (k_2k_4/k_{2'}k_{5'})^{1/2}\,[CH_4]$. The observed activation energy for $F_{\text{max.}}$ is then $E_F = \frac{1}{2}(E_2 + E_5 - E_{2'} - E_{5'})$. Since both the reactions of OH are exothermic, and that of HO_2 with methane is endothermic, E_2 and $E_{2'}$ are likely to be small while $E_5 - E_{5'}$ should be somewhat less than the difference in bond strength between methane and formaldehyde (about 25 kcal.). The experimental value of $E_F = 7{\cdot}8$ kcal. is obviously reasonable. The mechanism also predicts that the reaction should be of second order in methane and first order in oxygen, in reasonable agreement with experiment. The acceleration constant is $(k_2k_3/k_6)[CH_4][O_2]$. If the reaction accelerates exponentially during the induction period, t_i, the temperature dependence of $1/t_i$ should be the same as that of ϕ.

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[54] R. G. W. Norrish and S. G. Foord, *Proc. Roy. Soc.*, 1936, *A*, **157**, 503.

[55] L. V. Karmilova, N. S. Enikolopyan, and A. B. Nalbandyan, *Zhur. fiz. Khim.*, 1960, **34**, 990 (transl. 470).

[56] L. V. Karmilova, N. S. Enikolopyan, A. B. Nalbandyan, and N. N. Semenov, *Zhur. fiz. Khim.*, 1960, **34**, 1176 (transl. 562).

The experimental activation energy of the induction period was 36 kcal. and this agrees well with that predicted from the mechanism, since $E_\phi = E_{\text{max. rate}} - E_{\text{F}} = 33$ kcal. Furthermore, E_ϕ should be somewhat greater than E_3, which is expected to be about 30 kcal. The mechanism gives a very good account of the kinetics of the reaction up to the point of maximum rate and vindicates Norrish's original postulate [57] that formaldehyde is the branching intermediate. Features of the reaction which are not considered are (1) the role of hydrogen peroxide as a possible branching agent, (2) the maintenance of the maximum rate of reaction in spite of consumption of reactants, and (3) the formation of carbon dioxide.

In a fourth paper [58] the effect of added hydrogen peroxide is examined. Even in amounts several times in excess of those normally present at maximum rate, the induction period is only slightly reduced and the maximum rate unaltered. This has been confirmed by Mari *et al.*[59] It is, however, interesting that at 472° C, when 1·5 mm. of peroxide is added to 235 mm. of a stoicheiometric mixture, the yield of formaldehyde initially rises rapidly. Thereafter it rises more slowly to the same maximum as is obtained in the absence of peroxide. Meanwhile, the peroxide concentration falls gradually but is always greater than that normally present at maximum rate. It appears then, that hydrogen peroxide can act as an initiator in the earliest stages but not once any quantity of formaldehyde has appeared.

The constancy of the rate of oxidation, in spite of considerable consumption of the reactants, has been noted both by Karmilova *et al.*[52b] and by Mari *et al.*,[60] but their explanations are radically different. The former [61] suggest that a new chain-branching system appears in the later stages of the reaction which just compensates for the expected decline in rate as methane and oxygen are consumed. The system involves the formation of hydrogen atoms which can cause branching by reaction (9).

$$CO + OH = CO_2 + H \tag{7}$$

$$H_2 + OH = H_2O + H \tag{8}$$

$$H + O_2 = OH + O \tag{9}$$

$$H + RH = H_2 + R \tag{10}$$

This scheme also accounts for the formation of carbon dioxide. Application of the kinetic tracer method [62] has confirmed the general correctness of this idea by showing that all the carbon dioxide produced in the later stages arises from carbon monoxide. Additional confirmation comes from the calculation of the relative rates of removal of carbon monoxide and methane by using the known rate constant data for the reactions of OH.[18]

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[57] R. G. W. Norrish, *Proc. Roy. Soc.*, 1935, *A*, **150**, 36.

[58] L. V. Karmilova, N. S. Enikolopyan, and A. B. Nalbandyan, *Zhur. fiz. Khim.*, 1961, **35**, 1043 (transl. 512).

[59] R. Mari, M. Letort, M. Dzierzynski, and M. Niclause, *J. Chim. phys.*, 1962, **59**, 596.

[60] R. Mari, M. Letort, and M. Niclause, *J. Chim. phys.*, 1962, **59**, 324.

[61] L. V. Karmilova, N. S. Enikolopyan, A. B. Nalbandyan, and V. T. Il'in, *Zhur. fiz. Khim.*, 1961, **35**, 1435 (transl. 706).

[62] L. V. Karmilova, N. S. Enikolopyan, and A. B. Nalbandyan, *Zhur. fiz. Khim.*, 1961, **35**, 1458 (transl. 717).

Mari, Letort, and Niclause,[60] on the other hand, consider that the high rate of reaction is maintained because of modification of the surface of the reaction vessel. Mari *et al.*[63] have shown that it is necessary to add some eight times the quantity of formaldehyde normally present at maximum rate, in order to make the reaction start at this rate. But the pressure–time curves are then of an unexpected shape, starting at a high rate which then declines and finally increases again. This is thought to be due to acclimatisation of the reaction-vessel surface during the reaction, and pretreatment of the Pyrex reaction vessel with water vapour for several hours certainly accelerates the subsequent reaction. Although the theory of Karmilova *et al.* is the more attractive, some account should certainly be taken of surface modification during the course of a reaction.

The theory of Karmilova *et al.* supposes that all methyl peroxy radicals decompose to formaldehyde and hydroxyl. Fisher and Tipper [64] have shown that this may not be so. In an aged silica reaction vessel at 400° C measurable yields of methyl hydroperoxide are formed in the acetone-photosensitised oxidation of methane and, subsequently, in the oxidation of methane alone. Pyrolysis of methyl hydroperoxide at 345° C gives formaldehyde and methanol as the major products, probably mainly by heterogeneous decomposition. The methanol which Karmilova *et al.* report may have come from this source. The lifetime of the peroxide is about 30 sec. and its stability, as regards homogeneous decomposition, must be considerably greater than that of the higher alkyl hydroperoxides.[65] It is probable that CH_3O_2 abstracts hydrogen from formaldehyde rather than from methane.

The oxidation of methane by traces of oxygen has been studied at 950—1050° C by Germain and Sueur,[66] in a flow system. The reaction is autocatalytic and the maximum rate is held until all the oxygen (initially 0—5%) is consumed. The main products are H_2, H_2O, CO, CO_2, C_2H_4, and C_2H_6. The carbon dioxide probably arises by reaction (7), molecular hydrogen from H atoms, ethane from unoxidised methyl, and ethylene from ethane. The mechanism is thus similar to that at lower temperatures.

The high-temperature oxidation of methane has also been investigated by Cabannes and his co-workers [67] who passed a mixture of methane and oxygen over a platinum plate heated to between 600° and 1300° C. From the profile of gas velocity, temperature, and composition, determined by suitable probes, the degree of heterogeneity can be calculated. On clean platinum the reaction is 20% heterogeneous and on platinum coated with alumina it is entirely homogeneous.

Enikolopyan and Bel'gorskii [68] have compared the oxidation of methane and methanol in glass reactors, coated with potassium tetraborate and

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[63] R. Mari, M. Letort, M. Dzierzynski, and M. Niclause, *J. Chim. phys.*, 1962, **59**, 589; *Compt. rend.*, 1961, **252**, 3241.

[64] I. P. Fisher and C. F. H. Tipper, *Nature*, 1962, **195**, 489.

[65] A. D. Kirk and J. H. Knox, *Trans. Faraday Soc.*, 1960, **56**, 1296.

[66] J. E. Germain and R. Sueur, *Bull. Soc. chim. France*, 1961, 1008.

[67] F. Cabannes and Y. Fukuchi-Thibaut, *Bull. Soc. chim. France*, 1961, 947; F. Cabannes and P. Valentin, *ibid.*, 1962, 166.

[68] N. S. Enikolopyan and I. M. Bel'gorskii, *Zhur. fiz. Khim*, 1960, **34**, 1571 (transl. 749).

silver, using differential calorimetry. On the former surface both reactions are homogeneous and autocatalytic, and depend upon formaldehyde as the branching agent. On silver both are heterogeneous and, while the oxidation of methane produces no formaldehyde, that of methanol produces more formaldehyde than the homogeneous oxidation. Thus the effect of silver must be to destroy free radicals, rather than formaldehyde.

Barber and Cuthbert [69] have reported some preliminary work on the oxidation of methane in an electric discharge (200 w, 13,560 kc. sec.$^{-1}$), analysing the products by mass spectrometry. With the discharge through the methane the products are the same as without oxygen (ethane, hydrogen, traces of acetylene). With the discharge through the oxygen the major product is ethane, with smaller amounts of methane and carbon dioxide.

Enikolopyan and Konereva [70] have studied the oxidation of methane, catalysed by nitromethane, with the object of establishing whether nitromethane or nitrogen dioxide is the true catalyst. The results are inconclusive. The fall in the nitromethane concentration is slower in oxidising-methane than in the absence of oxygen, and kinetic-tracer experiments by Miller *et al.*[71] show that the nitromethane is not only destroyed in the reaction, but formed from CH_3 and NO_2. A striking feature is the sudden fall in the concentration of nitromethane at a certain stage in the reaction, coinciding with a peak in the heat evolution. This sudden burst of activity seems to be due to a partial ignition of the accumulated carbon monoxide. The ignition apparently produces a flood of radicals but is quickly inhibited and cannot be detected by any change in the CO concentration.

Alkanes.—The present state of knowledge of the oxidation of alkanes has been reviewed in a non-specialist article by Cullis.[72]

The lower alkanes. The most significant recent work is that of Zeelenberg *et al.* who have followed the oxidation of isobutane [73] and neopentane [74] in a static system, from the early stages of the induction period, by gas chromatography. Gas chromatography is now regarded as the most satisfactory tool for studying complex oxidations.[75] Sandler and Beech,[76] for example, determined some 30 products from the oxidation of n-pentane, and Wright [77] some 38 products from the oxidation of *o*-xylene. Zeelenberg's work on isobutane shows that all the initial products of the reaction increase exponentially with time. Isobutene is the major initial product (about 85% of isobutane oxidised) at about 300° c. Other initial products are

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[69] M. Barber and J. Cuthbert, *Nature*, 1961, **190**, 1001.

[70] N. S. Enikolopyan and G. P. Konereva, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1100; 1960, 419; 1961, 230 (transl. 210).

[71] V. B. Miller, P. L. Levin, G. P. Konereva, M. B. Neiman, and N. S. Enikolopyan, *Zhur. fiz. Khim.*, 1960, **34**, 1980 (transl. 940).

[72] C. F. Cullis, *Chem. and Ind.*, 1962, 23.

[73] A. P. Zeelenberg and A. F. Bickel, *J.*, 1961, 4014.

[74] A. P. Zeelenberg, *Rec. Trav. chim.*, 1962, **81**, 720.

[75] J. W. Falconer and J. H. Knox, *Proc. Roy. Soc.*, 1959, *A*, **250**, 493; R. E. Ferguson and C. R. Yokeley, 7th Internat. Symposium on Combustion, Butterworths Scientific Publns., London 1959, p. 113; G. Kyryacos, H. R. Menapace, and C. E. Boord, *Analyt. Chem.*, 1959, **31**, 222; C. F. Cullis, A. Fish, F. R. F. Hardy, and E. A. Warwicker, *Chem. and Ind.*, 1961, 1158.

[76] S. Sandler and J. A. Beech, *Canad. J. Chem.*, 1960, **38**, 1455.

[77] F. J. Wright, *J. Phys. Chem.*, 1962, **66**, 2023.

isobutene oxide (10%) and propionaldehyde (6%), with traces of acetone and propene. All can be derived from the decomposition of the two possible peroxy-radicals. The isobutene is probably formed by an HO_2 radical chain, which has been suggested for other hydrocarbons.[78]

With neopentane the HO_2 radical chain cannot operate, since there is no olefin with the neopentane carbon skeleton. The initial products at 260—290° C are isobutyraldehyde (85%), acetone (10%), and traces of pivalaldehyde, dimethyloxetan, epoxyisobutane, and neopentyl alcohol. Isobutene is the major hydrocarbon produced and becomes the major product when the isobutyraldehyde is being consumed during the later stages of the reaction. The main path of oxidation appears to be

$$\begin{aligned}(CH_3)_3C{\cdot}CH_3 + X &= (CH_3)_3C{\cdot}CH_2 + XH\\ (CH_3)_3C{\cdot}CH_2 + O_2 &= (CH_3)_3C{\cdot}CH_2{\cdot}O_2\\ &= (CH_3)_2CH{\cdot}CHO + CH_3O.\end{aligned}$$

Seakins [79] has reinvestigated the oxidation of propane, paying particular attention to the yields of peroxides and aldehydes. He has confirmed the existence of the negative temperature coefficient between 320° and 390° C and showed that coating the Pyrex reaction vessel with potassium chloride, while reducing the overall rate of reaction, does not affect the ratio of reaction rate to peroxide concentration. He deduces that the surface destroys the branching agent but does not affect the primary chain length, the peroxide being identified as the branching agent. Unfortunately the peroxide was not characterised. Since it is likely to be mainly hydrogen peroxide, which is inactive as a catalyst, the interpretation is doubtful.

A major problem in hydrocarbon oxidation is the source of methanol, which is often an important product. It is generally supposed to arise from the reaction

$$CH_3O + RH = CH_3{\cdot}OH + R$$

but Hanst and Calvert [80] have shown that methoxy-radicals, derived from the pyrolysis of dimethyl peroxide at 110—150° C, can be readily oxidised to formaldehyde, presumably by the reaction

$$CH_3O + O_2 = CH_2O + HO_2$$

which is 20 kcal. exothermic.

Neiman, Efremov, and Serdyuk [81] have gone some way to solving the problem by application of the kinetic-tracer method. By adding $^{14}CH_3{\cdot}CHO$ and $^{14}CH_3{\cdot}N{=}N{\cdot}CH_3$ to a propene–oxygen mixture at 315° C they have shown that ~75% of the methanol recovered arises from acetaldehyde, a primary product of the oxidation of propene, and that 75% of the acetaldehyde gives methanol. The experiments with azomethane establish that at least some of the methanol can come from methyl radicals, which also give formaldehyde and methane.

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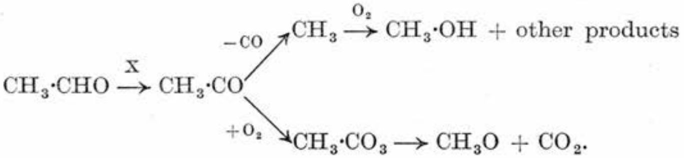
[78] (*a*) J. H. Knox, *Trans. Faraday Soc.*, 1960, **56,** 1225; (*b*) see ref. 24.

[79] M. Seakins, *Proc. Roy. Soc.*, 1961, *A*, **261,** 281.

[80] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, 1959, **63,** 104.

[81] M. B. Neiman, V. Y. Efremov, and N. K. Serdyuk, *Kinetika i Kataliz*, 1960, **1,** 345 (transl. 319).

Neiman *et al.*[81] postulate the following scheme



$$CH_3{\cdot}CHO \xrightarrow{X} CH_3{\cdot}CO \xrightarrow{-CO} CH_3 \xrightarrow{O_2} CH_3{\cdot}OH + \text{other products}$$

$$CH_3{\cdot}CO \xrightarrow{+O_2} CH_3{\cdot}CO_3 \rightarrow CH_3O + CO_2.$$

If all the methoxy-radicals form methanol the yield of methanol derived from acetylperoxy-radicals should equal the yield of carbon dioxide derived from the acetaldehyde. Tracer experiments with $CH_3{\cdot}{}^{14}CHO$ show, on this assumption, that 50% of the methyl groups in the acetaldehyde form methanol, *via* the acetylperoxy-radical, and the other 25% *via* methyl. Neiman *et al.* suggest that the methyl radicals give rise to methanol by way of $CH_3 + O_2 = CH_3O_2$ and $CH_3O_2 + RH = CH_3{\cdot}OH + RO$. The second reaction is implausible and the suggestion that methanol arises from the heterogeneous decomposition of methyl hydroperoxide [64] seems more reasonable. Neiman *et al.* also demonstrate the increasing ease of hydrogen abstraction, relative to oxidation, as the reaction proceeds. This is a general feature of oxidation, due to the formation of substances with weaker C–H bonds as oxidations proceed.

The results establish the molecular precursor of methanol in any system where acetaldehyde is formed, but they do not necessarily establish the free-radical precursor as methoxyl. Nor do they explain the formation of methanol in the oxidation of ethane and ethylene, where acetaldehyde was a minor product of the reaction.[82]

The importance of the surface in hydrocarbon oxidation has been re-emphasised by Satterfield and Reid,[83] who have correlated the effectiveness of surfaces in destroying hydrogen peroxide with the yields of other products. Thus aldehyde yields are low on surfaces which destroy peroxides, while ethylene yields are high under the same conditions. It has also been shown [84] that pretreatment of a reaction vessel with hydrogen fluoride accelerates the oxygen-induced pyrolysis of propane at 600° C, as does conditioning the reaction vessel by carrying out several runs with added nitric oxide.

Higher hydrocarbons. The oxidation of heptane has been studied by Ohlman *et al.*[85] at 200—250° C. The reaction is autocatalytic, starting with a pressure decrease, presumably due to the formation of a peroxide. The initial rate of pressure decrease is proportional to the hydrocarbon pressure. No pressure decrease is observed by Kende and Gal [86] in their work on the oxidation of n-hexane, inhibited by styrene, at about 230° C. This is probably because they used a reaction vessel coated with potassium chloride. The acceleration constant of the oxidation falls in proportion to the amount of styrene added. Tracer experiments show that a high proportion of the

[82] J. H. Knox and C. H. J. Wells, see p. 158 of ref. 2.

[83] C. N. Satterfield and R. C. Reid, *J. Chem. and Eng. Data*, 1961, **6**, 302.

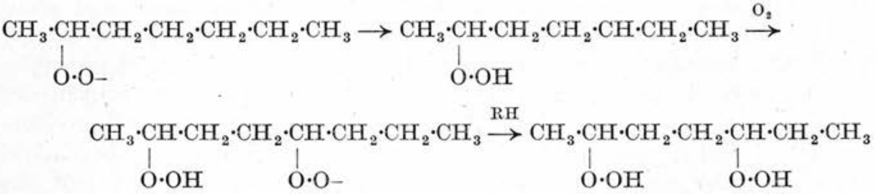
[84] (*a*) V. A. Poltorak and V. V. Voevodskii, *Zhur. fiz. Khim.*, 1961, **35**, 284 (transl. 176); (*b*) R. Martin, M. Niclause, and M. Dzierzynski, *Compt. rend.*, 1962, **254**, 1786.

[85] G. Ohlman, H. Steinert, G. Lischke, and E. Leibnitz, *Z. phys. Chem.* (*Leipzig*), 1962, **218**, 42.

[86] I. Kende and D. Gal, *Combustion and Flame*, 1962, **6**, 109.

carbon dioxide in the products comes from the styrene, and the inhibition is therefore due to the competitive oxidation of the styrene, rather than its action as a radical trap.

The nature of the peroxides formed in low-temperature oxidations has been clarified by Cartledge and Tipper [87] who have demonstrated the formation of mono-, di-, and tri-peroxides in the oxidation of heptane at 240—310° C. These are thought to arise from internal abstraction by peroxy-radicals.



$$CH_3\cdot\underset{O\cdot O-}{CH}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3 \rightarrow CH_3\cdot\underset{O\cdot OH}{CH}\cdot CH_2\cdot CH_2\cdot CH\cdot CH_2\cdot CH_3 \xrightarrow{O_2}$$

$$CH_3\cdot\underset{O\cdot OH}{CH}\cdot CH_2\cdot CH_2\cdot\underset{O\cdot O-}{CH}\cdot CH_2\cdot CH_2\cdot CH_3 \xrightarrow{RH} CH_3\cdot\underset{O\cdot OH}{CH}\cdot CH_2\cdot CH_2\cdot\underset{O\cdot OH}{CH}\cdot CH_2\cdot CH_3$$

Competitive oxidations. The wide differences in reactivity of different hydrocarbons towards oxygen are well known. They may arise from different rates of attack of the free radicals on the hydrocarbons, different rates of branching, and different efficiencies of production of the branching intermediates.[88] Competitive oxidation studies by Falconer, Knox, and Trotman-Dickenson [89] have shown that only small differences can be attributed to the chain-propagating steps. Between 320° and 495° C the radical or radical mixture attacking ethane, propane, cyclopropane, isobutane, and neopentane has a selectivity rather greater than Cl and less than CF_3, CH_3O, or CH_3. Individual oxidation studies strongly suggest that HO_2 is the chain-propagating radical, but the thermochemistry of the HO_2 radical reactions makes this questionable. Foner and Hudson [90] have redetermined the heat of formation of HO_2 by the electron-impact method. The new values for the bond strengths in H_2O_2 are $D[\text{H–OOH}] = 89{\cdot}6 \pm 2$ kcal.; $D[\text{H–OO}] = 45{\cdot}7 \pm 2$ kcal. Nearly all hydrogen-abstraction reactions by HO_2 are therefore endothermic, and its reactivity and selectivity should be comparable with that of a bromine atom for which $D[\text{H–Br}] = 87$ kcal. The competitive experiments taken alone would be better interpreted if OH were the radical removing the hydrocarbons.

Experiments at lower temperatures with ketone photosensitisation [91] have shown that the radicals removing the hydrocarbons have very similar reactivities to those at higher temperatures. The radicals were thought to be CH_3O_2, $C_2H_5O_2$, and $C_3H_7O_2$ but there is some doubt about this.

Olefins.—In the last few years there has been renewed interest in the oxidation of olefins.[92] Skirrow and Williams [93] have investigated the oxidation of isobutene between 250° and 320° C, analysing the products by gas

[87] J. Cartledge and C. F. H. Tipper, *Proc. Roy. Soc.*, 1961, *A*, **261**, 388; *Combustion and Flame*, 1961, **5**, 87.

[88] J. H. Knox, *Trans. Faraday Soc.*, 1959, **55**, 1362.

[89] W. E. Falconer, J. H. Knox, and A. F. Trotman-Dickenson, *J.*, 1961, 782.

[90] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 1962, **36**, 2681.

[91] W. E. Falconer, J. H. Knox, and A. F. Trotman-Dickenson, *J.*, 1961, 4285.

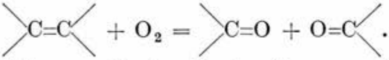
[92] G. Skirrow, *Proc. Roy. Soc.*, 1958, *A*, **244**, 345; A. Blundell and G. Skirrow, *ibid.*, p. 331; J. D. Mullen and G. Skirrow, *ibid.*, p. 312.

[93] G. Skirrow and A. Williams, *Proc. Roy. Soc.*, 1962, *A*, **268**, 537.

chromatography. The initial products are acetone and formaldehyde, in equimolar amounts. Isobutyraldehyde and α-methylacraldehyde may also be initial products. Later, carbon monoxide and dioxide, water, and propene appear. Hydrogen peroxide is the main peroxidic product, but some methallyl peroxide appears later in the reaction. Kinetic analysis of the reaction is difficult as it starts with a pressure decrease, a common although unexplained feature of many olefin oxidations.

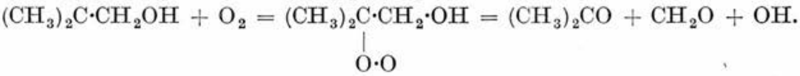
Cullis, Fish, and Turner [94] have studied the oxidation of 2-methylbut-2-ene (isopentene) at 265° C and find that acetaldehyde and acetone in equimolar amounts are the major initial products. Later products are carbon monoxide, dioxide, water, and methanol with smaller amounts of propaldehyde, isopropyl and t-butyl alcohol, and butan-2-one. Using isopentenes labelled with ^{14}C, at atoms 2 and 4, they have established that all products except t-butyl alcohol are formed without rearrangement of the carbon skeleton. The methanol appears to come from the CH_3 group of the acetaldehyde, as shown independently by Neiman *et al.*[81]

The first stage of the oxidation of an olefin now seems clear, and with ethylene,[82] propene,[81] isobutene,[93] and isopentene [94, 95] it can be represented by the stoicheiometric equation



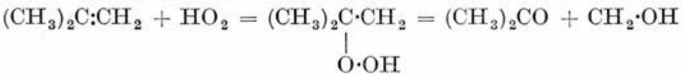
It is difficult to avoid the conclusion that a four-membered ring transition-state must be formed somewhere in this process. Cullis, Fish, and Turner believe that the oxygen molecule adds directly to the double bond, to give a ring peroxide which subsequently decomposes into two carbonyl compounds. This has the advantage of explaining the pressure decrease usually observed, but work on the oxidation of alkanes [78b, 88] rules this out. In the oxidation of propane,[78] for example, the yield of propene passes through a maximum due to its own oxidation. The maximum concentration and the dependence of propene yield on extent of reaction are independent of the rate of oxidation as a whole. Its consumption must therefore be controlled by the prevailing oxidation of the alkane, and can only be by a free-radical process. Skirrow and Williams [93] proposed a mechanism based upon OH as the chain carrier:

$$(CH_3)_2C{:}CH_2 + OH = (CH_3)_2C{\cdot}CH_2{\cdot}OH$$



$$(CH_3)_2C{\cdot}CH_2OH + O_2 = (CH_3)_2\underset{\underset{O\cdot O}{|}}{C}{\cdot}CH_2{\cdot}OH = (CH_3)_2CO + CH_2O + OH.$$

However, an equally plausible scheme, involving HO_2, can be written



$$(CH_3)_2C{:}CH_2 + HO_2 = (CH_3)_2\underset{\underset{O\cdot OH}{|}}{C}{\cdot}CH_2 = (CH_3)_2CO + CH_2{\cdot}OH$$

$$CH_2{\cdot}OH + O_2 = CH_2O + HO_2.$$

Thus the detailed mechanism for the formation of the carbonyl compounds is not finally established.

The oxidation of isobutene, catalysed by hydrogen bromide, has been

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[94] C. F. Cullis, A. Fish, and D. W. Turner, *Proc. Roy. Soc.*, 1961, *A*, **262**, 318.
[95] C. F. Cullis, A. Fish, and D. W. Turner, *Proc. Roy. Soc.*, 1962, *A*, **267**, 433.

studied by Hurst, Skirrow, and Tipper [96] and follows a similar study of the catalysed oxidation of isobutane.[97] The reaction between 145° and 195° c is autocatalytic, giving $Br{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}O{\cdot}OH$ as the major product. The kinetics are not fully explained, but the branching reaction seems to be bimolecular between RO·OH and HBr. The chain reaction must involve abstraction of H from HBr by RO_2 since the reaction stops when all the hydrogen bromide is exhausted.

Aromatics.—Drillat and his co-workers [98] have reinvestigated the oxidation of benzene at about 600° c and have confirmed that the reaction is of the degenerately branching type.

The slow oxidations of the three isomeric xylenes have been compared by Wright.[99] The *ortho*-isomer is the most reactive and the overall orders for *ortho*-, *meta*-, and *para*-isomers are 1·9, 2·8, and 1·5, respectively. The activation energies are all about 40 kcal. The rates of oxidation increase with xylene pressure, but are independent of oxygen pressure above a certain limit. Competitive-oxidation experiments show that the differences in reactivity do not lie in the chain-propagating steps; the dependence of the acceleration constants on xylene pressure suggests that the differences lie in the rates of branching.

In an analytical study of the oxidation of *o*-xylene [77] in a flow system, 38 products were identified by gas chromatography. The main products formed, without destruction of the benzene ring when 72% of the xylene had reacted, are 2-methylstyrene (14% molar of xylene reacted), toluene (10%), benzene (6%), *o*-tolualdehyde (5%), benzofuran (5%), and *o*-ethyltoluene (4%). Those formed by degradation of the ring are CO (200%), CO_2 (60%), H_2O (150%), CH_4 (25%), H_2 (20%), C_2H_4 (10%), and C_2H_6 (5%). Wright concludes that the initial step probably preserves the ring but, once it is ruptured, extensive degradation takes place rapidly. *o*-Tolualdehyde seemed the most likely branching agent.

Barnard and Hawtin [100] have examined the oxidation of *p*-xylene, in a static system, between 460° and 510° c. The main products are carbon monoxide and dioxide, with small amounts of toluene, hydrogen, and methane. The order of the reaction is 3, contrasting with Wright's value of 1·5.[77] Formaldehyde in 2% yield is also reported and, since its addition removes the induction period, it is considered to be the most likely branching agent. The mechanism suggested is similar to that of Enikolopyan *et al.* for methane.[56]

Jones *et al.*[101] have studied the oxidation of several aromatic hydrocarbons in a flow system, with a fine rain of metallic particles as heat exchangers. They agree with other workers that benzene, toluene, and the xylenes are relatively unreactive and tend to give extensively degraded

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[96] P. Hurst, G. Skirrow, and C. F. H. Tipper, *Proc. Roy. Soc.*, 1962, *A*, **268**, 405.

[97] E. R. Allen and C. F. H. Tipper, *Proc. Roy. Soc.*, 1960, *A*, **258**, 251.

[98] J. Drillat and P. Laffitte, *Compt. rend.*, 1960, **251**, 2359; J. Drillat, *ibid.*, 1961, **252**, 1155; R. Ben Aim and J. Drillat, *Bull. Soc. chim. France*, 1962, 519.

[99] F. J. Wright, *J. Phys. Chem.*, 1960, **64**, 1944.

[100] J. A. Barnard and P. Hawtin, *Combustion and Flame*, 1961, **5**, 249.

[101] J. H. Jones, M. R. Fenske, D. G. Hutton, and H. D. Allendorf, *J. Chem. and Eng. Data*, 1961, **6**, 623.

products, whereas ethyl- and isopropyl-benzenes gave large yields of styrene and methylstyrene, with smaller yields of benzaldehyde and acetophenone.

This is confirmed by Kroger and Bigorajski [102] who have oxidised ethylbenzene, styrene, benzene, and toluene, in a static system, at 380—410°, 310—340°, 415°, and 450° c, respectively. Styrene is the principal product of the oxidation of ethylbenzene, and formaldehyde and benzaldehyde are the principal products from styrene, accounting initially for about 70% of the hydrocarbons disappearing. With benzene and toluene the main products are oxides of carbon and water, although traces of benzaldehyde are obtained from toluene.

There seems little doubt that benzenes substituted only with methyl groups undergo extensive degradation. Whether the initial reaction preserves the ring or not is questionable, although Wright's results [77] certainly indicate that some of the initial reaction preserves the ring intact. With benzene substituted with higher alkyl groups, or olefinic groups, the situation is different. They are oxidised initially in the same way as the alkanes or olefins, obtained by replacing the phenyl group by hydrogen.

Oxygenated Compounds.—*Acetaldehyde*. Chamboux and Lucquin [103] have mapped the various oxidation regions of acetaldehyde-oxygen mixtures at temperatures between 200° and 500° c. Their results are similar to those of Ben Aim and Lucquin for n-pentane.[104] Six types of oxidation can be distinguished: (i) a slow straight-chain reaction at low temperatures and pressures; (ii) a slow branched-chain reaction; (iii) a slow branched-chain reaction showing a " pic d'arrêt " just before reaction ceases; and (iv) ignitions at low temperatures in an ignition peninsula, and at higher temperatures and pressures. Regions (iii) and (iv) enclose two further regions: (v) single and double cool flames and (vi) third stage ignitions which occur within a narrow peninsula, extending over a moderate pressure range but with narrow temperature limits from the ignition boundary into the cool flame region.

Sokoleva, Markevich, and Nalbandyan [105] have measured the rate o initiation of the oxidation of acetaldehyde between 320° and 380° c, by oxidising mixtures of about 1% of acetaldehyde in air in a flow reactor o molybdenum-glass, which preserves HO_2 and hydrogen peroxide. Yield of formaldehyde and hydrogen peroxide were determined for the first 20% consumption of the acetaldehyde. The peroxide yield rises linearly with time, and is unaffected by the addition of formaldehyde. Thus it does no arise from the secondary oxidation of formaldehyde. The initial rate o formation follows the equation

$$d[H_2O_2]/dt = k[O_2][CH_3{\cdot}CHO]^2.$$

The Authors deduce that the mechanism is

$$CH_3{\cdot}CHO + O_2 = CH_3{\cdot}CO + HO_2 \qquad (1$$

$$CH_3{\cdot}CHO + HO_2 = CH_3{\cdot}CO + H_2O_2 \qquad (2$$

$$HO_2 = \text{Wall termination} \qquad (3$$

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[102] C. Kroger and G. Bigorajski, *Erdöl u. Kohle*, 1962, **15,** 109.

[103] J. Chamboux and M. Lucquin, *J. Chim. phys.*, 1962, **59,** 797.

[104] R. Ben Aim and M. Lucquin, *J. Chim. phys.*, 1959, **56,** 475, 649.

[105] N. A. Sokoleva, A. M. Markevich, and A. B. Nalbandyan, *Zhur. fiz. Khim* **1961, 35,** 850 (transl. 415).

his scheme gives the observed rate expression only if reaction (2) is the ontrolling step in a long chain. Then $k = k_1k_2/k_3$. However, the other ain reaction product is formaldehyde and this is almost certainly formed *ia* the reactions

$$CH_3{\cdot}CO = CH_3 + CO; \qquad CH_3 + O_2 = CH_2O + OH$$

eactions (2) and (3) must therefore involve OH, not HO_2, if the overall rocess is a chain reaction as assumed. Denoting these reactions by (2′) nd (3′), $k = k_1k_{2\prime}/k_{3\prime}$. The observed activation energy of 30 kcal. is then $E_1 + E_2' - E_3'$. Thus 30 kcal. is the maximum value for E_1, giving $D[CH_3{\cdot}CO{-}H] \leqslant 76$ kcal., a rather low value.

Alcohols. The work of Cullis and Newitt [106] on ethanol has been exended to the propyl alcohols [107] and the four butyl alcohols,[108] in the temerature range 350—450° c.

The initial products, where possible, are an aldehyde, or ketone, and ydrogen peroxide in equimolar yields. The oxidations are similar to those f the alkanes, and are most simply explained by an HO_2 radical chain. For xample, with propan-2-ol

$$(CH_3)_2CH{\cdot}OH + X(HO_2) = (CH_3)_2C(OH) + XH(H_2O_2)$$
$$(CH_3)_2C(OH) + O_2 = (CH_3)_2CO + HO_2.$$

Vith t butyl alcohol this chain cannot occur; the alcohol is analogous to eopentane. It differs from the others in exhibiting only a high-temperaure oxidation region. The others show low-temperature oxidation zones, egative temperature coefficients, and sometimes cool flames. Other initial roducts may be formed in smaller quantities: isobutyl alcohol gives acetone nd formaldehyde, in addition to isobutyraldehyde and hydrogen peroxide, nd s-butyl alcohol gives acetaldehyde, in addition to ethyl methyl ketone nd hydrogen peroxide. These further products can arise from the decomosition of the relevant peroxy-radicals. t-Butyl alcohol gives as initial roducts only acetone and an unidentified C_1 compound. These findings ave been confirmed by experiments by Blumberg *et al.*[109] in which the iquid-phase and the gas phase oxidation of ethanol, under pressure, are ompared.

Esters. Fish and Waris [110] have started a programme of investigation f the oxidation of esters, with ethyl acetate in a flow system at 250—450° c. here is a negative temperature coefficient between 350° and 380° c. cetic acid and formaldehyde are the major low-temperature products (in he ratio of about 5 : 1); acetaldehyde begins to appear at 350° c. A perxide mechanism is invoked to account for the products.

Oxidation of Alkyl Radicals. The study of the direct oxidation of alkyl adicals formed by photolysis or pyrolysis has proved difficult, and much of

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[106] C. F. Cullis and E. J. Newitt, *Proc. Roy. Soc.*, 1956, *A*, **237**, 530; 1957, *A*, **242**, 16.

[107] C. F. Cullis and E. J. Newitt, *Proc. Roy. Soc.*, 1960, *A*, **257**, 402; A. R. Burgess, . F. Cullis, and E. J. Newitt, *J.*, 1961, 1884; A. R. Burgess and C. F. Cullis, *ibid.*, . 3014; A. R. Burgess, *J. Appl. Chem.*, 1961, **11**, 235.

[108] C. F. Cullis and E. A. Warwicker, *Proc. Roy. Soc.*, 1961, *A*, **264**, 392.

[109] E. A. Blumberg, G. E. Zaikov, Z. K. Maizus, and N. M. Emanuel, *Kinetika i ataliz*, 1960, **1**, 510 (transl. 477).

[110] A. Fish and A. Waris, *J.*, 1962, 4513.

the earlier work is conflicting and difficult to interpret. However, recen work on methyl gives a more consistent picture.

Methyl. There is no question that methyl radicals readily associate wit oxygen to give methylperoxy-radicals which, in the first instance, must b excited. It is gradually becoming evident that most of the chemical reactions which follow are those of thermalised peroxy-radicals, although thi still requires confirmation.

Subbaratham and Calvert,[111] and Drever and Calvert,[112] in complementary investigations have established the main features of the oxidatio of methyl at room temperature. They have made direct infrared absorptio measurements of photo-oxidising azomethane, in a 70-l. reaction vessel wit an optical system of 40 m. path-length. Reaction mixtures contained abou 1 mm. of azomethane and 1—740 mm. of oxygen. The total pressure wa made up to 740 mm. with inert gas. Irrespective of oxygen pressure roughly equimolar amounts of formaldehyde and methanol are obtaine with smaller amounts of formic acid and methyl hydroperoxide. Sinc different inert gases have no effect, $CH_3\cdot O\cdot OH$ does not arise from abstraction by activated $CH_3\cdot O\cdot O$, which would otherwise decompose. Experiments with hexadeuteroazomethane, $CD_3\cdot N{:}N\cdot CD_3$, in the presence of acetaldehyde, gave only $CD_3\cdot O\cdot OD$ and thus $CD_3\cdot O\cdot O$ does not abstract hydroge from acetaldehyde or azomethane. The products must therefore be explained by radical–radical reactions of thermalised peroxy-radicals. Th likely reactions are

$$2CH_3\cdot O\cdot O = 2CH_3O + O_2 \qquad (1$$

$$2CH_3O = CH_2O + CH_3\cdot OH \qquad (2$$

$$\begin{aligned} CH_3O + CH_3\cdot O\cdot O &= CH_3\cdot O\cdot OH + CH_2O \\ \text{or} \quad & CH_3\cdot OH + H\cdot CO_2H. \end{aligned} \qquad (3$$

In the presence of added formaldehyde the peroxide yield falls and that c methanol rises. This means that the CH_3O radical can abstract from CH_2C while $CH_3\cdot O\cdot O$ cannot:

$$CH_3O + CH_2O = CH_3\cdot OH + CHO. \qquad (4$$

Shanin and Kutschke[113] have studied the same reaction between 20 and 160° c, using mass-spectrometric analysis. They have established tha $CH_3\cdot O\cdot OH$ is a reaction product at all temperatures, but considerable precautions have to be taken to prevent its destruction on the metal parts c the apparatus. The addition of tetradeuteromethane gives no $CH_3O\cdot O\cdot I$ and so $CH_3\cdot O\cdot O$ does not abstract deuterium from tetradeuteromethane a 100° c, confirming Calvert's results.[111, 112] At this temperature the quantum yield of peroxide was about 0·5 and much greater than the valu obtained by Calvert.

Blake and Kutschke[114] have oxidised di-t-butyl peroxide at 160° c The overall rate of decomposition is unaffected by added oxygen and s the reaction is non-chain. The main initial product is formaldehyde, i

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[111] N. R. Subbaratham and J. G. Calvert, *J. Amer. Chem. Soc.*, 1962, **84,** 111

[112] D. F. Drever and J. G. Calvert, *J. Amer. Chem. Soc.*, 1962, **84,** 1362.

[113] M. Shanin and K. O. Kutschke, *J. Phys. Chem.*, 1961, **65,** 189; *Canad. J. Chem* 1961, **39,** 73.

[114] A. R. Blake and K. O. Kutschke, *Canad. J. Chem.*, 1961, **39,** 278.

similar yield to acetone. Small quantities of methanol are also formed. Later in the oxidation the formaldehyde pressure reaches a stationary value, carbon monoxide appears, and the pressure of methanol increases more rapidly. Kinetic tracer experiments show that all the carbon monoxide arises from formaldehyde, indicating that some species abstract from CH_2O giving CHO which is oxidised to HO_2 and CO.

The absence of methanol as a major initial product indicates that most of the $CH_3{\cdot}O{\cdot}O$ radicals decompose by

$$CH_3{\cdot}O{\cdot}O = CH_2O + OH \qquad (5)$$

The formation of methanol later in the reaction, when the formaldehyde has accumulated, together with the previous observation of methyl hydroperoxide,[113] indicates that reaction (6) occurs:

$$CH_3{\cdot}O{\cdot}O + CH_2O = CH_3{\cdot}O{\cdot}OH + CHO. \qquad (6)$$

That methyl hydroperoxide would decompose to give methanol was found by independent experiments, when the peroxide was admitted to the reaction vessel. Reaction (6) does not occur at room temperature, according to the results of Calvert.

The results of Kutschke are in general agreement with those of Fisher and Tipper,[64] who introduced reaction (6) to explain the formation of methanol and methyl hydroperoxide in the photo-oxidation of methane at 400° C.

Hoare and Wellington [115] have also studied the oxidation of methyl radicals, formed by the photolysis and pyrolysis of di-t-butyl peroxide, at 50°, 100°, and 135° C, and by the photolysis of acetone at 200° C. Oxygen pressures were 0—5 mm. There is no evidence for any change of mechanism over this range as would have been expected by comparison of the results of Calvert and Kutschke. The initial products are formaldehyde and methanol, carbon monoxide appearing later. As the reaction proceeds the quantum yield of formaldehyde falls and that of methanol rises to a maximum; the quantum yield of carbon monoxide rises continuously. Adding formaldehyde increases the initial quantum yield of methanol towards unity and also that of carbon monoxide. Hoare and Wellington claim that the initial quantum yields of formaldehyde and methanol are both 0·5. This conflicts with Blake and Kutschke's result [114] and, indeed, their own experimental data [115] suggest that the true initial quantum yield of formaldehyde is considerably greater than that of methanol. There is therefore some doubt as to the interpretation of their results. The authors assume that the methanol which they observe is initially formed as methanol, not methyl hydroperoxide, but there is no real evidence that this is the case. In order to explain the methanol formed, in the presence of added formaldehyde, they propose reaction (4), but this conflicts with the evidence of Hanst and Calvert [80] that methoxyl radicals oxidise to formaldehyde and HO_2 at about 200° C.

There is obviously more work still to be done in this field. The main pitfall seems to be failure to distinguish between methanol and methyl hydro-

[115] D. E. Hoare and C. A. Wellington, 8th Internat. Symposium on Combustion, Williams and Wilkins, Baltimore, Md., 1962, p. 472.

peroxide in the products. Further work is required on the oxidation of methoxyl, to establish whether reaction (4) can occur at high temperatures. This is relevant in connexion with the source of methanol in hydrocarbon oxidation. The effect of inert gases requires further investigation, to establish finally whether activated peroxy-radicals are chemically important or not.

The general picture which emerges is that $CH_3{\cdot}O{\cdot}O$ radicals, at about room temperature, undergo only disproportionation. At higher temperatures they mostly decompose to formaldehyde but some abstract to give methyl hydroperoxide, which will generally be analysed as methanol.

Johnson and Salmon [116] have shown that the only important product from the γ-ray-initiated oxidation of methane at room temperature is methyl hydroperoxide. This conflicts with the results of photochemical experiments, but can probably be explained by the presence of HO_2 radicals which react by

$$CH_3{\cdot}O{\cdot}O + HO_2 = CH_3{\cdot}O{\cdot}OH + O_2. \qquad (7)$$

The results are similar to those of photosensitised oxidations.[117]

The predominant decomposition of methylperoxy to formaldehyde and OH, which is assumed in all mechanisms for the oxidation of methane, has been confirmed by the flash photolysis work of McKellar and Norrish,[118] who have observed the spectra of both OH and CH_2O in the flash photolytic oxidation of methyl iodide, some 30 μsec. after the initiating flash.

The results of the fast-flow experiments of Avramenko and Postnikov [119] conflict with those of the photochemical work. When methyl radicals, produced by the pyrolysis of acetone, are oxidised at a total pressure of 0·6—3 mm. Hg, methyl hydroperoxide is the only product detected in the products condensed on a cold finger. No formaldehyde is found even with the reactor at 450° c, although some carbon dioxide is obtained (about 30% of the peroxide). The system was checked by measuring the rate constant for recombination of methyl radicals by determining the saturation yield of methyl hydroperoxide, when the oxygen was added at different distances downstream from the methyl radical source. The rate constant was in good agreement with the accepted value. The rate constant for $CH_3 + O_2 = CH_3{\cdot}O{\cdot}O$ was determined from the variation of the yield of peroxide with oxygen concentration, and the value is almost the same as that found by Hoare and Walsh,[120] although obtained at a much lower total pressure. The authors [119] propose that two reactions are involved, a bimolecular reaction which gives activated $CH_3{\cdot}O{\cdot}O$ radicals, which then abstract from acetone, and a thermolecular reaction which gives thermalised $CH_3{\cdot}O{\cdot}O$ radicals which also abstract hydrogen from acetone:

$$CH_3 + O_2 = CH_3{\cdot}O{\cdot}O^* \longrightarrow CH_3{\cdot}O{\cdot}OH \qquad (8)$$

$$CH_3 + O_2 + M = CH_3{\cdot}O{\cdot}O + M \longrightarrow CH_3{\cdot}O{\cdot}OH. \qquad (9)$$

Their rate constant is then k_8 while that of other workers is $k_8 + k_9[M]$.

[116] G. R. A. Johnson and G. A. Salmon, *J. Phys. Chem.*, 1961, **65**, 177.

[117] J. S. Watson and B. de B. Darwent, *J. Phys. Chem.*, 1957, **61**, 577; A. B. Nalbandyan, *Doklady Akad. Nauk S.S.S.R.*, 1952, **86**, 589; J. Gray, *J.*, 1952, 3150.

[118] J. F. McKellar and R. G. W. Norrish, *Proc. Roy. Soc.*, 1961, *A*, **254**, 147.

[119] L. I. Avramenko and L. M. Postnikov, *Izvest. Akad. Nauk S.S.S.R.*, 1960, 1921 (transl. 1796).

[120] D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, 1957, **53**, 1102.

The complete absence of formaldehyde in the products is difficult to explain and makes it questionable whether the peroxide could have arisen from a gas-phase abstraction from acetone. It could have been formed in the cold trap used to collect the products. The formation of unexpected products seems to be a feature of the fast flow experiments of Avramenko and his co-workers.

A complementary study has been made by Avramenko and Kolesnikova [121] on the oxidation of the radical derived by reaction of hydrogen atoms with methanol. This may be either CH_2OH or CH_3O. The authors favour the former. The oxidation products are formaldehyde and hydrogen peroxide in yields consistent with the reactions

$$CH_2OH + O_2 = CH_2O + HO_2 \qquad (10)$$

$$2HO_2 = H_2O_2 + O_2.$$

The rate constant is

$$k_{10} = 2{\cdot}4 \times 10^{12} \exp[-2500/1{\cdot}987T] \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}.$$

Other alkyl radicals. Bell and Macdowell [122] have studied the mercury-photosensitised oxidation of isobutane between 30° and 100° C. The main product is t-butyl hydroperoxide, with about half the amount of acetone + t-butyl alcohol. The dependence of the quantum yield, which is low, on light intensity and reactant concentration shows that the reaction is non-chain and that the peroxide is probably formed by

$$C_4H_9{\cdot}O{\cdot}O + HO_2 = C_4H_9{\cdot}O{\cdot}OH + O_2.$$

The results are thus in agreement with those from other mercury-photosensitised oxidations.[117]

The oxidation at 25° C of t-butyl radicals, generated by photolysis of azoisobutane, has been studied by Thomas and Calvert,[123] using the long-path infrared technique.[111, 112] Azoisobutane pressures were about 0·1 mm. and oxygen pressures 20 and 740 mm. The main initial products are acetone, formaldehyde, and t-butyl alcohol and hydroperoxide, in comparable yields, with smaller quantities of methanol. As with methyl radicals there is no chain reaction and all the products can be explained on the basis of radical-radical reactions with the addition of $C_4H_9{\cdot}O = CH_3{\cdot}CO{\cdot}CH_3 + CH_3$, which accounts for the acetone and provides a source of CH_3, $CH_3{\cdot}O{\cdot}O$ and CH_3O.

The Reactions of Oxygen Atoms.—The literature on the reactions of oxygen atoms, up to the end of 1959, has been authoritatively reviewed by Kaufman.[124] We mention here the more recent work on the reactions of oxygen atoms with organic compounds.

For the purpose of deriving kinetic data oxygen atoms can be generated in several ways: (1) by the mercury photosensitised decomposition of nitrous oxide [125a] which gives $N_2 + O$; (2) by photolysis of nitrogen dioxide,[125b]

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[121] L. I. Avramenko and R. V. Kolesnikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 591 (transl. 545).

[122] K. M. Bell and C. A. Macdowell, *Canad. J. Chem.*, 1961, **39**, 1419, 1424.

[123] S. S. Thomas and J. G. Calvert, *J. Amer. Chem. Soc.*, 1962, **84**, 4207.

[124] F. Kaufman, "Progress in Reaction Kinetics," ed. G. Porter, Pergamon Press, London and New York, 1961, Vol. I, p. 1.

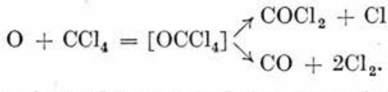
[125] (*a*) R. J. Cvetanovic, *J. Chem. Phys.*, 1955, **23**, 1203; (*b*) S. Sato and R. J. Cvetanovic, *Canad. J. Chem.*, 1958, **36**, 970.

giving NO + O; (3) by passing a silent discharge through oxygen,[126] giving $O + O_2$; and (4) by titrating nitrogen atoms with nitric oxide, giving $O + N_2$.[22a]

The reactions of oxygen atoms are hydrogen-abstraction, addition to double bonds and possibly insertion into C–H and C–C bonds. The existence of the insertion reactions proposed by Avramenko and his co-workers has been doubted by Kaufman,[124] who does not accept their mechanisms.

The recent work concerns carbon tetrachloride,[127] benzene,[128] toluene,[129] methanol,[130] acetaldehyde,[131] and 1,2-dichloroethane.[132]

Ung and Schiff,[127] using methods (3) and (4) for generating oxygen atoms, find that with carbon tetrachloride the products are chlorine, carbonyl chloride, and carbon monoxide and dioxide. They propose that oxygen atoms add to carbon tetrachloride and that the complex decomposes



$$O + CCl_4 = [OCCl_4] \begin{array}{l} \nearrow COCl_2 + Cl_2 \\ \searrow CO + 2Cl_2. \end{array}$$

Carbon dioxide is then formed by a rapid reaction of carbonyl chloride with oxygen atoms. The rate constant for the addition reaction is

$$k = 2{\cdot}0 \times 10^{10} \exp\,[-4500/1{\cdot}987\,T]\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}.$$

The low A factor is noteworthy. Boocock and Cvetanovic,[128] and Jones and Cvetanovic [129] [method (1)] have found that the reactions with benzene and toluene are some 100 times slower than with olefins. The products are mainly polymeric and no mechanism could be derived.

Avramenko, Kolesnikova, and Kuznetsova [130] [method (3)] have found that with methanol the only products are formaldehyde and a small yield of hydrogen peroxide. Since the radical derived by hydrogen-abstraction from methanol [121] gives a substantial yield of hydrogen peroxide on oxidation they conclude that the oxygen atom must react directly with methanol, to give formaldehyde and water:

$$O + CH_3{\cdot}OH = CH_2O + H_2O.$$

The rate constant of the reaction is

$$k = 5 \times 10^{11} \exp\,[-3100/1{\cdot}987\,T]\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}.$$

With acetaldehyde, the products are methyl hydroperoxide, keten, and glycollaldehyde, and completely different from those obtained by Cvetanovic [133] (only biacetyl). The products suggest that insertion into C–H

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[126] L. I. Avramenko and R. V. Kolesnikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1955, 386; 1958, 277.

[127] A. Y. M. Ung and H. I. Schiff, *Canad. J. Chem.*, 1962, **40,** 486.

[128] G. Boocock and R. J. Cvetanovic, *Canad. J. Chem.*, 1961, **39,** 2436.

[129] G. R. H. Jones and R. J. Cvetanovic, *Canad. J. Chem.*, 1961, **39,** 2444.

[130] L. I. Avramenko, R. V. Kolesnikova, and N. L. Kuznetsova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 599 (transl. 522).

[131] L. I. Avramenko, R. V. Kolesnikova, and M. F. Sorokin, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 1005 (transl. 930); 1231 (transl. 1141).

[132] L. I. Avramenko, R. V. Kolesnikova, and N. L. Kuznetsova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 1565 (transl. 1462).

[133] R. J. Cvetanovic, *Canad. J. Chem.*, 1956, **34,** 775.

bonds occurs. The rate constant, based upon the rate of formation of acetic acid, is

$$k = 3{\cdot}6 \times 10^{11} \exp\,[-2750/1{\cdot}987\,T]\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}.$$

The value calculated for 300° K is about 30 times lower than Cvetanovic's value.

With 1,2-dichloroethane the main products are hydrochloric acid and carbon monoxide. It is suggested that O attacks the C–C bond, with rupture of the molecule and formation of CH_2 as one product. As this reaction is endothermic, it is most improbable. The rate constant for the reaction, whatever its nature, is

$$k = 1{\cdot}2 \times 10^{13} \exp\,[-5500/1{\cdot}987\,T]\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}.$$

Elias and Schiff [20] [method (4)] have obtained the rate constant for reaction with n-butane as

$$k = 3{\cdot}1 \times 10^{13} \exp\,[-4200/1{\cdot}987\,T]\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}.$$

The picture of activation energies is reasonably consistent, but that of the *A* factors is unsatisfactory. Further work is required to resolve the disagreement between the results of Avramenko and those of Schiff, Cvetanovic, and Kaufman.

J. H. K.

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COMPETITIVE CHLORINATION REACTIONS IN THE GAS PHASE: HYDROGEN AND C_1—C_5 SATURATED HYDROCARBONS

COMPETITIVE CHLORINATION REACTIONS IN THE GAS PHASE: HYDROGEN AND C_1—C_5 SATURATED HYDROCARBONS

By JOHN H. KNOX AND ROBERT L. NELSON
Dept. of Chemistry, Edinburgh University

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By carrying out competitive chlorination reactions with hydrogen, the C_1—C_4 alkanes, cyclopropane, cyclobutane and *neo*pentane, accurate values for the activation energy differences and *A* factor ratios have been obtained for the reactions RH + Cl = R + HCl. Use of the accepted value for the absolute rate constant of the reaction with hydrogen [3] then yields absolute values for the Arrhenius parameters. The experimental activation energies of attack at primary bonds decrease as the hydrocarbon RH becomes more complex, tending to a limiting value of about 750 cal mole^{-1} for long-chain hydrocarbons; values for attack at secondary bonds are some 300 cal mole^{-1} lower and for tertiary some 700 cal mole^{-1} lower. Evaluation of the internal energies of activation at absolute zero ($\Delta U_0^{\ddagger}$) leads to the unexpected result that two of the values are negative by more than can reasonably be attributed to experimental error. Discussion of the *A* factors in the light of transition-state theory indicates that the vibrational entropy of activation increases as RH becomes more complex. While the major part of this arises from the introduction of the low-frequency bending and wagging of the R—H—Cl part of the complex, alteration in the frequencies of the low-energy chain deformation vibrations must be invoked to account for secondary effects such as the higher vibrational entropy of activation for attack at secondary than at primary C—H bonds.

The work described in the present paper concerns the absolute rate constants k_{RH} of reactions of the type

$$\mathrm{Cl} + \mathrm{RH} = \mathrm{HCl} + \mathrm{R}, \tag{1}$$

where RH is hydrogen or a hydrocarbon.

Early work on chlorination reactions was mainly concerned with the overall mechanism of the reactions which were soon recognized as examples of free-radical chain reactions in which reaction (1) was coupled with

$$\mathrm{R} + \mathrm{Cl_2} = \mathrm{RCl} + \mathrm{Cl}. \tag{2}$$

Owing to the concern with overall mechanism, little attention was paid to the actual rate constants of the individual steps, their activation energies or *A* factors. However, as a result of the extensive development of our understanding of free-radical reactions since 1945, these Arrhenius factors have assumed great importance, but it is only for one reaction of the above type, namely, that in which RH is H_2, that these factors are known with any accuracy. Ashmore and Chanmugam, using the results of several other workers [1, 2] in addition to their own [3] give

$$k_{\mathrm{HH}} = 0{\cdot}8 \times 10^{14} \exp\,[5{,}500 \pm 200 \text{ cal mole}^{-1}/\boldsymbol{R}T]\text{ mole}^{-1}\text{ cm}^3\text{ sec}^{-1}$$

for a temperature range 300-1000°K. The value for the activation energy agrees with earlier work [4, 5] carried out at low temperatures on the temperature coefficient of the photochemical reaction ($E_{\mathrm{HH}} = 5{,}800 \pm 500$ cal mole^{-1}).

The position regarding the rate factors of the reactions of Cl with hydrocarbons is, however, unsatisfactory. Values of between 2 and 8 kcal mole^{-1} have been suggested for the activation energy of the reaction with methane.[6-9] The position with regard to the higher hydrocarbons is still worse and all that was generally known until recently was that the chlorinations were chain reactions whose chain lengths were comparable to those of the methane chlorination.[10, 11]

The chief difficulty in determining directly the rate constants or even the activation energies of these reactions lies in the extraordinary length of the chains and the consequent extreme sensitivity of the reaction rates to traces of inhibitors. This overriding difficulty can, however, be overcome by the use of a competitive method if one is temporarily willing to sacrifice the determination of absolute rate constants. These can be found later if the absolute rate constant is known for one of the competing reactions. The accuracy of the results obtained in a competitive experiment is unaffected by the nature of the chain initiation or chain termination steps provided that the chains are not too short. Since the results always give ratios of rate constants, they should, in principle, enable highly accurate values to be obtained for activation energy differences and *A* factor ratios since, when differences in reactivity are small, experiments can be carried out over a very wide temperature range. The same proportional accuracy should be obtainable whatever the actual magnitude of the activation energy differences.

When hydrogen and a hydrocarbon RH are chlorinated simultaneously the rates of the two reactions removing the two substances are:

$$-R_{\mathrm{HH}} = k_{\mathrm{HH}}[\mathrm{H_2}][\mathrm{Cl}] \text{ and } -R_{\mathrm{RH}} = k_{\mathrm{RH}}[\mathrm{RH}][\mathrm{Cl}],$$

and the relative rates are

$$\frac{R_{\mathrm{HH}}}{R_{\mathrm{RH}}} = \frac{\mathrm{d}[\mathrm{H_2}]/\mathrm{d}t}{\mathrm{d}[\mathrm{RH}]/\mathrm{d}t} = \frac{k_{\mathrm{HH}}[\mathrm{H_2}]}{k_{\mathrm{RH}}[\mathrm{RH}]},$$

giving on integration

$$\frac{k_{\mathrm{HH}}}{k_{\mathrm{RH}}} = \frac{\ln([\mathrm{H_2}]_i/[\mathrm{H_2}]_f)}{\ln([\mathrm{RH}]_i/[\mathrm{RH}]_f)},$$

where $[\mathrm{RH}]_i$ and $[\mathrm{RH}]_f$ are the initial and final hydrocarbon concentrations. If the amount of reaction is assumed to be small, then the approximation

$$\ln(1+x) \approx x,\ (x \to 0)$$

may be used giving

$$\frac{k_{\mathrm{HH}}}{k_{\mathrm{RH}}} = \frac{\Delta[\mathrm{H_2}]}{\Delta[\mathrm{RH}]}\frac{[\mathrm{RH}]}{[\mathrm{H_2}]},$$

where $\Delta[\mathrm{RH}]$ is the change in hydrocarbon concentration during the reaction and [RH] is taken as the initial hydrocarbon concentration.

In order to obtain the rate constant ratio, it is therefore necessary to measure only the initial concentrations of hydrogen and the hydrocarbon and to determine the quantities of each consumed. One does not require to know the concentration of free radicals. Hydrogen is, however, not always a convenient substance to use as a direct competitor with a hydrocarbon, mainly because of its relative unreactivity, and in the present work we have proceeded stepwise from the less reactive substances to the more reactive, using hydrogen only in competition with methane.

Direct measurement of the quantities of various hydrocarbons consumed in competitive chlorination reactions was employed by Pyke, Pritchard and Trotman-Dickenson.[12] Mixtures of hydrocarbons and chlorine were sealed up in small bulbs, brought up to reaction temperature and then illuminated. Analysis was carried out for the hydrocarbon content of the products using a controlled temperature still. The accuracy of their results was limited by the difficulties of measuring relatively small changes in the hydrocarbon concentrations. Their method also suffered from the serious disadvantage that it was impossible by measurement of the disappearance of the hydrocarbon alone to determine the relative rates of attack of Cl atoms at different points in the same molecule. This could only have been achieved by analysis for products characteristic of the initial point of attack. The alkyl chlorides formed inevitably by reaction (2) following reaction (1) are such substances and analysis for the chlorides can thus yield the relative rates of attack at different points in the same molecule. The relative rate constants for two different modes of attack are then given by

$$\frac{k_{\mathrm{RH}}}{k_{\mathrm{R'H}}} = \frac{[\mathrm{RCl}][\mathrm{R'H}]}{[\mathrm{R'Cl}][\mathrm{RH}]},$$

where the initial concentrations of the hydrocarbons are [RH] and [R′H] and the final concentrations of the chlorides are [RCl] and [R′Cl], consumption of the hydrocarbon being assumed small. When RH and R′H are the same substance the equation takes a particularly simple form.

Use of product analysis in this way was first made by Hass, McBee and Weber[13] in their study of the thermal chlorination of propane and *iso*butane. However, a number of complicating factors appear to have arisen in their experiments which render their results somewhat misleading. These are mentioned later.

In the past, one of the chief difficulties in the way of applying product analysis to competitive reactions in anything but flow systems has been that of the accurate analysis for very small quantities of closely similar chemical substances. This difficulty has now fortunately been solved by the rapid development of gas chromatography which has been used throughout the present work as the main analytical tool.

EXPERIMENTAL

APPARATUS

Chlorine atoms were generated photolytically in a 100 ml Pyrex reaction vessel using light from a 250 W projection lamp. In order to eliminate heat from the lamp the light was filtered by passage through 10 cm of a 10 % solution of copper sulphate. The reaction vessel had an internal thermometer pocket and was thermostatted by suitable vapour baths or freezing mixtures. Reactant mixtures were normally made up in a darkened mixing vessel of similar volume to the reaction vessel and usually contained approximately 1/10 of chlorine/hydrocarbon with chlorine pressures between 0·025 and 0·25 mm Hg, these being measured on a sensitive glass spoon-gauge. The mixtures were then made up to a total pressure of about 50 cm Hg by addition of nitrogen. In this way both the formation of secondary products and self-heating of the reaction mixture were avoided. The time of illumination in all experiments was about 30 min. After an experiment the products were frozen out by liquid oxygen and the uncondensable gases pumped off. The reaction products were then distilled into the U-tube of the chromatography apparatus.

Modifications of this procedure were employed for two of the mixtures studied. In the chlorination of $CH_4 + H_2$ mixtures the characteristic product from hydrogen, HCl, could not be determined on the chromatography column used owing to irreversible adsorption. The HCl was accordingly converted into an equivalent amount of benzene by reaction *in vacuo* with mercury diphenyl at 80°C. The chromatographic analysis was then carried out for methyl chloride and benzene. After allowance for the HCl arising from the chlorination of the methane, the HCl resulting from the reaction of the hydrogen was determined. To be directly comparable with the CH_3Cl formed, this amount of HCl was finally halved.

In the experiments with cyclopropane it was found that an appreciable dark reaction took place which did not, however, form cyclopropyl chloride. This product may have been 1 : 3-dichloropropane. Although the dark reaction would not have affected the subsequent competitive reaction induced by light, it was considered best to modify the usual procedure and admit the chlorine to the reaction vessel first and add the hydrocarbon + nitrogen mixture later. The mixture was then immediately illuminated to minimize any subsequent " dark reaction ".

The chromatography apparatus was of conventional design, employing hydrogen as carrier gas and a brass block thermal conductivity gauge at room temperature as detector.

The column used in all experiments was of 6 mm int. diam. and contained 25-52 mesh Firebrick (Fosalsil no. 6 powder made by Moler Products, Colchester) moistened with 25 % w/w of dioctyl phthalate. For separation of the different mixtures the temperature, flow rate and length of the column were suitably adjusted. (Typical operating conditions for the separation of ethyl and butyl chlorides were, for example: column length 300 cm; column temperature 60°C; flow rate 50 cm^3/min.) Calibration of the apparatus for each product was carried out with authentic samples, peak areas being used throughout as a measure of quantity. Where the identity of a product was in doubt, for example in the chlorination of cyclopropane, this was proved by infra-red analysis. The quantities of product generally used for analysis were of the order of 5 micromoles and the overall reproducibility of identical experiments was about 5 %. However, when products of high molecular weight were obtained, such as benzene, *neo*pentyl chloride and the butyl chlorides, the reproducibility was considerably poorer, the main source of error probably being caused by solution of these compounds in tap grease.

MATERIALS

The materials used in the work were obtained as follows.

CHLORINE: I.C.I. cylinder.

NITROGEN (oxygen-free): B.O.G. cylinder.

HYDROGEN: B.O.G. cylinder.

METHANE: B.O.G. cylinder. This methane contained a small amount of ethane which caused interference owing to its very much higher rate of chlorination. This was removed by prechlorination which reduced the ethane to insignificant proportions.

ETHANE: B.O.G. cylinder, containing about 2 % of ethylene.

PROPANE: sample given by I.C.I. containing about 0·6 % *iso*butane and traces of ethane and propylene.

*iso*BUTANE: sample given by I.C.I.

n-BUTANE: sample given by I.C.I.

*neo*PENTANE: pure hydrocarbon sample supplied by D.S.I.R., Chemical Research Laboratories, Teddington.

CYCLOPROPANE: B.O.G. (medicinal) cylinder.

CYCLOBUTANE: prepared by photolysis of cyclopentanone in the gas phase.[14] Cyclopentanone at a pressure of 50 cm Hg was illuminated at about 100-200°C in a 5 l. spherical bulb for 120 h using a 250 W Hg lamp. The cyclobutane was separated from the other products by gas chromatography and its identity checked by infra-red.

MERCURY DIPHENYL: B.D.H. laboratory reagent was purified by sublimation under reduced pressure.

The chlorine and hydrocarbon gases were normally subjected to several trap-to-trap distillations from − 80°C in order to remove any uncondensable gases and traces of water. In view of the nature of the experiments small impurities of the order of 1 % would not influence the accuracy of the results and no special steps were taken to purify the reagents further.

RESULTS

The rate constant ratios, k_{R_aH}/k_{R_bH}, have been obtained for the following mixtures over the temperature ranges between − 80°C and 320°C: hydrogen + methane; (methane + ethane);[12, 15] ethane + propane; ethane + *iso*butane; ethane + *n*-butane; propane + *neo*pentane; ethane + cyclopropane, and propane + cyclobutane. The appropriate activation energy plots are given in fig. 1, 2 and 3. Each point in these figures represents the mean of all experimental values obtained for that temperature. The values of the activation energy differences and A factor ratios are given in table 1 and were calculated by the method of least squares.

Although the ratios $[R_aH]/[R_bH]$ were normally adjusted to give approximately equal amounts of the two chlorides, experiments in which this ratio was varied over wide limits showed that the mixture composition had no effect upon the final rate constant ratio. Similarly, variation of the $[RH]_{total}/[Cl_2]$ likewise had no effect on the rate constant ratios, provided always that secondary chlorination of the products was avoided.

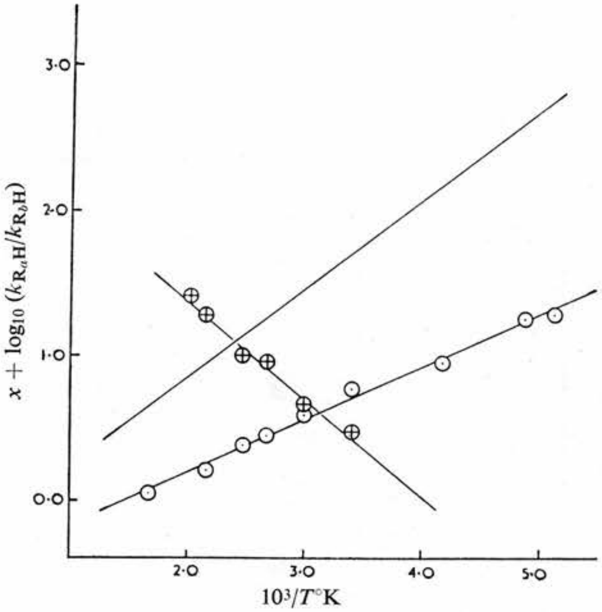

FIG. 1.—Arrhenius plots for chlorination of mixtures.
⊙, k(methane)/k(hydrogen) ; ⊕, k(cyclopropane)/k(ethane), $x = 3·0$.
Full line, k(ethane)/k(methane) ($x = 1·0$) results from ref. (15).

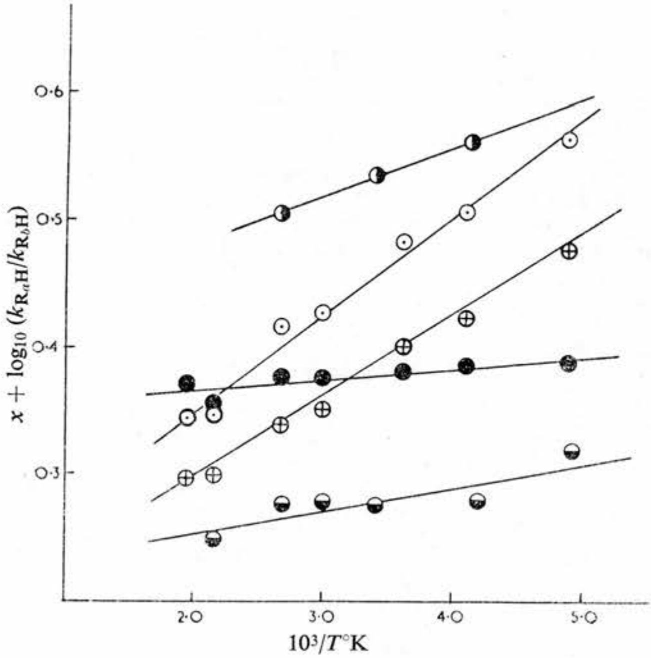

FIG. 2.—Arrhenius plots for chlorination of mixtures.
⊙, k(*sec*-propane)/k(ethane), $x = 0·3$; ●, k(*pri*-propane)/k(ethane), $x = 0·3$;
⊕, k(*sec*-propane)/k(*pri*-propane), $x = 0·3$; ◒, k(*neo*pentane)/k(*pri*-propane),
◑, k(cyclobutane)/k(*pri*-propane).

The occurrence of the back reaction

$$\mathrm{HCl + R = RH + Cl}$$

to any extent would have resulted in spurious values of the rate constant ratios. However, in the presence of a tenfold excess of HCl over Cl_2 no change was observed in the rate constant ratios for the chlorination of *iso*butane at 0°C and 100°C. We have therefore assumed that the back reaction was negligible in our experiments.

Decomposition of the products was, however, found to be important in some experiments. In the chlorination of *iso*butane at temperatures above 100°C and in the chlorination of propane above 300°C the experimental values of k_{tert}/k_{pri} and k_{sec}/k_{pri} were

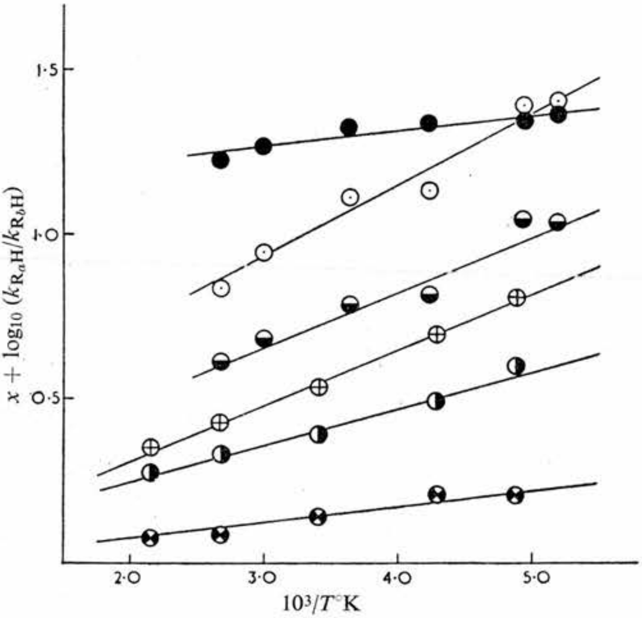

FIG. 3.—Arrhenius plots for chlorination of mixtures.
⊙, *k*(*tert-iso*butane)/*k*(ethane), $x = 1{\cdot}0$; ●, *k*(*pri-iso*butane)/*k*(ethane), $x = 1{\cdot}0$; ◒, *k*(*tert-iso*butane)/*k*(*pri-iso*butane), $x = 1{\cdot}0$; ⊕, *k*(*sec-n*-butane)/*k*(ethane); ⊗, *k*(*pri-n*-butane)/*k*(ethane); ◑, *k*(*sec-n*-butane)/*k*(*pri-n*-butane).

TABLE 1.—RELATIVE RATE FACTORS FOR COMPETING REACTIONS

$$\mathrm{R}_a\mathrm{H} + \mathrm{Cl} = \mathrm{R}_a + \mathrm{HCl}$$
$$\mathrm{R}_b\mathrm{H} + \mathrm{Cl} = \mathrm{R}_b + \mathrm{HCl}$$

mixture $\mathrm{R}_b\mathrm{H}$ + $\mathrm{R}_a\mathrm{H}$	$A_{\mathrm{R}_a\mathrm{H}}/A_{\mathrm{R}_b\mathrm{H}}$		$E_{\mathrm{R}_b\mathrm{H}} - E_{\mathrm{R}_a\mathrm{H}}$
	per molecule	per H atom	cal mole^{-1}
$H_2 + CH_4$	0·30	$0{\cdot}15 \pm 0{\cdot}01_5$ (*a*)	1,650 ± 60
$CH_4 + C_2H_6$ (*b*)	3·85	2·57 ± 0·16	2,810 ± 45
C_2H_6 + *pri*-C_3H_8	1·11	$1{\cdot}11 \pm 0{\cdot}02_5$	40 ± 10
C_2H_6 + *sec*-C_3H_8	0·78	2·34 ± 0·04	360 ± 10
C_2H_6 + *pri-n*-C_4H_{10}	0·89	0·89 ± 0·04	250 ± 30
C_2H_6 + *sec-n*-C_4H_{10}	0·94	1·41 ± 0·08	770 ± 35
C_2H_6 + *pri-iso*C_4H_{10}	1·30	0·87 ± 0·04	220 ± 25
C_2H_6 + *tert-iso*C_4H_{10}	0·18	1·08 ± 0·10	1,020 ± 45
pri-C_3H_8 + *neo*C_5H_{12}	1·65	0·82 ± 0·02	80 ± 20
C_2H_6 + cycloC_3H_6	0·56	0·56 ± 0·02	− 3,100 ± 30
pri-C_3H_8 + cycloC_4H_8	2·54	1·90 ± 0·13	175 ± 40

(*a*) Errors quoted are 50 % probability limits.
(*b*) result taken from ref. (15).

found to be lower than expected and to depend upon the duration of the experiment. This was traced to the decomposition of the alkyl chlorides; for example, *tert*-butyl chloride was found to have almost completely decomposed into *iso*butene and HCl after 30 min at 194°C. Although addition of a tenfold excess of HCl suppressed this decomposition it caused considerable isomerization of *iso*butyl chloride so that when the chlorination of *iso*butane was carried out at 194°C in the presence of excess HCl, the observed values of k_{tert}/k_{pri} were unduly high. We have therefore included in fig. 1-3 only results of those experiments where there was no evidence of thermal decomposition of the reaction products.

The occurrence of thermal decomposition of the chlorides is probably the explanation of the curvature of the activation energy plots obtained by Hass, McBee and Weber[13] for high temperatures. It is, however, difficult to see why their low-temperature results are so much higher than ours unless secondary chlorination of the products also took place in their experiments. Their rate constant ratios k_{tert}/k_{pri} and k_{sec}/k_{pri} for *iso*butane and propane would be high if the primary chlorides were more readily chlorinated than the secondary and tertiary. This appears likely in view of the deactivating effect of chlorine substitution observed in the chlorination of various alkyl chlorides.[16, 17]

DISCUSSION

The absolute values of the rate constants of the chlorination reactions studied are obtained by assuming the value of Ashmore and Chanmugam [3] for reaction (1) with hydrogen. The values so obtained for A_{RH}, E_{RH} and k_{RH} at 298°K are presented in table 2. The errors quoted are the cumulative 50 % probability limits assuming that the value for hydrogen is exact.

TABLE 2.—ABSOLUTE RATE FACTORS FOR THE REACTIONS

$$RH + Cl = R + HCl$$

assuming $k_{HH} = 8{\cdot}0 \times 10^{13} \exp[-5500/RT]$ mole^{-1} cm^3 sec^{-1}

type of bond attacked	RH	$10^{-13} \times A_{RH}$ per H atom	E_{RH} cal mole^{-1}	$10^{-13} \times k_{RH}$ per H atom at 298°K
	H_2	4·0	5500	$3{\cdot}6 \times 10^{-4}$
	CH_4	0·6 ± 0·1	3850 ± 60	$0{\cdot}9 \times 10^{-3}$
primary	C_2H_6	1·5 ± 0·2	1040 ± 75	$0{\cdot}25_5$
"	C_3H_8	1·7 ± 0·2	1000 ± 75	0·31
"	*n*-C_4H_{10}	1·4 ± 0·2	790 ± 80	0·37
"	*iso*C_4H_{10}	1·3 ± 0·2	820 ± 80	$0{\cdot}32_5$
"	*neo*C_5H_{12}	1·4 ± 0·2	920 ± 80	$0{\cdot}29_5$
secondary	C_3H_8	3·6 ± 0·5	680 ± 75	1·14
"	*n*-C_4H_{10}	2·2 ± 0·3	270 ± 80	1·40
"	cycloC_3H_6	0·9 ± 0·1	4140 ± 80	$0{\cdot}8 \times 10^{-3}$
"	cycloC_4H_8	3·2 ± 0·4	825 ± 85	0·79
tertiary	*iso*C_4H_{10}	1·7 ± 0·3	20 ± 90	1·64

The activation energies, in general, fall as the hydrocarbon becomes more complex. This applies both to primary and secondary C—H bonds. A limiting value of 700-750 cal mole^{-1} appears to be reached for the E of attack at primary bonds as the length of the hydrocarbon chain increases. The values for secondary attack are some 300-500 cal mole^{-1} lower than for primary attack in the same molecule. The effect of branching in a hydrocarbon of given carbon number is to raise the E for primary attack slightly. The E's for abstraction from cyclic hydrocarbons were higher than for the corresponding alkanes. The very high value for cyclopropane ($E = 4140$ cal mole^{-1}) is in accord with the views of Brown [18] on the effect of ring strain on activation energies and with the findings of Skinner [19] and Linnett [20] that the C—H bonds in cyclopropane are stronger than normal secondary bonds, being near-ethylenic in character. In cyclobutane the effect of ring strain is much less ($E = 825$ cal mole^{-1}) although still noticeable.

When considering activation energies of the order of a few hundred cal it is important to remember that E differs from the critical internal energy increment at absolute zero $\Delta U_0^{\ddagger}$ according to [21]

$$\Delta U_0^{\ddagger} = E - \boldsymbol{R}T - \int_0^T \Delta C_v^{\ddagger} \mathrm{d}T$$

where $\Delta C_v^{\ddagger}$ is the difference between the constant volume specific heats of RHCl and RH + Cl. If the frequencies of the additional modes of vibration introduced on formation of RHCl are assumed to have values consistent with those necessary for explanation of the A factors (see later), it may readily be shown that at 298°K,

$$\Delta U_0^{\ddagger} < E - 500 \text{ cal mole}^{-1}.$$

Thus for attack at the tertiary bond in *iso*butane ($E = 20$ cal mole^{-1}) and at the secondary bond in *n*-butane ($E = 270$ cal mole^{-1}), $\Delta U_0^{\ddagger}$ is negative. Although negative activation energies are now well established for some third-order reactions [22] they have not so far been reported for bimolecular reactions such as (1). However, there seems no fundamental reason why they should not be observed. It is of course possible that the rather small negative values found here simply reflect an experimental error in the value assumed for the hydrogen reaction and clearly further work is necessary before a definite conclusion can be reached. We require firstly a further absolute determination of a rate constant of some reaction of the type (1) and secondly the examination of further reactions where E is likely to be very low or even negative.

While activation energies cannot yet be calculated absolutely the position regarding A factors is much more satisfactory. According to transition state theory A for a bimolecular reaction is given by [21]

$$A = e^2 \frac{\boldsymbol{k}T}{\boldsymbol{h}} \exp\,[(\Delta S_{\text{tr}}^{\ddagger} + \Delta S_{\text{rot}}^{\ddagger} + \Delta S_{\text{vib}}^{\ddagger})/\boldsymbol{R}].$$

The translational entropy of activation, at a standard state of 1 mole cm^{-3} and 298°K, for reaction (1) is

$$\Delta S_{\text{tr}}^{\ddagger} = \tfrac{3}{2}\boldsymbol{R} \ln (M^{\ddagger}/M) - 16{\cdot}60 \text{ cal/mole deg.},$$

where $M^{\ddagger}$ and M are the molecular weights of RHCl and RH, and the rotational entropy of activation per H atom is

$$\Delta S_{\text{rot}}^{\ddagger} = \tfrac{1}{2}\boldsymbol{R} \ln (A^{\ddagger}B^{\ddagger}C^{\ddagger}/ABC)$$

where $A^{\ddagger}B^{\ddagger}C^{\ddagger}$ and ABC are the products of the principal moments of inertia of RHCl and RH. Values for these products may be calculated with sufficient accuracy for the present purpose by making reasonable assumptions about the structures of RHCl and RH. Calculations for H_2, CH_4, C_2H_6, C_3H_8, *iso*C_4H_{10} and *neo*C_5H_{12} have been made by Knox and Trotman-Dickenson [23] and for n-C_4H_{10}, cycloC_3H_6 and cycloC_4H_8 by the present authors.

Using the values so obtained a rotational/translational A factor may be calculated according to the equation

$$A_{\text{calc.}} = e^2 \frac{\boldsymbol{k}T}{\boldsymbol{h}} \exp\,[(\Delta S_{\text{tr}}^{\ddagger} + \Delta S_{\text{rot}}^{\ddagger})/\boldsymbol{R}].$$

The vibrational entropy of activation is then given by

$$\Delta S_{\text{vib}}^{\ddagger} = \boldsymbol{R} \ln (A_{\text{expt.}}/A_{\text{calc.}}).$$

The relevant values are given in table 3.

Theoretical calculations of A factors have been made by Pitzer [24] and by Wilson and Johnston.[25] The basic assumption made in both treatments is that the force constants for the new vibrations introduced in forming a complex of a given type such as RHCl do not change with R. Using the experimental value for A_{HH}, Pitzer calculated a value for A_{CH_4} within 50 % of the experimental value. The procedure employed may readily be extended to other hydrocarbons by making allowance for the changes in reduced mass and reduced moment of inertia in going from HHCl to RHCl. The values of $\Delta S^{\ddagger}_{\text{vib}}$ obtained in this way are recorded in table 4, column 3. These values take account only of the bending and long stretching of the R—H—Cl bonds in the complex. The calculations of Wilson and Johnston take account of other modes of vibration whose frequencies change in forming the complex, particularly the wagging of R against the rest of the molecule. Their calculations were, however, for CH_3, CD_3, H and Br, not for Cl, but, as seen from the figures given in table 4, columns 4 and 5, the values of $\Delta S^{\ddagger}_{\text{vib}}$ for CH_3 and Br are comparable and probably do not differ much from those for Cl.

TABLE 3.—CALCULATED AND EXPERIMENTAL *A* FACTORS FOR THE REACTION

$RH + Cl = R + HCl$

RH	$\Delta S^{\ddagger}_{\text{tr}}$ + 16.60 cal/mole deg.	$\Delta S^{\ddagger}_{\text{rot}}$	$10^{-13} \times A_{\text{calc.}}$ per H	$10^{-13} \times A_{\text{expt.}}$ per H	$A_{\text{expt.}}/A_{\text{calc.}}$	$\Delta S^{\ddagger}_{\text{vib}}$ cal/mole deg.
H_2	8·73	5·51	1·40	4·0	$2{\cdot}8_5$	2·1
CH_4	3·48	6·25	0·144	0·6	4·1	2·8
C_2H_6	2·32	4·96	0·042	1·5	36	7·1
pri-C_3H_8	1·77	3·45	0·0150	1·7	115	9·4
pri-n-C_4H_{10}	1·42	3·15	0·0107	1·4	130	9·6
pri-isoC_4H_{10}	1·42	2·77	0·0089	1·3	145	9·8
neoC_5H_{12}	1·19	2·63	0·0074	1·4	190	10·4
sec-C_3H_8	1·77	3·70	0·0170	3·6	210	10·6
sec-n-C_4H_{10}	1·42	2·74	0·0089	2·2	250	10·9
cycloC_3H_6	1·83	4·05	0·0208	0·9	43	7·5
cycloC_4H_8	1·45	3·36	0·0121	3·2	270	11·1
tert-isoC_4H_{10}	1·42	2·67	0·0084	1·7	200	10·5

TABLE 4.—COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF $\Delta S^{\ddagger}_{\text{vib}}$

RH	$\Delta S^{\ddagger}_{\text{vib}}$ expt. for Cl (*a*)	$\Delta S^{\ddagger}_{\text{vib}}$ calc. for: Cl (*b*)	CH₃ (*c*)	Br (*c*)
H_2	2·1	1·0	1·3	3·6
CH_4	2·8	5·8	3·6	—
C_2H_6	7·1	8·1	6·1	—
cycloC_3H_6	7·5	8·4	—	—
pri-C_3H_8	9·4	8·5	—	—
sec-C_3H_8	10·6	8·4	—	—
cycloC_4H_8	11·1	8·8	—	—
pri-n-C_4H_{10}	9·6	9·0	—	—
sec-n-C_4H_{10}	10·9	8·8	7·0	—
sec-n-C_5H_{12}	—	—	7·0	—
sec-n-C_6H_{14}	—	—	7·0	—
pri-isoC_4H_{10}	9·8	9·0	—	—
tert-isoC_4H_{10}	10·5	8·8	—	8·0
neoC_5H_{12}	10·4	9·2	—	—
C_∞	—	9·7	—	—

(*a*) values from table 3.

(*b*) values obtained assuming that force constants for stretching and bending of R—H—Cl bonds in complex same as for H—H—Cl; cf. ref. (22).

(*c*) values obtained from data in ref. (23).

There are three notable points of disagreement between the experimental and calculated values. (i) The experimental value for methane is considerably smaller than any of those calculated. There is no obvious explanation of this and it is most unlikely that the experimental value is seriously in error since it agrees well with the value obtained independently by Pritchard, Pyke and Trotman-Dickenson.[12]

(ii) While there is reasonable agreement between the experimental and calculated values for ethane and cyclopropane, the experimental values increase much more rapidly than do the calculated ones as the hydrocarbon becomes larger. This can only mean that the calculations ignore contributions to $\Delta S^{\ddagger}_{\text{vib}}$ from vibrational modes which become important in the more complex molecules. The largest contributions will probably come from changes in the lowest vibration frequencies. Since the lowest frequencies in cyclopropane and ethane are about 800 cm^{-1}, changes in them resulting from the attachment of a Cl atom to the molecule will only give small entropy contributions. However, when RH contains three or more C atoms in a straight chain, chain deformation vibrations of much lower frequencies occur, and in a complex hydrocarbon may [26] be as low as 150 cm^{-1}. Changes in these frequencies will result in much larger contributions to the entropy of activation, and the contributions will be larger the longer the chain and the more complex the molecule.

(iii) While the calculations suggest that $\Delta S^{\ddagger}_{\text{vib}}$ should be slightly less for secondary attack than primary attack experiment shows the opposite to be true. It again seems likely that the participation of low frequency chain deformation modes may account for the disagreement since the attachment of a Cl atom to the centre of a hydrocarbon chain will reduce the vibration frequency more than attachment at the end. Thus the entropy of activation should be larger for the secondary attack.

Thus while the major part of the vibrational entropy of activation can be accounted for by the introduction of vibrational modes peculiar to the complex (namely the stretching and bending of the R—H—Cl bonds) significant contributions may also arise from changes in the frequencies of low frequency modes in the original hydrocarbon, such as chain deformation. The vibrational entropy of activation then increases steadily as the hydrocarbon becomes larger but this is almost exactly offset by the decreases in the translational and rotational entropies of activation.

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THE REACTIONS OF CHLORINE ATOMS—A TEST OF THE TRANSITION STATE THEORY

BY J. H. KNOX AND A. F. TROTMAN-DICKENSON

Chemistry Department, The University, Edinburgh

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The relative A factors for reactions of the type $Cl + RH = HCl + R$ have been calculated on the assumptions of the transition state theory. A comparison of these values with the accurate experimental data reveals considerable discrepancies.

The transition state theory of chemical kinetics has been applied with fair success to the calculation of the order of magnitude of the Arrhenius A factors of bimolecular reactions.[1] Little more can however be claimed for two reasons: firstly, doubtful assumptions as to the configurations of the activated complexes had to be made which led to considerable uncertainty in the calculated values, and secondly, experimental results of sufficient accuracy to sustain an unambiguous test were not available. The usual errors in the measurement of activation energies of these reactions were, under the most favorable conditions, of the order of ± 300 cal./mole. The corresponding error in the A factor is then $10^{\pm 0.2}$ (about ± 60%).

In the present paper, relative A factors calculated from transition state theory are compared with those determined experimentally by us[2,3] for the competitive reactions of chlorine atoms with several hydrocarbons. Calculated A factor ratios are also given for a number of reactions which have not yet been studied but which we hope to investigate in due course. These reactions of chlorine atoms offer a number of advantages for such a study. In the first place there is much less doubt about the configuration of the activated complexes in reactions of atoms than in the corresponding reactions of free radicals, there being no uncertainty about the free rotation of the radical in the former case. Secondly, the activation energies of the reactions are low and may therefore be measured with very small absolute errors (although the percentage error will be of the usual magnitude). It may furthermore be assumed that in such cases the bond lengths C–H–Cl will vary little from complex to complex and that the C–H and C–Cl bond lengths will be only slightly longer than those in normal molecules. Thirdly, by employing a competitive technique, relative A factors can be determined with unusual precision. In the most favorable cases relative activation energies have been measured to within 30 cal./mole giving relative A factors to within 5%.

These relative A factors can therefore provide a stringent test of the transition state theory since not only can they be measured experimentally with

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high precision but they may also be calculated with high accuracy making use of fewer assumptions than are required in the calculation of absolute values.

According to transition state theory the relative A factors for the competitive reaction of chlorine atoms with methane and ethane are given by the equation

$$\frac{A_{\mathrm{CH_4}}}{A_{\mathrm{C_2H_6}}} = \frac{[\phi^{\mathrm{tr}}_{\mathrm{CH_4Cl}}\ \phi^{\mathrm{rot}}_{\mathrm{CH_4Cl}}\phi^{\mathrm{vib}}_{\mathrm{CH_4Cl}}]/[\phi^{\mathrm{tr}}_{\mathrm{CH_4}}\ \phi^{\mathrm{rot}}_{\mathrm{CH_4}}\ \phi^{\mathrm{vib}}_{\mathrm{CH_4}}]}{[\phi^{\mathrm{tr}}_{\mathrm{C_2H_6Cl}}\ \phi^{\mathrm{rot}}_{\mathrm{C_2H_6Cl}}\ \phi^{\mathrm{vib}}_{\mathrm{C_2H_6Cl}}]/[\phi^{\mathrm{tr}}_{\mathrm{C_2H_6}}\ \phi^{\mathrm{rot}}_{\mathrm{C_2H_6}}\ \phi^{\mathrm{vib}}_{\mathrm{C_2H_6}}]}$$

$$= \exp\left[\frac{1}{R}(\Delta S^{\mathrm{tr}}_{\mathrm{CH_4}} - \Delta S^{\mathrm{tr}}_{\mathrm{C_2H_6}} + \Delta S^{\mathrm{rot}}_{\mathrm{CH_4}} - \Delta S^{\mathrm{rot}}_{\mathrm{C_2H_6}} + \Delta S^{\mathrm{vib}}_{\mathrm{CH_4}} - \Delta S^{\mathrm{vib}}_{\mathrm{C_2H_6}})\right]$$

where the partition functions, denoted by ϕ's, are measured from the ground state of the parent molecule and of the complex, respectively. The activation energy appropriate to these theoretical A factors is therefore the activation energy at absolute zero which may be denoted ΔE°_0. The ΔS values are the entropies of activation appropriate to the translational, rotational and vibrational degrees of freedom. In the above expression for the A factors the transmission coefficients have been omitted, and the symmetry numbers are taken to be included in the rotational partition functions. If the partition functions are evaluated without the symmetry numbers the values for the A factors are those for individual hydrogen atoms. Denoting such factors by A' the above equation can be written

$$\frac{A'_{\mathrm{CH_4}}}{A'_{\mathrm{C_2H_6}}} = \left\{\frac{M_{\mathrm{CH_4Cl}}/M_{\mathrm{CH_4}}}{M_{\mathrm{C_2H_6Cl}}/M_{\mathrm{C_2H_6}}}\right\}^{3/2} \times \left\{\frac{(ABC)_{\mathrm{CH_4Cl}}/(ABC)_{\mathrm{CH_4}}}{(ABC)_{\mathrm{C_2H_6Cl}}/(ABC)_{\mathrm{C_2H_6}}}\right\}^{1/2} \times \exp\left[\frac{1}{R}(\Delta S^{\mathrm{vib}}_{\mathrm{CH_4}} - \Delta S^{\mathrm{vib}}_{\mathrm{C2H_6}})\right]$$

where M's are the molecular weights of the various substances and the product (ABC) is the product of the moments of inertia about the three principal axes of the molecules. While the masses are known exactly, the values of (ABC) are not known with the same precision because of the slight uncertainty (probably less than 0.2 Å.) as to the C–H–Cl distances. Values of (ABC) can however be calculated to any degree of accuracy once a configuration has been accepted. Since any error in the C–H–Cl distances will affect the (ABC)'s of all complexes in the same sense and roughly in the same proportion, any error of choice will largely cancel out. There are three likely sources of error in comparing the calculated values with the experimental ones. The calculation of the vibrational entropy term is not possible with any certainty. It will however almost certainly be small. The vibrational entropies of methane and ethane are both less than 1.e.u. and the vibrational entropies of activation will therefore be much smaller than 1 e.u. Differences in vibrational entropies of activation as between say methane and ethane will be even smaller and probably not greater than ±0.1 e.u. The vibrational term which might at first sight appear to result in large uncertainty in the calculation of the theoretical A factor should not therefore contribute more than about $\exp 0.1/R$, that is, about 5% uncertainty.

In these calculations the contributions from internal rotations in the parent molecules and the complexes have been neglected. The appropriate allowance may readily be made only in the simplest cases where the rotators are symmetrical tops. In the case of ethane, for example, the contribution to the entropies of the parent and the complex due to free internal rotation are, ignoring the symmetry factor, 5.06 and 5.66 e.u., respectively. An error of about 30% may therefore be introduced in the particular case of ethane/methane by ignoring internal rotation. For higher homologs the contributions due to changes in internal rotation will be smaller than this. In the cases considered we are moreover concerned with restricted rotation rather than free rotation, and the effect of neglecting rotations is thus further reduced.

Lastly, there is likely to be a discrepancy between the theoretical and experimental A factors resulting from the fact that the experimental activation energy and the theoretical activation energy differ according to the equation

$$\Delta E_{\mathrm{exp}} = \Delta E_0{}^\circ + \int_0^T \Delta C_{\mathrm{v}}\, \mathrm{d}T$$

giving $$A_{\mathrm{exp}} = A_{\mathrm{calc}} \exp[(\textstyle\int \Delta C\mathrm{v}/\mathrm{d}T)/RT]$$

The difference in ΔC_{v} for two similar reactions will however be very small since the translational and rotational specific heat changes will be identical for the two reactions and only the changes in vibrational specific heats will be important. As with the vibrational entropy contributions, these will be very small indeed.

We therefore conclude that the major factors influencing the relative A factors for two similar reactions are the changes in the translational and rotational entropies. Errors of up to some 5% are introduced by ignoring the vibrational contributions, and rather more by ignoring internal rotation. The latter is however never likely to be more than about 20%, even in an extreme case such as the comparison of the chlorinations of methane and ethane.

The details of the calculations are given below and a summary of the results appears in Table I. It already has been shown[2] that A factors of the right order of magnitude may be calculated for these chlorination reactions so that considerable interest attaches to the much more accurate values found for the relative A factors. These are given in Table II where they are compared with the experimentally determined values. Examination of the table reveals that the simple transition state theory predicts only approximately the relative A factors and that the discrepancy between the calculated and the experimental values is in the sense that too large an A factor is predicted for the lighter relative to the heavier molecules except in the indirect comparison of neopentane with isobutane where the mass difference is relatively small. These discrepancies (factors of up to ten) are well without both experimental error and any reasonable estimate of the theoretical error in our calculations. They may possibly be resolved in terms of transmission coefficients which we have neglected, but as yet no general method has been suggested by which such allowance might be made. The calculations show clearly the limits of the application of the simple transition state theory, and

TABLE I

TRANSLATIONAL AND ROTATIONAL ENTROPIES

Compound	S_{trans}	$\log_{10}$ ABC[a]	σ	S_{rot}
Cl	36.6	0	..	0
H_2	28.1	$\bar{1}.68$[b]	2	4.1
H_2-Cl	36.8	0.89[b]	1	11.0
CH_4	34.3	1.56	12	10.3
CH_4–Cl	37.8	4.29	3	19.3
C_2H_6	36.1	3.62	18	14.2
C_2H_6–Cl	38.9	5.78	3	22.7
C_3H_8	37.2	4.84	18	17.0
C_3H_8 cond.[c]	37.2	4.65	18	16.5
p-C_3H_8–Cl (a)	39.0	6.36	3	24.0
p-C_3H_8–Cl (a) cond.	39.0	6.26	3	23.8
p-C_3H_8–Cl (b)	39.0	6.35	3	24.0
p-C_3H_8–Cl (b) cond.	39.0	6.31	3	23.9
s-C_3H_8–Cl	39.0	6.47	9	22.1
s-C_3H_8–Cl cond.	39.0	6.43	9	22.0
iso-C_4H_{10}	38.1	5.76	81	16.1
iso-C_4H_{10} cond.	38.1	5.46	81	15.4
p-iso-C_4H_{10}–Cl (a) cond.	39.5	6.91	9	23.1
p-iso-C_4H_{10}–Cl (b) cond.	39.5	6.75	9	22.7
t-iso-C_4H_{10}–Cl	39.5	6.93	81	18.7
t-iso-C_4H_{10}–Cl cond.	39.5	6.79	81	18.4
$C(CH_3)_4$[d]	38.8	6.18	324	14.3
$C(CH_3)_4$–Cl[d]	40.1	7.33	27	21.9
CF_3H	38.7	5.11	3	21.2
CF_3H–Cl	40.0	6.86	3	26.2
CCl_3H	40.1	6.88	3	26.2
CCl_3H–Cl	41.1	7.73	3	28.2

[a] Units of ABC are [molecular weight × Å.^{2}]^3. [b] These values are $\log_{10}$ A where A is the moment of inertia. [c] "cond." stands for the condensed CH_3 approximation. [d] The molecule was treated as a series of spherical shells.

TABLE II

RELATIVE *A* FACTORS FOR CHLORINE ATOM REACTIONS

$Cl + RH = HCl + R$

Compounds X Y	Relative *A* factors/H atom A'_X/A'_Y Calcd.	 Exptl.
Hydrogen/methane	9.8	6.3 ± 2
Methane/ethane	3.58	0.39 ± 0.03
Ethane/neopentane	5.43	2.0 ± 0.1
Ethane/chloroform	9.46	.....
Ethane/fluoroform	2.08	.....
p-Propane/*sec*-propane (a)	0.89[a]; 0.82[b]	0.61 ± 0.05
p-Propane/*sec*-propane (b)	0.87[a]; 0.87[b]	
p-isobutane/*t*-isobutane (a)	1.14[c]	0.75 ± 0.1
p-isobutane/*t*-isobutane (b)	0.95[c]	
	Relative *A* factors per molecule,[c] A_X/A_Y	
Ethane/propane[c]	1.9[a] ; 1.6[b]	0.68 ± 0.04
Ethane/isobutane[c]	2.8[b]	0.61 ± 0.04

[a] Calculated for the complete molecule. [b] Calculated using the condensed approximation. [c] These results are given in terms of the molecule as a whole because no experimental distinction was made between the different types of hydrogen atoms.

invite further work on other series of reactions which might likewise be compared with theoretical predictions.

The Calculations.—Values for the translational and rotational entropies have been calculated for each of the reactants and complexes studied. The translational entropies were calculated from the Sackur–Tetrode equation; the values are given in Table I. The values obtained for the rotational entropies depend upon the precise configurations assumed for the molecules (see below). These calculations of the moments of inertia can be considerably simplified if the hydrogen atoms of the methyl groups are "condensed" into the appropriate carbon atom; each methyl group is then treated as a mass of 15 located at the center of gravity of the original methyl group. Some examples of such condensations are given in Table I, and it can be seen from Table II that this simplification yields values of the relative *A* factors which are only slightly different from those obtained by more laborious means.

The Configurations.—It was assumed throughout that the carbon valency angles were all equal to 109.5°. In the linear C–H–Cl groups of the activated complexes the C–H distance was taken as 1.15 Å. and the H–Cl as 1.45 Å.; other bond lengths assumed were C–C 1.54 Å., C–H 0.98 Å., C–F 1.36 Å. and C–Cl 1.76 Å. The following points may be mentioned in connection with the configurations of individual reactants and complexes.

Propane.—Calculations were made for two different configurations of the complex obtained by attack of the chlorine atom at the primary position: (a) in which the chlorine atom in the complex is at the greatest possible distance from the third carbon atom (*i.e.*, with the C–H–Cl bond parallel to the opposite C–C bond) (b) in which the chlorine atom is as close as possible to the third carbon atom.

Isobutane.—Calculations were again made for two configurations of the complex: (a) in which the chlorine atom was at the greatest possible distance from the tertiary hydrogen atom (*i.e.*, the C–H–Cl bond parallel to the tertiary C–H bond); (b) in which the chlorine atom is as close as possible to the tertiary hydrogen atom.

Neopentane.—This molecule was treated as a central atom of mass 12 surrounded by two spherical shells one of mass 48 and radius 1.54 Å. and the other of mass 12 and radius 2.20 Å.; the chlorine atom in the complex was taken to be a distance of 3.65 Å. from the central carbon atom.

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[12]

218. *The Reactions of Fluorine Atoms with Alkanes.*

By G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson.

The hydrogen transfer reactions of fluorine atoms with methane, ethane, propane, cyclopropane, n-butane, isobutane, and neopentane have been studied between $-95°$ and $100°$ by a competitive method based on analysis of the fluorides produced. The activation-energy differences are very small. The A factors of the reactions have been discussed in terms of transition-state theory and compared with those found for chlorine atoms.

THE gas-phase reactions of chlorine atoms with saturated hydrocarbons have recently been extensively studied.[1,2] Kistiakowsky, Van Artsdalen, and their co-workers have investigated the reactions of bromine atoms with alkanes.[3] Much less is known about the reactions by which fluorine atoms abstract hydrogen atoms from saturated compounds. These reactions are interesting because they form a unique series involving three similar atomic reactants. The only comparable series of reactions about which much is known is that involving the lower alkyl radicals, but our knowledge of these reactions is still fragmentary. The halogen atoms offer the considerable advantage for theoretical interpretation in that we know the strengths of the bonds involved to a high accuracy. It might therefore be possible to interpret the activation energies or differences in the activation energies of their reactions. There is more hope, however, that the variations in the A factors of the reactions can be understood. The transition states for the reaction of a hydrocarbon with the different halogens differ only in the mass of the attacking atoms and slightly in the lengths of the bonds and their flexibility.

The rate constants for the attack of bromine atoms on hydrocarbons, according to the equation $Br + RH = R + HBr$, have been measured absolutely, though the values obtained for the higher hydrocarbons are doubtful. The chlorinations have been followed competitively both by the study of the relative rates of consumption of two hydrocarbons in a mixture [1] and by measuring the rates of formation of the distinctive products from the reactions [2] $R + Cl_2 = RCl + Cl$. Reactions in solution have been studied in this way for some years. The very small amounts of the products formed in gaseous systems made the analyses difficult until the invention of gas chromatography. Knox [4] first applied this technique to the chlorination of methane, ethane, and propane. He made use of the fact that when the consumption of RH is small the rate constants for the attack of a chlorine atom on two hydrocarbons R^1H and R^2H are given by:

$$\frac{k_1}{k_2} = \frac{R^1Cl}{R^2Cl} \times \frac{[R^2H]}{[R^1H]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This approach has the advantage that attack on different positions in a molecule yields different products.

The present work involves the application of this technique to the study of fluorine atoms about which very little is known, though the reactions of fluorine with n-butane and isobutane have recently been investigated.[5] The reactions of fluorine atoms have been neglected partly because of experimental difficulty and partly because the reactions are so exothermic that they have been difficult to control. Consequently the reactions of elementary fluorine have been chiefly studied in ill-defined systems designed to conduct away the excessive heat. The products obtained were usually polyfluorides and the analyses are not susceptible to kinetic evaluation.

EXPERIMENTAL

Materials.—Fluorine was generated with an I.C.I. medium-temperature 10 A cell and collected in a soft-glass bulb from which oxygen was removed by flushing with nitrogen. Samples were taken after generation for 5 A-hr. (longer if the cell had not been used for some time). The fluorine was distilled into a soft-glass storage vessel cooled in oxygen boiling under reduced pressure. Fresh samples were taken every 3 days.

The nitrogen (oxygen-free), hydrogen, methane, and cyclopropane were from commercial cylinders. Methane was purified by bulb-to-bulb distillations from liquid oxygen which removed most of the propane, ethane, and ethylene. Carbon dioxide was obtained from a solid block. The butanes were given by the British Petroleum Company and the propane by Imperial Chemical Industries Limited. The ethane and neopentane were of high purity and were obtained from the National Chemical Laboratory. The condensable gases were purified and degassed by bulb-to-bulb distillations and analysed by gas chromatography.

Apparatus.—The high-vacuum system, apart from the fluorine storage vessels, was constructed of Pyrex glass. Stopcocks in contact with fluorine or the reaction products were lubricated with Florube A. The volume of the reaction vessel was 60 c.c. The gas-chromatography system was of standard design with 6 mm. bore columns and a brass thermal conductivity cell with tungsten filaments as detector. Firebrick was of 25—52 mesh.

Procedure.—Small pressures of fluorine were measured on a spoon gauge and introduced by several expansions into a vessel held at the reaction temperature. Either carbon dioxide or nitrogen was mixed with the fluorine as a diluent. The hydrocarbons were measured on a mercury manometer, mixed by convection in a suitable vessel, and expanded into the reaction vessel, the temperature of which was thermostatically controlled by a cooling mixture or vapour jacket. The fluorinating mixture was then expanded into the reaction vessel, where the total pressure was about 16 cm. and the fluorine : hydrocarbon : inert gas ratio was 1 : 20 : 120. The reaction time was varied between 2 and 30 min. without affecting the products. No illumination was required if the fluorine was carefully handled, in agreement with calculations based on the known dissociation constant of elementary fluorine and the probable absolute rate constants of these reactions. The reaction of fluorine with glass, especially Pyrex, yields an inhibitor; oxygen also seems to have some effect. The products were condensed out after passage through a tube of sodium fluoride crystals to remove the hydrogen fluoride.

Hydrogen gas (30—40 $\text{cm.}^3\ \text{min.}^{-1}$) carried the products to the chromatography columns. The products were identified by their elution times, confirmed for n-butyl fluoride by comparison with a sample kindly supplied by Dr. J. M. Tedder. The amounts of products were found by measurement of peak areas, calibrated by collection of individual products as they came off the column, measurement of their volume on a gas burette, and repassage through the chromatography system to check that there was no loss. Each run yielded about 3 μmoles of fluorides. Within experimental error the sensitivities of the monofluorides were identical with the exception of methyl fluoride which gave a 3% lower response.

*Results.**—Runs were done with the following mixtures and pure hydrocarbons. The ratios of the hydrocarbons in the mixtures were varied between 1·5 : 1 and 1 : 1·5. The fluorine : hydrocarbon ratio was varied between 1 : 10 and 1 : 20. No changes in reactivity accompanied these variations. The fluorine : inert gas ratio was varied between 1 : 70 and 1 : 160, without affecting the results except in the cases noted. The choice of mixtures was determined largely by the ease of analysis. The errors quoted are standard errors throughout, determined by normal statistical procedures.

(1) *Methane–ethane.* 31 Runs were carried out between −75° and 78° with nitrogen as inert gas. Analysis was with 32 ft. columns of 20% nitrobenzene–firebrick. A least-squares treatment of the results shown as an Arrhenius plot in Fig. 1 gave

$$k(\text{ethane})/k(\text{methane}) = (0{\cdot}38 \pm 0{\cdot}04) \exp\,[(928 \pm 41)/\boldsymbol{R}T]$$

This expression is obtained directly from the analyses of ethyl fluoride and methyl fluoride and the equation analogous to (1). No allowance is made in this section for the numbers of hydrogen atoms in the reactant molecules.

(2) *Ethane–propane.* 21 runs were carried out at 20° and −60° with carbon dioxide as the inert gas. The columns for analysis were 15 ft. of 25% diethyl phthalate–washed Celite, 2 ft. of 25% nitrobenzene–washed Celite, plus 10 ft. of 25% diethyl phthalate–firebrick. The ratio ethyl fluoride : n-propyl fluoride appeared to fall slightly when the fluorine : carbon dioxide ratio was greater than 1 : 100. It was supposed that this indicated that the ethyl

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* k^{p}, k^{s}, k^{t} relate to reaction at a primary, secondary, or tertiary carbon atom, respectively. Where all the carbon atoms of a molecule are equal this suffix is omitted.

fluoride molecules which are formed by an exothermic reaction were not deactivated sufficiently rapidly at the lower relative pressure of inert gas. Some ethyl fluoride then decomposed to ethylene and hydrogen fluoride. Similar behaviour was observed with cyclopropane. It is not easy to determine very small quantities of an alkene in the presence of large amounts of alkane of the same carbon number but the indications were that in no case did the amount of alkene formed exceed 5% of the amount of appropriate alkyl fluoride. The rate constants are again plotted in Fig. 1:

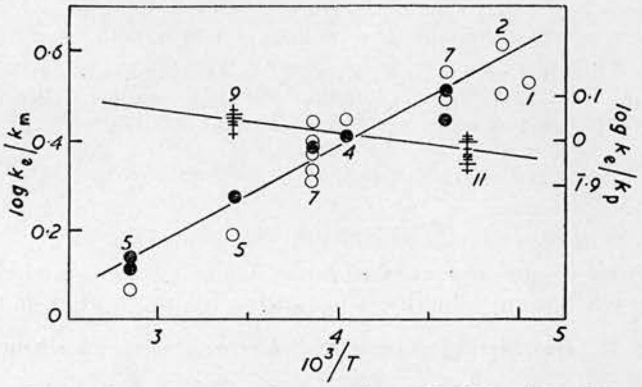


FIG. 1. *Arrhenius plots for the reactions of fluorine atoms with ethane–methane (k_e/k_m; circes) and ethane–propane (k_e/k_p; crosses) mixtures. The filled circles and widened lines indicate two or more coincident points. The figures indicate the number of runs at each temperature.*

$$k(\text{ethane})/k^p(\text{propane}) = (1{\cdot}84 \pm 0{\cdot}05) \exp[-(279 \pm 12)/\boldsymbol{R}T]$$

(3) *Propane–n-butane.* 14 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as the inert gas. The columns were 12 ft. of 25% diethyl phthalate–washed Celite, 2 ft. of 25% nitrobenzene–washed Celite plus 5 ft. of diethyl phthalate–firebrick. No activation energy was found.

$$k^p(\text{propane})/k^p(\text{n-butane}) = 1{\cdot}11 \pm 0{\cdot}06$$
$$k^s(\text{propane})/k^s(\text{n-butane}) = 0{\cdot}56 \pm 0{\cdot}04.$$

(4) *Isobutane–n-butane.* 17 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as the inert gas [analysis as for (3)].

$$k^p(\text{isobutane})/k^p(\text{n-butane}) = 1{\cdot}57 \pm 0{\cdot}06$$

(5) *n-Butane–cyclopropane.* 19 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as the inert gas. Columns were 12 ft. of 25% diethyl phthalate–washed Celite plus 5 ft. of 25% diethyl phthalate–firebrick. When the carbon dioxide : fluorine ratio fell below 100 : 1 a three-carbon product other than cyclopropyl fluoride was formed. At a ratio of 60 : 1 it constituted 50% of the C_3 products and at 80 : 1, 30%. It is likely that the unknown product was a fluoride of propene formed by a typical isomerization of the cyclopropane nucleus activated from its exothermic mode of formation. No activation energy was found at high pressures of the inert gas.

$$k^p(\text{n-butane})/k(\text{cyclopropane}) = 1{\cdot}02 \pm 0{\cdot}06$$
$$k^s(\text{n-butane})/k(\text{cyclopropane}) = 0{\cdot}80 \pm 0{\cdot}06$$

(6) *Propane–cyclopropane.* 25 Runs were carried out in the same manner as for (3). The same dependence of the products on carbon dioxide was found as with (5). Propyl fluorides were not formed by the attack of hydrogen fluoride on cyclopropane.

$$k^p(\text{propane})/k(\text{cyclopropane}) = 1{\cdot}13 \pm 0{\cdot}15$$
$$k^s(\text{propane})/k(\text{cyclopropane}) = 0{\cdot}45 \pm 0{\cdot}05$$

(7) *Isobutane–neopentane.* 14 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as inert gas. Columns were 12 ft. of 25% diethyl phthalate–washed Celite plus 2 ft. of 25% nitrobenzene–washed Celite.

$$k(\text{neopentane})/k^p(\text{isobutane}) = 1{\cdot}22 \pm 0{\cdot}04$$

(8) *Propane.* 74 Runs were carried out (25 with cyclopropane, 21 with ethane, 14 with n-butane) between 36° and −99°. Carbon dioxide and nitrogen were used separately as inert gases with similar results. Columns of 15 ft. of 15% nitrobenzene–firebrick were sometimes used.

$$k^{p}(\text{propane})/k^{s}(\text{propane}) = 2{\cdot}48 \pm 0{\cdot}08$$

(9) *n-Butane.* 124 Runs were carried out (14 with propane, 17 with isobutane, 19 with cyclopropane) at 25°, −25°, and −60° with carbon dioxide as the inert gas. Columns of 10 ft. of 25% dinonyl phthalate–firebrick plus 2 ft. of 25% nitrobenzene–washed Celite were sometimes used.

$$k^{p}(\text{n-butane})/k^{s}(\text{n-butane}) = 1{\cdot}30 \pm 0{\cdot}09$$

(10) *Isobutane.* 16 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as inert gas. Columns were 12 ft. of 25% diethyl phthalate–washed Celite plus 5 ft. of 25% diethyl phthalate–firebrick. An amount of olefin equal to about 5% of the fluorides was always formed.

$$k^{p}(\text{isobutane})/k^{t}(\text{isobutane}) = 6{\cdot}41 \pm 0{\cdot}34.$$

DISCUSSION

The experimental results are summarized in Table 1. For convenience it has been assumed that the reaction of a fluorine atom with a hydrogen atom in one of the higher hydrocarbons requires no activation energy. It has also been assumed that the logarithm of the A factor for the attack of a fluorine atom on a single hydrogen atom in ethane is 12·90 mole^{-1} cm.^{3} sec.$^{-1}$. All the results for fluorine atoms were obtained in this work with the exception of the results for hydrogen which are taken from Mercer and Pritchard [6] who used Pritchard, Pyke, and Trotman-Dickenson's [1] method to study hydrogen–methane mixtures. They found

$$k(\text{methane})/k(\text{hydrogen}) = 1{\cdot}05 \exp\left[-(500 \pm 200)/\boldsymbol{R}T\right]$$

Hydrogen–methane mixtures were not studied in the present work because the hydrogen fluoride formed could not be determined accurately.

TABLE 1. *Reactions of fluorine and chlorine atoms with alkanes.*

	$\log_{10} A$ (mole^{-1} cm.^{3} sec.$^{-1}$)	E (kcal. mole^{-1})	E (kcal. mole^{-1})
Tond Type	Fluorine		Chlorine
H_2	13·67	1710[6]	5500 [a]
CH_4	13·39	1210	3850[1], 3850[2]
Primary C–H bonds			
C_2H_6	12·90 *	280	1000[1], 1040[2]
C_3H_8	12·64	0	1000[2]
n-C_4H_{10}	12·59	0	790[2]
iso-C_4H_{10}	12·61	0	820[2]
neo-C_5H_{12}	12·58	0	920[2]
Secondary C–H bonds			
cyclo-C_3H_6	12·59	0	4140[2]
C_3H_8	12·71	0	680[2]
n-C_4H_{10}	12·67	0	270[2]
Tertiary C–H bond			
iso-C_4H_{10}	12·76	0	20[2]

The A factors listed are for reactions of individual hydrogen atoms of the standard type.

* Assumed value.

[a] Ashmore and Chanmugam, *Trans. Faraday Soc.*, 1953, **49**, 254. Other references as in text.

The present results with the butanes are in good agreement with those of Anson, Fredericks, and Tedder [5] who found at 25° that $k^{p}(\text{n-butane})/k^{s}(\text{n-butane}) = 1{\cdot}20 \pm 0{\cdot}17$ $(1{\cdot}30 \pm 0{\cdot}09)$ and $k^{p}(\text{isobutane})/k^{t}\text{isobutane} = 6{\cdot}47 \pm 0{\cdot}70$ $(6{\cdot}41 \pm 0{\cdot}34)$; the present values are placed in parentheses.

Activation Energies of Fluorine Atom Reactions.—Although the assumption that fluorine atoms react with no activation energy with the higher hydrocarbons may not be precisely correct, it is unlikely that any of the activation energies are large. First, the absence of any activation-energy difference between the attack on the primary and tertiary hydrogen atoms in isobutane, together with the absence of differences for the other higher hydrocarbons, is an indication that no activation energies are involved. Secondly, there is a marked parallelism between the activation energies for the attack of fluorine and chlorine atoms on hydrogen, methane, and ethane. The activation energies for the attack of chlorine atoms on the higher hydrocarbons are very small, those for fluorine must be smaller. The assumption of zero energies of activation is therefore not likely to be in error by more than a few tens of calories at the most. Too little is known about the factors that determine activation energies for the detailed consideration of these small energies to be profitable.

A *Factors of Fluorine Atom Reactions.*—According to transition-state theory the A factor for a bimolecular reaction is given by [7]

$$A = e^2 \,.\, (\boldsymbol{k}T/\boldsymbol{h}) \exp\left[(\Delta S^{\ddagger}_{\mathrm{tr}} + \Delta S^{\ddagger}_{\mathrm{rot}} + \Delta S^{\ddagger}_{\mathrm{vib}})/\boldsymbol{R}\right]$$

The translational entropy of activation for reaction

$$\mathrm{RH + F \rightleftharpoons RHF \longrightarrow R + HF}$$

is given exactly by

$$\Delta S^{\ddagger}_{\mathrm{tr}} = 1{\cdot}5\boldsymbol{R} \ln (M^{\ddagger}/M) - 14{\cdot}75 \text{ cal. mole}^{-1}$$

where $M^{\ddagger}$ and M are the molecular weights of RHF and RH respectively and the standard state is 1 mole cm.$^{-3}$.

The rotational entropy of activation may be obtained from

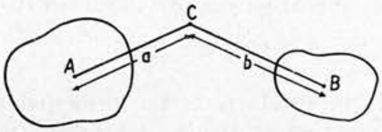
$$\Delta S^{\ddagger}_{\mathrm{rot}} = 0{\cdot}5\boldsymbol{R} \ln (A^{\ddagger}B^{\ddagger}C^{\ddagger}/ABC)$$

where $A^{\ddagger}B^{\ddagger}C^{\ddagger}$ and ABC are the products of the principal moments of inertia of RHF and RH. This value is for reaction at a single hydrogen atom of any type; inclusion of the symmetry numbers in the expression would yield $\Delta S^{\ddagger}_{\mathrm{rot}}$ appropriate to reaction with all the hydrogen atoms of a given type in the molecule. The ABC values can be evaluated graphically with sufficient accuracy by assuming suitable configurations and bond lengths in RH and RHF. C–H and C–C distances have been taken throughout as 1·10 and 1·54 Å except for the half-order bonds in the complexes, *i.e.*, the bonds $\geqslant$C–H–F. After Pauling [8] we have assumed that they are 0·18 Å longer than the corresponding single bonds. All bond angles have been taken as tetrahedral. $A^{\ddagger}B^{\ddagger}C^{\ddagger}/ABC$ is not very sensitive to the exact lengths chosen and increases in the C–F distances by 0·1 Å, for example, lead to increases of only about 3% in the ratio. More serious errors arise from the difficulty of choosing the correct configuration of the molecules, since any molecule containing three or more carbon atoms in an unlinked chain may have an infinite number of configurations depending upon the degree of rotation about each C–C bond. An approximate method of dealing with the situation is to work out ABC values for a few extreme configurations and to take the average value.[9] Fortunately the errors introduced are probably not greater than ±10%. For n-propyl fluoride two configurations were chosen with the fluorine atom as near to and as far from the centre of gravity of the propane molecule as possible. The values of $A^{\ddagger}B^{\ddagger}C^{\ddagger}$ were respectively $1{\cdot}04 \times 10^5$ and $0{\cdot}99 \times 10^5$ AMW (Ångström molecular weight units). For 2-methylpropyl fluoride [$(CH_3)_2CH{\cdot}CH_2F$] the two configurations chosen were those with the fluorine atom as near to and as far from the tertiary hydrogen atom as possible. Rather more divergent values were obtained, $4{\cdot}7 \times 10^6$ and $3{\cdot}7 \times 10^6$ AMW. For the n-butane molecule an expanded chain and bent chain structure are possible. However, calculations by Knox and Nelson for the corresponding chlorine atom complexes showed that almost identical results were obtained with the two structures. Accordingly the moments of inertia have been calculated only for the extended form of the hydrocarbon and for the complex with the fluorine atom as close to the centre of gravity of the butane molecule as possible.

The calculation of the vibrational entropy of activation is much less certain. It is difficult to assign frequencies to the vibrations in RH but quite impossible to do so accurately for the complexes. However, it is likely that many of the vibrations in RH will be little changed by the addition of a fluorine atom and their contributions to $\Delta S^{\ddagger}_{\text{vib}}$ will largely cancel. Only a few vibrations intimately connected with the part of the molecule to which the fluorine atom is attached will give rise to important contributions. These vibrations will be the C–H stretching and C–H wagging in the hydrocarbon which are replaced by five new vibrations in the activated complex. The C–H stretching becomes the reaction co-ordinate and the C–H wagging becomes the wagging of H–F against the rest of the hydrocarbon. The three additional vibrations are the symmetrical stretching of the C–H–F bonds and the doubly-degenerate bending of the C–H–F bonds.

Approximate calculations on this basis have been made by Pitzer [10] and by Wilson and Johnston [11] for various abstraction reactions. They hinge upon the assumption that the force constants for these vibrations do not change with R. Pitzer used the observed A factor of the reaction $\mathrm{Cl} + \mathrm{H}_2 = \mathrm{HCl} + \mathrm{H}$ to deduce $\Delta S^{\ddagger}_{\text{vib}}$ and calculated that the probable bending and stretching frequencies in the complex were 560 cm.^{-1} and 1460 cm.^{-1} respectively. Assuming that the force constants for these modes of vibration were the same in the $\mathrm{CH_3{-}H{-}Cl}$ complex he calculated an A factor for the reaction of chlorine with methane. No account was taken in this calculation of the wagging vibration of the H–Cl against the methyl group in the complex. To calculate the change of frequency due to a change of R, the stretching frequencies are reduced in the ratio of the root of the reduced mass, and the bending frequencies in the ratio of the root of the reduced moment of inertia. For a molecule (see Fig. 2) consisting of two molecular fragments A and B joined to a common atom C the reduced mass is

FIG. 2.



$$\mu = m_a m_b/(m_a + m_b)$$

The reduced moment of inertia is given by

$$\lambda = J_a J_b/(J_a + J_b)$$

where $$J_a = \frac{(m_a + m_c)m_b}{(m_a + m_b + m_c)}\,a^2 + I_a\,; \quad J_b = \frac{(m_b + m_c)m_a}{(m_a + m_b + m_c)}\,b^2 + I_b$$

The m's are the masses of A, B, and C; I_a, I_b are the moments of inertia of A and B about axes through their centres of gravity and perpendicular to the plane of vibration and a and b are the distances of C from the centres of gravity of A and B respectively (Schlapp's formula). When m_c is small in comparison with m_a and m_b (true for all complexes except H–H–F), the formulæ reduce approximately to

$$J_a = \mu a^2 + I_a; \quad J_b = \mu b^2 + I_b$$

Calculations for the RHCl complexes have been carried out by Knox and Nelson [2] and are now extended to the fluorine atom complexes. The values for the various $\Delta S^{\ddagger}_{\text{vib}}$ are given in Table 2.

With chlorine atoms the absolute rate constant for the reaction with hydrogen is known over a range 25—700° and Pitzer's calculations refer to the mid-temperature of this range. The discrepancy in Table 2 between the calculated and theoretical values for the reaction

TABLE 2. *A Factors for Fluorine and Chlorine Atom Reactions.*

	F + RH						Cl + RH[2]		
Bond type RH	$\Delta S^\ddagger_{tr}$ $+14{\cdot}75$	$\Delta S^\ddagger_{rot}$	$\Delta S^\ddagger_{vib}$	log A (calc.)	log A (exp)	$\log \frac{A_{exp}}{A_{calc}}$	log A (calc.)	log A (exp)	$\log \frac{A_{exp}}{A_{calc}}$
H_2	6·99	4·92	0·8	13·22	13·67	+0·50	13·37	13·60	+0·23
CH_4	2·31	5·51	4·8	13·20	13·39	+0·24	13·46	12·78	−0·68
Primary C–H bonds									
C_2H_6	1·46	3·73	6·1	12·90	12·90	0·00	13·28	13·18	−0·10
C_3H_8	1·07	2·66	6·6	12·69	12·64	−0·05	12·98	13·23	+0·25
n-C_4H_{10}	0·84	2·33	6·9	12·62	12·59	−0·03	12·95	13·15	+0·20
iso-C_4H_{10}	0·84	2·05	6·9	12·57	12·61	+0·04	12·87	13·11	+0·24
neo-C_5H_{12}	0·68	1·70	7·1	12·52	12·58	+0·06	12·84	13·15	+0·31
Secondary C–H bonds									
cyclo-C_3H_6	1·11	3·13	6·4	12·76	12·59	−0·17	13·11	12·95	−0·16
C_3H_8	1·07	2·88	6·6	12·74	12·71	−0·03	13·04	13·56	+0·52
cyclo-C_4H_8							12·95	13·51	+0·56
n-C_4H_{10}	0·84	2·33	6·7	12·59	12·67	+0·08	12·84	13·34	+0·50
Tertiary C–H bond									
iso-C_4H_{10}	0·84	1·99	7·1	12·61	12·76	+0·15	12·82	13·23	+0·41

arises because the calculated value used here was for 25°. For the reactions of fluorine atoms there is no such absolute measurement. Therefore equality between the experimental and theoretical A factors for the reactions of fluorine atoms with ethane has been assumed.

The similarity of the pattern of the A factors for the reactions of fluorine atoms to that for the chlorine atoms is demonstrated by the following points: (1) There is a fall in log (A_{exp}/A_{calc}) from hydrogen to ethane, followed by a slight rise as the hydrocarbons become more complex. This rise may be attributed to the part played by alterations in the frequencies of the chain deformations which have been ignored in the calculations. (2) The values of log (A_{exp}/A_{calc}) are slightly higher for attack on a hydrogen atom attached to a secondary than a primary carbon atom. (3) Cyclopropane has the lowest value of log (A_{exp}/A_{calc}) for hydrocarbon higher than methane.

In general, apart from the apparently anomalous position of methane in the chlorinations, the results for fluorine atoms show similar but less marked trends than those for chlorine. The lower mass of the fluorine atom leads to smaller differences in the entropies of activation and to smaller errors resulting from assumptions about the vibrational frequencies. The differences between calculated and experimental A factors for reactions of bromine atoms may be more marked than those for reactions of chlorine atoms.

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UNIVERSITY OF EDINBURGH. [*Received, May* 19*th*, 1959.]

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[13]

818. *The Reactions of Bromine Atoms with Alkanes and Methyl Halides.*

By G. C. FETTIS, J. H. KNOX, and A. F. TROTMAN-DICKENSON.

The reactions of bromine atoms with alkanes and with methyl halides have been studied by competitive bromination in the gas phase and analysis of the products by gas chromatography. Absolute rate constants and Arrhenius parameters are given, based on those previously found for attack on methyl bromide. The activation energies for hydrogen abstraction are probably closely related to the strengths of the C–H bonds broken. The *A* factors predicted by transition-state theory agree well with those found. The deviations are similar to those obtained for chlorine- and fluorine-atom reactions.

INVESTIGATORS have studied the hydrogen-abstraction reactions of bromine atoms both because of the intrinsic interest of the rate constants and the reaction systems and because measurement of the activation energies of the reactions could lead to more accurate values for bond-dissociation energies. The first rate constant of a reaction of an atom or radical with a molecule to be accurately measured was that of the bromine atom with hydrogen. Bodenstein and Lind [1] obtained expressions for the rate of disappearance of bromine from mixtures with hydrogen by thermal processes. The value of the rate constant for reaction (1) derived from their work is shown in Table 1. Their values of the activation energy and *A* factor have been amply confirmed. Kistiakowsky and Van Artsdalen [2] showed that the gas-phase bromination of methane proceeded by the same mechanism as the reaction with hydrogen. The currently accepted value for $D(CH_3–H)$, the strength of the C–H bond in methane, is largely based on their activation energy for the attack on methane (2).

$$Br + H_2 = HBr + H \quad . . . . (1)$$

$$Br + RH = HBr + R \quad . . . . (2)$$

The heat of reaction (2) is related to the activation energies of the forward (E_2) and the reverse (E_{-2}) reaction by the equation:

$$\Delta H_2 = E_2 - E_{-2}$$

Since the heats of formation of H, Br, and HBr are accurately known, the value of $D(CH_3–H)$ can be derived from the equation

$$D(CH_3–H) = (E_2 - E_{-2}) + D(H–Br)$$

The principal uncertainty is in the value of E_{-2}. Andersen and Van Artsdalen [3] also deduced $D(C_2H_5–H)$ from less detailed studies and measured the activation energy for attack of bromine on methyl bromide.[2] Van Artsdalen and his collaborators later studied the reactions of bromine with neopentane,[4] isobutane,[5] and toluene.[6] Although the work was careful and yielded acceptable values for the bond strengths, the results have been suspected because the *A* factors of the abstraction reactions were very high. Benson and Buss [7] explained the discrepancies on the grounds that assumptions made in interpreting the results were invalid for the more reactive compounds. These necessary assumptions were that steady-state concentrations of bromine atoms were reached in times short compared with the lengths of the runs. They calculated that a steady state was only attained for hydrocarbons less reactive than ethane. They also postulated that the reactions were partially heterogeneous, but there is no direct evidence for this.

One reason for adopting a competitive method to study brominations in this investigation was that no assumption had to be made about the rate at which steady-state concentrations were attained. Two hydrocarbons, R^3H and R^4H, were mixed in known

$$\mathrm{Br_2} \longrightarrow \mathrm{2Br}$$

$$\mathrm{Br + R^3H} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{R^3 + HBr} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{Br + R^4H} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \mathrm{R^4 + HBr} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$\mathrm{R^3 + Br_2} \longrightarrow \mathrm{R^3Br + Br} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\mathrm{R^4 + Br_2} \longrightarrow \mathrm{R^4Br + Br} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

proportion and then admitted to a reaction vessel containing bromine. Alkyl bromides were formed by reactions (3), (4), (5), and (6). Reactions (5) and (6) are fast, so we can write, for low percentage consumption of the hydrocarbons:

$$k_3/k_4 = \mathrm{R^3Br[R^4H]/R^4Br[R^3H]}$$

where R^3Br is the total amount of the bromide formed. The bromine-atom concentration does not appear in this expression; therefore steady-state conditions are unnecessary. The rate-constant ratio should also be independent of the molecular bromine and hydrocarbon concentrations in agreement with experiment. The back reactions (−3) and (−4) were found by previous workers to be sufficiently fast to influence the overall rate of bromination of several hydrocarbons. It would be expected that the back reactions should influence k_3/k_4 less than the overall rate because the effect on the formation of R^3Br and R^4Br would tend to cancel out. Experiment showed that k_3/k_4 could be only slightly altered by the addition of far greater quantities of hydrogen bromide than were normally formed in the reactions.

The competitive method yields only relative values of the Arrhenius parameters A_3/A_4 and $E_3 - E_4$ when the reactions are investigated over a range of temperature. Consequently, all values of A_2 and E_2 depend upon an absolute determination. All the results

TABLE 1. *Rate constauts,* A *factors, and activation energies for reactions of type* (2).

RH	log k_2 (100°) (mole⁻¹ cm.³ sec.⁻¹)	log A_2 (mole⁻¹ cm.³ sec.⁻¹)	E_2 (kcal. mole⁻¹)	Ref.
H_2	3·36	14·2	18·5	1, *a*
	3·43	13·8	17·7	*b*
	3·48	13·8	17·6	*c*
	3·28	13·7	17·5	2
	3·27	13·7	17·8	*d*
	3·32	14·0	18·3	
D_2	2·23	13·9	19·9	*b*
CH_4	3·07	13·8	18·3	2
	3·3	14·0	18·3	This work †
C_2H_6	—	—	13·9	3
	6·05	13·895 ± 0·035	13·396 ± 0·088	This work
$C_3H_8^s$	7·76	13·712 ± 0·069	10·149 ± 0·139	This work
$C_4H_{10}^n$	7·23	13·221 ± 0·137	10·225 ± 0·234	This work
$C_4H_{10}^i$	(10·7)	(17·6)	(11·7)	5
	8·90	13·303 ± 0·112	7·509 ± 0·204	This work
Neo-C_5H_{12}	(6·3)	(17·0)	(18·2)	4
	5·87	14·244 ± 0·061	14·289 ± 0·132	This work
$C_6H_5{\cdot}CH_3$	(9·1)	(13·5)	(7·6)	6
CH_3Br *	4·33 *	13·730 *	16·050 *	2
CH_3Cl	5·15	13·616 ± 0·057	14·451 ± 0·156	This work
$CHCl_3$	6·8	12·3	9·3	*e*

* Taken as standard. † These values are less reliable than those given for other compounds.

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obtained in this work are related to the rate constants for the bromination of methyl bromide. It would have been more satisfactory if the bromination of methane could have been used as the standard but the present results with methane were not sufficiently reliable to justify this choice. For many purposes it is the relative rates of reaction of members of series of compounds that are of greatest interest. The competitive method is ideal for such determinations.

Table 1 lists the Arrhenius parameters and rate constants that have been found. The values obtained in this work are for reaction with the indicated hydrogen atoms; as they are much the most reactive atoms, the overall rates are very little different. Those values that are considered incorrect are placed in parentheses. The errors quoted are the 50% probable errors derived by the method of least squares.

Two comparisons can be made with results obtained by Anson, Fredricks, and Tedder.[8] They found that k^{s}(n-butane)/k^{p}(n-butane) = 82 and k^{t}(isobutane)/k^{p}(n-butane) = 1640 at 146°.* Our results give k^{s}(n-butane)/k(ethane) = 143 and k^{t}(isobutane)/k(ethane) = 1820 at 146°. The discrepancy between k^{s}/k^{p} is outside experimental error and it is surprising that the values of k^{t}/k^{p} which were found from $(k^{t}/k^{s})\,.\,(k^{s}/k^{p})$ agree so well. No explanation can be advanced for these observations. It may be noted that k^{s}(propane)/k(ethane) = 83 at 146°. Fredricks and Tedder [9] also found that attack on a hydrogen atom in the 1-position in n-butyl chloride occurred 34 times as fast as attack on a primary hydrogen in n-butane at 146°. The agreement with our value of k(methyl chloride)/k(methane) = 50 for each hydrogen atom is as close as could be expected.

A *Factors of Bromine-atom Reactions.*—According to transition-state theory the A factor for a bimolecular reaction is given by

$$A = e^{2}(\boldsymbol{k}T/\boldsymbol{h}) \exp\,[(\Delta S^{\ddagger}_{\mathrm{tr}} + \Delta S^{\ddagger}_{\mathrm{rot}} + \Delta S^{\ddagger}_{\mathrm{vib}})/\boldsymbol{R}]$$

The translational entropy of activation for reaction

$$\mathrm{RH} + \mathrm{Br} \rightleftharpoons \mathrm{RHBr} \longrightarrow \mathrm{R} + \mathrm{HBr}$$

is given exactly by

$$\Delta S^{\ddagger}_{\mathrm{tr}} = 1{\cdot}5\boldsymbol{R}\ln\,(M^{\ddagger}/M) - 19{\cdot}02 \text{ cal. mole}^{-1}\text{ deg.}^{-1}$$

where $M^{\ddagger}$ and M are the molecular weights of RHBr and RH respectively and the standard state is 1 mole cm.$^{-3}$.

The rotational entropy of activation can be obtained from

$$\Delta S^{\ddagger}_{\mathrm{rot}} = 0{\cdot}5\boldsymbol{R}\ln\,(A^{\ddagger}B^{\ddagger}C^{\ddagger}/ABC)$$

where $A^{\ddagger}B^{\ddagger}C^{\ddagger}$ and ABC are the products of the principal moments of inertia of RHBr and RH. This value is for reaction at a single hydrogen atom of any type; inclusion of the symmetry numbers in the expression would yield $\Delta S^{\ddagger}_{\mathrm{rot}}$ appropriate to all the hydrogen atoms of a given type in the molecule. The ABC values can be evaluated graphically with sufficient accuracy by assuming suitable configurations and bond lengths in RH and RHBr. C–H and C–C distances have been taken as 1·10 and 1·54 Å except for the half-order bonds in the complexes, *i.e.*, the bonds $\geqslant$C–H–Br. Following Pauling, we have assumed that they are 0·18 Å longer than the corresponding single bonds, *i.e.*, C–H = 1·28 Å, H–Br = 1·59 Å. All bond angles have been taken as tetrahedral with the exception of ∠CHBr which has been taken as 180°. It was found that the results of similar calculations for the reactions of chlorine and fluorine atoms depended little on the precise dimensions assumed for the complex. The products of the moments of inertia are therefore unlikely to be in error by more than a few units %.

The calculation of the vibrational entropies of activation is much less certain. The procedure followed is that adopted for the chlorine [10] and fluorine atoms.[11] Briefly, it was

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* k^{p}, k^{s}, k^{t} relate to reaction at a primary, secondary, or tertiary carbon atom, respectively. Where all the carbon atoms of a molecule are identical this suffix is omitted.

assumed that most of the molecular motions of the complex would be the same as those of the reactant. Hence they could be disregarded in calculating the change of vibrational entropy. Only those vibrations most intimately associated with the site of the reaction should be greatly altered. The alteration will be similar for the members of a series such as the paraffins. It has been assumed that the only new vibrations that have to be considered are the symmetrical stretching and double degenerate bending of the R–H–Br bond. The stretching of the C–H bond that becomes the reaction co-ordinate makes a negligible contribution to the initial vibrational entropy. This simplification might introduce an error into the absolute values calculated for the *A* factors but should have little effect on the accuracy of the relative *A* factors calculated for different members of a series. The frequencies of the bending motion of the R–H–Br bonds were calculated in the same way as those for fluorine atoms, the same force constant being assumed. This is a straightforward application of classical mechanics; the frequency is simply a function of the masses of R, H, and Br and the internuclear distances. The force constants selected were those derived by Pitzer[12] to equate the calculated and experimental *A* factors for the reaction $Cl + H_2 = HCl + H$. The calculations are summarized in Table 2, and the results for $\log (A_{exp.}/A_{calc.})$ for bromine atoms are compared with the equivalent quantities for chlorine and fluorine atom reactions.

The absolute rate constant for the reaction of chlorine atoms with hydrogen was determined between 25° and 700°. Pitzer's calculations refer to the mid-temperature of this range. The discrepancy in Table 2 between the calculated and experimental values for the reaction arises because the calculated value here was for 25°. No rate constant of a fluorine-atom reaction has been measured absolutely. The values in Table 2 are based on the assumption that the calculated and experimental *A* factors for ethane are equal.

TABLE 2. A *Factors for bromine-, chlorine-, and fluorine-atom reactions.*

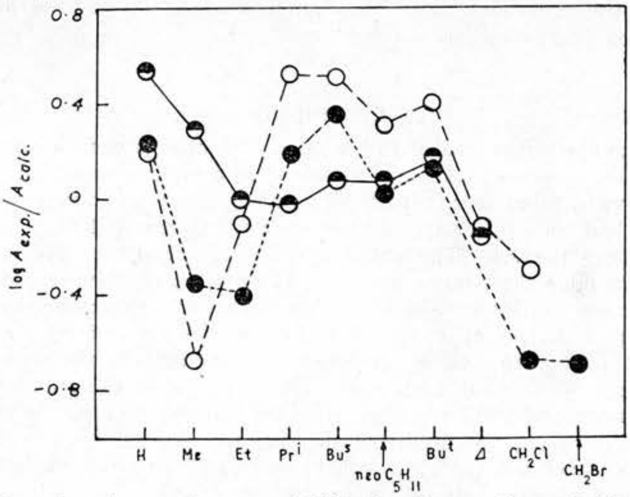
	Br						Cl	F
Bond type RH	$\Delta S^{\ddagger}_{tr}$ +19·02	$\Delta S^{\ddagger}_{rot}$	$\Delta S^{\ddagger}_{vib}$	log *A* (calc.)	log *A* (exp.)	$\log \frac{A_{exp.}}{A_{calc.}}$	$\log \frac{A_{exp.}}{A_{calc.}}$	$\log \frac{A_{exp.}}{A_{calc.}}$
H_2	11·05	6·85	1·1	13·66	13·90	+0·24	+0·23	+0·54 *
CH_4	5·34	7·06	7·2	13·78	13·42	−0·36	−0·68	+0·29 *
Primary C–H bonds								
C_2H_6	3·86	5·50	9·0	13·53	13·12	−0·41	−0·10	0·00 †
neo-C_5H_{12} ...	2·22	3·34	11·3	13·20	13·17	+0·03	+0·31	+0·06
Secondary C–H bonds								
C_3H_8	3·08	4·90	9·0	13·23	13·41	+0·18	+0·52	−0·03
n-C_4H_{10}	2·58	4·05	10·5	13·26	13·62	+0·36	+0·50	+0·08
Tertiary C–H bonds								
iso-C_4H_{10} ...	2·58	3·66	10·5	13·18	13·30	+0·12	+0·41	+0·15
Halides								
CH_3Cl	2·83	6·61	10·3	13·82	13·14	−0·68	−0·29	—
CH_3Br	1·83	6·90	11·6	13·95	13·25	−0·70	—	—

S in cal. $mole^{-1}$ $deg.^{-1}$; *A* in $mole^{-1}$ $cm.^3$ $sec.^{-1}$.
* The figure in ref. 11 is incorrect. † Assumed, see ref. 11.

No adjustable parameters were involved in the calculations of the *A* factors for the bromine atoms. The good agreement with the experimental values is therefore most satisfactory. Wilson and Johnston[13] calculated a similar value for the reaction of hydrogen ($\log A_{calc.} = 14{\cdot}1$) but a rather lower value for isobutane (12·4). The smallness of $\log (A_{exp.}/A_{calc.})$ for the reactions is a strong argument that the experimental values obtained in this work are approximately correct and that those previously reported for the higher hydrocarbons are wrong.

The probable errors for the $\log A_{exp.}$ derived by the method of least squares are lower than those usually found in kinetic studies. Nevertheless, little significance can be attached to the fourth significant figure, and there must frequently be an error in the third figure even if relative values only are considered. The parallelism, shown in the Figure, between the values of $\log (A_{exp.}/A_{calc.})$ for the three series of halogen-atom reactions is more marked than could resonably have been expected. Two features that were noted for chlorine and fluorine are again found for bromine, *viz.*: (1) There is a fall in log ($A_{\text{exp.}}/A_{\text{calc.}}$) from hydrogen to ethane followed by a slight rise as the hydrocarbons become more complex. (2) The values of log ($A_{\text{exp.}}/A_{\text{calc.}}$) are slightly higher for attack on a hydrogen atom attached to a secondary than to a primary carbon atom. It was suggested that these features could be attributed to the part played by alterations in the frequencies of the chain deformations that were ignored in the calculations. The bromine results support this conclusion. The fact that the bromine results resemble those for chlorine more closely than those for fluorine was also expected. It is therefore reasonable to suppose that a coherent theory could be developed that would reduce the size of log ($A_{\text{exp.}}/A_{\text{calc.}}$) and that their present sizes are not solely determined by experimental error.

log $A_{\text{exp.}}/A_{\text{calc.}}$ *for the reactions of bromine, chlorine, and fluorine atoms with hydrocarbons.*



●- - - -● Bromine atoms. ○— —○ Chlorine atoms. ◓——◓ Fluorine atoms.

Activation Energies of Bromine-atom Reactions.—The activation energies found for the attack of bromine atoms on the hydrocarbons are close to those that might have been expected, for the activation energies for the abstraction reactions of all the more selective radicals are in the order methyl > primary > secondary > tertiary.[14] The value of E_2 for neopentane is perhaps high but it lies within the limits of the experimental error of most work with other radicals. The strengths of the C–H bonds cannot be directly deduced until the activation energies of the back reactions, E_{-2}, have been measured. Some information can be derived if the Polanyi relation $E = \alpha\Delta H + c$, where c is a constant, is accepted. The difference in ΔH for the reactions of methyl and t-butyl is equal to D(Me–H) − D(Bu^t–H) = 12·5 kcal. mole^{-1}.[21] This figure is derived from electron-impact measurements and may be in error by 2 or 3 kcal. mole^{-1}. Hence α lies between 0·72 and 1 (α cannot be greater than unity) with a most probable value of 0·86. This value has been used to obtain the intermediate values of D(R–H) shown in Table 3. The bond strengths are very reasonable and agree well with those obtained by electron impact. On the other hand, the Polanyi relation has not been clearly established for any series of reactions, largely because

TABLE 3. D(R–H) *for alkanes and Arrhenius parameters for the reaction of alkyl radicals with hydrogen bromide.*

Alkyl	S	E_{-2}	log A_{-2}	D(R–H)	Alkyl	S	E_{-2}	log A_{-2}	D(R–H)
Methyl	47·2	1·8	12·2	102·5 *	Isopropyl ...	65·9	(3·1)	12·2	93·1
Ethyl	58·5	(2·5)	11·9	96·9	s-Butyl	76·8	(3·1)	12·4	93·2
Neopentyl ...	78·2	(2·4)	12·0	97·9	t-Butyl	70·4 †	(3·6)	12·1	90·0

S is in cal mole^{-1} deg.$^{-1}$, D and E in kcal. mole^{-1}, and A_{-2} in mole^{-1} cm.^{3} sec.$^{-1}$.

* Long, *Proc. Roy. Soc.*, 1949, **198**, 62. † Benson and Buss [7] recommend 79·5 cal. mole^{-1} deg.$^{-1}$, which seems much too high.

of the lack of an adequate knowledge of bond strengths. It would be expected that the relation would hold best when α is high, as in the present instance. At the moment the use of the relation should be regarded as no more than a plausible method of interpolation.

E_{-2} for methyl radicals has been estimated kinetically on a rather dubious basis. E_{-2} for the other radicals has been deduced from E_2 and ΔH_2 and is given in parentheses in col. 3 of Table 3. Values of A_{-2} have also been calculated from A_2 and ΔS_2 on the assumption that the entropies of the radicals are as listed in col. 2. The entropies have been derived from those of the parent hydrocarbon; 1·4 cal. mole^{-1} deg.$^{-1}$ have been added to allow for the electron degeneracy, and the symmetry numbers have been calculated on the assumption that the bonds from the carbon atom carrying the free electron are coplanar. Free rotation may occur slightly more readily in some of the radicals than in the parent molecules, hence the entropies may be slightly underestimated. Direct experimental evidence on reaction (−2) is clearly needed.

EXPERIMENTAL

Apparatus.—The apparatus was of Pyrex glass. Stopcocks were lubricated with Silicone grease. The reaction vessel (92 c.c.) was contained in a vapour-jacket that could be kept at suitable temperatures by filling it with different liquids. The temperature was measured with a thermocouple that had been calibrated against standard thermometers, placed in a well down the centre of the reaction vessel. The reaction vessel was joined by capillary tubing to the rest of the apparatus through a three-way stopcock. The hydrocarbons were generally measured in quantities sufficient for a series of runs into a 500 c.c. spherical mixing vessel that had a cold finger to contain liquid oxygen let into it. Small quantities were mixed in a toroidal trap with a flame applied to one side to induce convection. This trap was also used for degassing and remixing the hydrocarbons before each run. The stopcock on the reaction vessel separated the hydrocarbon dosage and storage system, from the bromine storage and the analysis system. Pressures in the former were measured by a mercury manometer.

The detector for the chromatography system was a katharometer made from a brass block with coiled tungsten filaments. Hydrogen was the carrier gas.

Procedure.—Known amounts of hydrocarbons were mixed with the less reactive hydrocarbon in considerable excess. Bromine was admitted into the reaction vessel up to a pressure determined by the temperature of the storage vessel. The pressure was 4 cm. (0°) for most runs. The hydrocarbon mixture was then expanded into the reaction vessel. The vapour-bath was painted black except for a window fitted with a shutter. Slow reactions were accelerated by illumination with a 125 w mercury arc. At the end of the reaction, the products were frozen into the injection trap of the chromatography system. The products were then injected into the column through a short tube of 30% *NN*-dimethyl-*p*-toluidine on 52/72 mesh firebrick or a mixture of tetramethyldiaminodiphenylmethane with dinonyl phthalate on firebrick which absorbed the bromine.

Materials.—The rate-constant ratios were very sensitive to impurities in the bromine which was stored for several weeks over potassium bromide. Small samples were distilled from potassium bromide and phosphoric oxide with rejection of head and tail fractions. They were degassed many times by distillation under a high vacuum into traps cooled with liquid oxygen.

The methane generally contained some impurities which made it difficult to obtain reproducible results. B.O.G. methane passed over heated copper and subsequently degassed was unsatisfactory. Some satisfactory work was done with methane obtained from the National Chemical Laboratory, Teddington, but only a limited supply was available. Prebromination of the methane in the presence of ethane partially removed the impurity. Manganese dioxide that had been reduced by hydrogen at 300° was a more convenient and equally effective reagent for removing the impurity. The purifications were followed by several trap-to-trap distillations (−183° to −210°) under a high vacuum. The nature of the more successful methods of purification indicates that the impurity is probably oxygen and that it is very difficult to remove it completely. Ethylene was removed from B.O.G. ethane with an absorbent. Propane was an N.C.L. sample. n-Butane and isobutane were given by the British Petroleum Co.; the latter contained 0·3% of propane. The neopentane (Phillips Petroleum pure grade) contained 1% of isobutane that was removed by bromination of the mixture for 10 min. in diffused sunlight. The product was distilled from a trap at −80° through tubes of potassium hydroxide and Anhydrone. The residual bromine was removed by passage through a tube filled with *NN*-diethyl-*p*-toluidine supported on three times its weight of firebrick. The methyl chloride (B.O.G.) and methyl bromide (B.D.H.) were degassed. All gases were dried (P_2O_5).

RESULTS

Calibrations.—The relative sensitivity of the katharometer to the products was determined by measurements on known mixtures of selected pairs of bromides. The sensitivities found (relative to ethyl bromide) were as follows: EtBr, 1; CH_2ClBr, 0·98; MeBr, 1·08; CH_2Br_2, 1·11; Pr^iBr, 1·02; Bu^sBr, 1·02; Bu^tBr, 1·10. Neopentyl bromide was assumed to have the same sensitivity as Bu^tBr.

The reaction systems are described in the order in which they were studied.

n-Butane–Isobutane.—Between −6° and 98° the only measurable products were t- and s-butyl bromide. They were separated on a 50 cm. column of 25% dimethyl phthalate–Celite (80—100 mesh). Details of the conditions and results are given in Table 4, which shows that the relative rate constants are independent of the proportions of the reactants, their total pressure, the amount of bromine, and the presence of added hydrogen bromide. Tests showed that no bromination occurred in the chromatography system and that the products did not decompose. A least-squares treatment gave

TABLE 4. *Results of isobutane–n-butane bromination.*

	Hydrocarbon press (cm.)		Peak areas (units)		k^t (isobutane)
Temp.	n-Butane	Isobutane	Bu^tBr	Bu^sBr	k^s (n-butane)
−11·5°	4·73	1·88	9·48	1·00	23·93
,,	,,	,,	12·30	1·12	27·60
,,	,,	,,	8·36	0·82	25·84
,,	,,	,,	8·59	0·86	25·12
−6·0	,,	,,	11·73	1·29	22·89
,,	,,	,,	10·33	1·28	20·30
11·38	5·29	1·51	6·20	1·40	15·58
,,	4·10	2·72	10·30	0·95	16·35
,,	5·80	2·31	5·36	0·86	15·65
,,	3·00	1·20	5·34	0·77	16·94
,,	4·73	1·88	9·03	1·38	16·46
,,	,,	,,	5·57	0·88	15·92
,,	,,	,,	11·25	1·67	16·95
,,	,,	,,	6·04	0·96	15·83
35·0	5·19	2·07	7·68	1·81	10·63
,, [a]	3·82	1·52	3·05	0·69	11·09
,, [a]	3·26	1·30	2·11	0·49	10·80
,, [b]	4·73	1·88	3·03	0·68	11·16
,, [c]	3·51	1·40	16·04	3·61	11·14
58·3	4·73	1·88	6·04	1·73	8·78
,,	,,	,,	3·14	0·98	7·96
,,	,,	,,	2·77	0·79	8·83
,,	,,	,,	5·21	1·65	7·94
,,	,,	,,	9·08	3·02	7·56
98·0	,,	,,	5·08	2·29	5·58
,,	,,	,,	1·86	0·93	5·03
,,	,,	,,	3·17	1·46	5·45
,,	,,	,,	1·60	0·77	5·23
,,	,,	,,	1·29	0·61	5·32
,,	,,	,,	2·52	1·13	5·61

[a] Bromine pressure = 15 cm. [b] Bromine pressure = 3·4 cm. Bromine pressure for all other runs = 6 cm. [c] 3 mm. HBr also present.

$$k^t(\text{isobutane})/k^s(\text{n-butane}) = (0{\cdot}132 \pm 0{\cdot}009) \exp{(2716 \pm 30/\boldsymbol{RT})}$$

Propane–Isobutane.—In 27 runs between 34° and 148°, the only measurable products were isopropyl and t-butyl bromide. They were separated on a 60 cm. column of 25% dimethyl phthalate–Celite. The total pressure of hydrocarbon was 6·6 cm. in most runs with propane/isobutane = 3·45. Variation of hydrocarbon pressure between 4 and 8 cm. and of the proportion between 2 and 4 did not affect the results; nor did the addition of hydrogen bromide.

$$k^t(\text{isobutane})/k^s(\text{propane}) = (0{\cdot}418 \pm 0{\cdot}04) \exp (2640 \pm 65/\boldsymbol{R}T)$$

Propane–Ethane.—In 32 runs between 12·5° and 145°, the only measurable products were isopropyl and ethyl bromide which were separated on the column used in the previous experiment. The total pressure of hydrocarbon was 7·6 cm. in most runs, with ethane/propane = 4·9. Variation of hydrocarbon pressure from 5 to 8·4 cm., of the proportion from 4·9 to 1·43, and of the bromine pressure from 3·4 to 15 cm. had no effect. As the proportion of propane was normally small, the extent of the reaction was kept low to restrict its relative depletion. The addition of 20 times the normal amount of hydrogen bromide formed had only a very small effect.

$$k^s(\text{propane})/k(\text{ethane}) = (0{\cdot}669 \pm 0{\cdot}053) \exp (3247 \pm 51/\boldsymbol{R}T)$$

Methyl Bromide–Ethane.—In 23 runs between 58·5° and 199°, the only measurable products were methylene dibromide and ethyl bromide. These were passed through 150 cm. of 25% dinonyl phthalate–Celite (70°) and on to 50 cm. of 25% dimethyl phthalate–Celite (25°). When the ethyl bromide was eluted the second column was by-passed, and the methylene bromide carried through a column of glass beads that maintained the flow of carrier gas constant. The pressure of reactants was between 6 and 9 cm., and the methyl bromide/ethane ratio between 2·1 and 4·3. Variation of the bromine pressure between 3·4 and 15 cm. had no effect. Previous work had shown that hydrogen bromide had no effect on these reactants separately.

$$k(\text{ethane})/k(\text{methyl bromide}) = (1{\cdot}364 \pm 0{\cdot}050) \exp (2654 \pm 88/\boldsymbol{R}T).$$

Neopentane–Ethane.—In 23 runs between 57° and 200°, the only products were ethyl bromide and a compound with an elution time appropriate to neopentyl bromide. They were separated on a 60 cm. column of 25% dimethyl phthalate–Celite (20°). Hydrocarbon pressures were between 4 and 8 cm., with ethane/neopentane between 1·5 and 0·67. The bromine pressure was between 3·4 and 15 cm.

$$k(\text{neopentane})k(\text{ethane}) = (2{\cdot}235 \pm 0{\cdot}117) \exp (-893 \pm 44/\boldsymbol{R}T)$$

Methyl Chloride–Ethane.—In 26 runs between 58·5° and 200° the only measurable products were ethyl bromide and bromochloromethane. The column was 60 cm. of 25% dimethyl phthalate–Celite (20°). Total reactant pressure was 4—8 cm., methyl chloride/ethane = 2·9—1, and bromine pressure 3·4—15 cm. Addition of more hydrogen bromide than was formed in a normal run did not affect the rate constants.

$$k(\text{ethane})/k(\text{methyl chloride}) = (1{\cdot}897 \pm 0{\cdot}109) \exp (1055 \pm 68/\boldsymbol{R}T)$$

Methane–Methyl Chloride.—23 Runs were carried out between 204° and 341°. The products were analysed on a 150 cm. column of 25% diethyl phthalate–Celite (37°). Most of the runs were done with a total reactant pressure of about 7·6 cm., made up in the proportions $MeCl : CH_4 : C_2H_6$ of 1·3 : 5 : 0·7. The addition of the ethane greatly improved the reproducibility and yield of the C_1 products, presumably because the ethyl radicals formed reacted with the impurities. Total pressure was varied between 5 and 10 cm., CH_3Cl/CH_4 between 2 and 5, and ethane between 0·3 and 2 cm. The bromine pressure was kept at about 10 cm. Many runs were wasted because the precautions taken to eliminate impurities were insufficient. The amounts of products found were then small, and the ratio of rate constants was low. The scatter of the points obtained when reasonable quantities of products were formed was not excessive. From the mean points at each temperature we found

$$k(\text{methyl chloride})/k(\text{methane}) = 0{\cdot}36 \exp (3800/\boldsymbol{R}T)$$

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THE UNIVERSITY, EDINBURGH. [*Received, April 20th*, 1960.]

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[14]

THE TRANSFER REACTIONS OF HALOGEN ATOMS[1]

G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson

ABSTRACT

Extensive results on the reactions of fluorine, chlorine, and bromine atoms with alkanes and with some other molecules have been obtained from the study of competitive halogenations. The comparison of the A factors of the reactions provides an excellent test of the transition state theory. The activation energies of the bromine atom reactions can be combined with measurements of the activation energies for the reactions of alkyl radicals with hydrogen bromide to yield unusually reliable values of bond strengths. Information on the influence of polar effects on the activation energies of atomic reactions can be obtained from results on the reactions of fluorine and chlorine atoms with methyl halides.

The reaction of a halogen with a pair of hydrocarbons can be represented by the following steps:

$$\begin{aligned} X + R^1H &= XH + R^1 \\ R^1 + X_2 &= R^1X + X \end{aligned} \qquad [1]$$

$$\begin{aligned} X + R^2H &= XH + R^2 \\ R^2 + X_2 &= R^2X + X \end{aligned} \qquad [2]$$

In this paper we shall be concerned with the rate constants and Arrhenius factors for reactions [1] and [2] and for those of the reverse processes [−1] and [−2]. The relative values of k_1 and k_2 can be found by competitive methods in two ways. The first is the consumption method in which the amounts of R^1H and R^2H removed from a mixture during reaction with a halogen are determined. Then

$$\frac{k_1}{k_2} = \frac{-d[R^1H]/dt.\ [R^2H]}{-d[R^2H]/dt.\ [R^1H]}\,.$$

In practice this relation is used in its integrated form and the conversions are kept below about 20–30%. This method was particularly attractive before the development of gas chromatography for it was much simpler to analyze for small quantities of R^1H and R^2H than of the corresponding halides. It was employed by Pritchard, Pyke, and Trotman-Dickenson (1) to study chlorine atom reactions and later by Mercer and Pritchard (2) to study fluorine atoms.

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[1] *Contribution from the Chemistry Department, Edinburgh University, Edinburgh 9, Scotland; paper presented at the Symposium on the Fundamental Aspects of Atomic Reactions held at McGill University, Montreal, Que., September 1960.*

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The second method depends upon the measurement of the rate of formation of the halides formed. The rate constants are then obtained from

$$\frac{k_1}{k_2} = \frac{d[R^1X]/dt.\ [R^2H]}{d[R^2X]/dt.\ [R^1H]}\ .$$

The integrated form of the equation need not be used as the percentage conversions should be kept very low to avoid secondary reactions of the halides. Fortunately halides are not more than 10 times as reactive as their parent alkanes. This approach was first used by Hass, McBee, and Weber (3) in their studies of chlorinations. Their work was done on a large scale in flow systems, so that sufficient chlorides were formed for analysis by distillation. They worked at high temperatures. Some isomerization of the chlorides probably occurred so that the results do not agree well with those of later workers. Knox (4) applied gas chromatography to the problem and was able to reduce the scale of reaction by about 10^4 and at the same time improve the accuracy. The method has the great advantage that isomeric products can be distinguished and reactivities directly assigned to specific types of hydrogen atom. The attack on hydrogen is not simply followed because hydrogen halides are not easily determined by gas chromatography and are produced in reactions of all hydrogen-containing compounds.

Relative rate constants obtained by competitive methods can be placed on an absolute scale if the constant for one member of the series can be absolutely determined. Fortunately the rate constant for the attack of a chlorine atom on molecular hydrogen has been determined by three groups of workers whose results are in good agreement. Kistiakowsky and Van Artsdalen have carefully measured the rate of reaction of bromine atoms with methyl bromide and methane (5). No rate constant for a fluorine atom reaction has been measured. In this work it has been assumed that the value of the A factor calculated for the reaction of fluorine atoms with ethane is correct and that the activation energies for attack on hydrocarbons heavier than ethane are zero. The justification for these assumptions will be apparent in what follows.

Table I summarizes the results that have been obtained at Edinburgh, together with

TABLE I

Rate constants, A factors, and activation energies for reactions of the type $X + RH = HX + R$

	Fluorine atoms (8)			Chlorine atoms (9)			Bromine atoms (10)		
RH	log k (25°)	log A	E	log k (25°)	log A	E	log k (100°)	log A	E
H_2	12.8	14.0	1.71[2]	9.8	13.9	5.50[7]	3.3[5]	13.7	17.5
CH_4	13.1	14.0	1.21	10.6	13.4	3.85[1]	3.3	14.0	18.3
Primary									
C_2H_6	13.5	13.7	0.28	13.2	14.0	1.04[1]	6.1	13.9	13.4
C_3H_8	13.4	13.4	0	13.3	14.0	1.00	—	—	—
n-C_4H_{10}	13.3	13.3	0	13.2	13.9	0.79	—	—	—
iso-C_4H_{10}	13.6	13.6	0	13.5	14.1	0.82	—	—	—
neo-C_5H_{12}	13.7	13.7	0	13.6	14.3	0.92	5.9	14.2	14.3
Secondary									
C_3H_8	13.0	13.0	0	13.3	13.9	0.68	7.7	13.7	10.1
n-C_4H_{10}	13.3	13.3	0	13.8	13.9	0.27	7.2	13.2	10.2
cyclo-C_3H_6	13.4	13.4	0	10.7	13.7	4.1	—	—	—
cyclo-C_4H_8	—	—	—	13.8	14.4	0.83	—	—	—
Tertiary									
iso-C_4H_{10}	12.8	12.8	0	13.2	13.2	0.02	8.9	13.3	7.5

NOTE: A and k are in $cm^3\ mole^{-1}\ sec^{-1}$; E is in kilocalories $mole^{-1}$.

a few other results of our own and of other workers. The experimental details and a full comparison of the results with the rather small number available from other sources are fully discussed in the original papers to which reference is made. With the notable exception of the bromination results of Van Artsdalen's group the present work is in excellent agreement with the small amount of recent work by other authors. Benson and Buss (6) have discussed at length the probable reasons for the unreliability of the results of Van Artsdalen's very careful work. These results were always suspect because they appeared to be out of line with those for all other atomic reactions.

The A Factors

According to transition state theory the A factor for a bimolecular reaction is given by

$$A = e^2.(kT/h)\exp[(\Delta S^{\ddagger}_{\mathrm{tr}}+\Delta S^{\ddagger}_{\mathrm{rot}}+\Delta S^{\ddagger}_{\mathrm{vib}})/R].$$

The translational entropies of activation can be calculated exactly from the molecular weights of the reactants and complexes. The accuracy of the calculated value of the rotational entropy of activation is limited by the uncertainty of the exact configuration of the complex and, to a lesser degree, of the reactant. The C—H and C—C bond lengths have throughout been assumed to be 1.10 and 1.54 Å except that the half-order bonds $\gt$C—H—X have been taken as 0.18 Å longer than the corresponding single bonds. The two extreme forms of the *n*-butane – halogen complexes in which the molecule is fully extended or completely curled up yield rotational entropies of activation that differ by less than 10%. Since intermediate configurations are much more profitable, it is unlikely that the error arising from assumptions about the configurations are as large as this.

The calculation of the vibrational entropies of activation is less certain and has a greater effect upon the result obtained. It has been assumed that many of the vibrations in RH will be little changed by the addition of the halogen atom and that their contributions to $\Delta S^{\ddagger}_{\mathrm{vib}}$ will largely cancel. Only a few vibrations intimately connected with the part of the molecule to which the halogen atom is attached will give rise to important contributions. These vibrations are the C—H stretching and C—H wagging in the hydrocarbon which are replaced by five new vibrations in the activated complex. The C—H stretching becomes the reaction co-ordinate and the C—H wagging becomes the wagging of H—X against the rest of the hydrocarbon. The three additional vibrations are the symmetrical stretching of the C—H—X bonds and the doubly degenerate bending of the C—H—X bonds. Pitzer (11) deduced $\Delta S^{\ddagger}_{\mathrm{vib}}$ for the reaction

$$\mathrm{Cl} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{H}$$

from the observed A factor and found that the bending and stretching frequencies were 560 cm^{-1} and 1460 cm^{-1} respectively. It has here been assumed that the force constants for these modes of vibration are the same for all the complexes and that the corresponding frequencies can therefore be calculated by classical mechanics for the different groups, R, and atoms, X.

The calculated and experimental A factors are compared for each type of halogen in Table II. In only one instance does A_{exp} differ from A_{calc} by more than a factor of 4. The transition state theory, therefore, accounts very well for the magnitude of the A factors. Even the deviations from the calculated values show a fairly regular pattern as can be seen by comparing the columns of ratios. This encourages us to think that the experimental results are adequate to sustain the test of a more precise theory if

TABLE II

A factors for halogen atom reactions

RH	log A_{exp}/A_{calc}		
	F	Cl	Br
H_2	+0.29	+0.01	+0.24
CH_4	+0.24	−0.68	−0.36
Primary C—H bonds			
C_2H_6	0.00*	−0.10	−0.41
C_3H_8	−0.05	+0.25	—
n-C_4H_{10}	−0.03	+0.20	—
iso-C_4H_{10}	+0.04	+0.24	—
neo-C_5H_{12}	+0.06	+0.31	+0.03
Secondary C—H bonds			
C_3H_8	−0.03	+0.52	+0.18
n-C_4H_{10}	+0.08	+0.50	+0.08
cyclo-C_3H_6	−0.17	−0.16	—
cyclo-C_4H_8	—	+0.56	—
Tertiary C—H bonds			
iso-C_4H_{10}	+0.15	+0.41	+0.12

*This value is assumed and the others for fluorine based on it.

one could be found. Since the deviations are more extreme for the heavier halogens, it is likely that the wagging of the H—X bond or the bending of the C—H—X bonds have not been correctly accounted for.

The Activation Energies

The activation energies of the reactions of the higher hydrocarbons with chlorine closely approach zero. It is not surprising that no differences between the activation energies for attack on the higher hydrocarbons by fluorine could be detected. There is probably no energy barrier to attack on these compounds.

The activation energies of the bromine atom reactions vary widely and are of greater interest because of the relation that they bear to the strengths of the bonds broken. The heat of reaction is related to the activation energies for the forward and reverse reactions by the equation

$$\Delta H_1 = E_1 - E_{-1}.$$

Since $D(\text{H—Br})$ is known, $D(\text{R}^1\text{—H})$ can be found if E_1 and E_{-1} are measured. At the moment, the values of E_{-1} are not accurately known and consequently the measurements do not yield the bond strengths directly. Until the E_{-1}'s have been determined it is convenient to use the Polanyi relation as a method of interpolation. This leads to the results shown below, which is based on the currently accepted values of $D(\text{Me—H})$ and $D(\text{Bu}^t\text{—H})$.

R	E_1	E_{-1}	$D(\text{R—H})$
Me	18.3	1.8	102.5
Et	13.4	(2.5)	96.9
Pr^i	10.2	(3.1)	93.1
Bu^t	7.5	(3.6)	90.0

Information about E_{-1} can be obtained by photolysing a source of R^1 in a mixture of hydrogen bromide and iodine. The products are then analyzed for RH and RI. Hence

$$\frac{k_{-1}}{k_2} = \frac{R_{\text{R}^1\text{H}}}{R_{\text{R}^1\text{I}}} \, \frac{[\text{I}_2]}{[\text{HBr}]}$$

where k_3 refers to

$$R^1 + I_2 = R^1I + I. \qquad [3]$$

So far preliminary experiments have been carried out with methyl ethyl ketone as the source of ethyl radicals. Hence we find that

$$E_{-1} - E_3 = 2.3 \text{ kcal mole}^{-1}.$$

It seems likely that the activation energies for the attack of radicals on iodine are very small and may well be zero. The value for ethyl agrees well with that listed above. Further investigations along these lines are clearly required.

Polar Effects

Although bond strengths largely determine the activation energies of the reactions of halogen atoms, polar effects are also important. This has been realized for some years. Recent experiments by Fredricks and Tedder (12) have extended our knowledge. We have attempted to study polar effects in the fluorination, chlorination, and less systematically, in the bromination of halogenated methanes. Fluorination is the most satisfactory because the reactions are so exothermic that the bond strengths are unlikely to be important, and all variations can be ascribed to the polar nature of the activated complexes. The available results are shown in Table III. The first conclusion to be drawn from the table is that more results are needed. The second is that there is little parallelism between the reactivities of the halogenated methanes and the α-hydrogen atoms in the halogenated *n*-butanes.

TABLE III

Relative rate constants for the reactions of halogen atoms with halogenated methanes

	F	Cl	Br
CH_4	1	1	1
CH_3Cl	0.33*	4.9, 0.7†	90, 34†
CH_2Cl_2	0.07*	7.5	—
$CHCl_3$	0.6*	3.9	—
CH_3Br	0.23*	0.3†	14
CH_3F	0.3†	0.9†	10†
Temp., °C	25	100, 146†	100, 146†

*Values obtained at Edinburgh by Dr. R. Foon.
†Reactivities of α-hydrogen atoms in halogenated butanes.

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COMPETITIVE CHLORINATIONS

PART 2.—CHLOROMETHANES

Competitive Chlorinations

PART 2.—CHLOROMETHANES*

By John H. Knox

Dept. of Chemistry, University of Edinburgh

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The competitive gas-phase chlorination of each pair of successive substances in the following series has been carried out, each series providing its own internal check:

(i) methane, ethane, propane, methylene chloride, methane.

(ii) methane, ethane, propane, methyl chloride, chloroform, methane.

Measurements of the yields of the appropriate chlorinated products give the relative rate constants of pairs of reactions

$$Cl+R_aH = HCl+R_a, \qquad (2a)$$

$$Cl+R_bH = HCl+R_b. \qquad (2b)$$

Using the absolute value of k_2 for methane obtained in part 1, the following Arrhenius equations are obtained for methane and the three chloromethanes between 0 and 300°C:

$$k_2 \text{ (methane)} = 2{\cdot}4\times 10^{13} \exp[-3850/RT] \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

$$k_2 \text{ (methyl chloride)} = 3{\cdot}4\times 10^{13} \exp[-3300/RT] \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

$$k_2 \text{ (methylene chloride)} = 2{\cdot}7\times 10^{13} \exp[-3000/RT] \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

$$k_2 \text{ (chloroform)} = 0{\cdot}69\times 10^{13} \exp[-3350/RT] \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

These results are compared with relative values obtained by Goldfinger and coworkers and are discussed in terms of transition state theory.

The chlorination of hydrocarbons and their derivatives in the gas phase proceeds by mechanisms of the following general type:

$$\text{initiation}\begin{cases} Cl_2+h\nu = 2Cl & (1a)\\ Cl_2+M = 2Cl+M & (1b)\end{cases}$$

$$\text{propagation}\begin{cases} Cl+RH = HCl+R & (2)\\ R+Cl_2 = RCl+Cl & (3)\end{cases}$$

$$\text{termination}\begin{cases} Cl+Cl+M = Cl_2+M & (6)\\ R+Cl = \text{inactive products} & (7)\\ R+R = \text{inactive products.} & (8)\end{cases}$$

When RH is hydrogen or methane, (2) has a higher activation energy than (3) and the chain termination reaction is probably (6). In principle it is then possible in a photo-chemical system to obtain an overall activation energy which is close to that of (2); by using intermittent light it is possible to obtain an absolute rate constant for (2). In practice, this is difficult since the overall reaction is exceedingly sensitive to small traces of impurity and it is only for the reaction with hydrogen that a rough value of $5{\cdot}8\pm0{\cdot}5$ kcal mole^{-1} has been obtained for the overall activation

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* part 1, Knox and Nelson.[1]

energy.[2, 3] However, k_2 for this reaction has been measured absolutely by a number of quite independent methods which when combined give [4]

$$k_2\,(\text{hydrogen}) = 8\times10^{13} \exp\left[-5500/RT\right] \text{cm}^3\,\text{mole}^{-1}\,\text{sec}^{-1}.$$

The value for the activation energy agrees well with the overall activation energy of the reaction.

With chlorinated methanes and highly chlorinated hydrocarbons in general, the free radicals formed in (2) are rather unreactive and (3) has the higher activation energy. Because of this and the fact that (6) is termolecular, chain termination is predominantly by (8) at moderate temperatures. Any measurement of the overall rate of reaction under constant or intermittent light then gives only the activation energy or rate constant of reaction (3).[5, 6]

The rate constants of (2) with such compounds can only be obtained absolutely by a method in which they are chlorinated competitively either directly or indirectly with hydrogen, a method such as that previously employed for the C_1—C_5 hydrocarbons.[1]

Provided that the chains are relatively long (say, more than 100 units) and the radical R does not decompose, the rate of (2) will be very close to that of (3) and can be obtained from the rate of formation of RCl provided RCl itself is stable. In the competitive method, when two substances R_aH and R_bH are chlorinated simultaneously, the ratio of the rate constants of (2*a*) and (2*b*) is given to a high degree of accuracy by

$$\frac{k_{2a}}{k_{2b}} = \frac{[R_aCl][R_bH]_m}{[R_bCl][R_aH]_m}, \tag{A}$$

where $[R_aCl]$ and $[R_bCl]$ are the amounts of the two chlorides formed and $[R_aH]_m$ and $[R_bH]_m$ are the mean concentrations of the H-donors during the chlorination. The approximation (A) is accurate to better than 1 % when consumption of either H-donor is less than 30 %.

Recently, Goldfinger and co-workers [7, 8] have investigated the chlorination of methane and the chloromethanes by a slightly different competitive method in which they were competed against tetrachloroethylene. The chlorination of the latter has been extensively investigated by Goldfinger and co-workers [6] and conforms to the general mechanism already given, except that (2) is replaced by the reversible reaction,

$$C_2Cl_4+Cl\underline{\rightleftharpoons}C_2Cl_6. \quad \overset{\rightarrow}{(2)};\ \overset{\leftarrow}{(4)}.$$

Since the chlorination of the olefin is accompanied by a pressure decrease and that of the methane or chloromethane by none, the relative rates of the two reactions can be obtained by measuring the rates of pressure change and of chlorine consumption. This method suffers from several disadvantages as a means of determining the rate constants of reactions (2) with saturated compounds: (i) the temperature range over which experiments can be conducted is limited to about 100 deg.; (ii) the instability of the C_2Cl_5 radical means that an extrapolation to infinite chlorine pressure must be made in order to obtain the true rate of (2) with C_2Cl_4; and (iii) only relative rates of reaction can be obtained since the absolute rate constant for the addition of Cl to tetrachloroethylene is not known independently. Nevertheless the fact that the relative values obtained by Goldfinger and coworkers agree with those now reported is an excellent check on the general mechanism of the chlorinations. Furthermore, by combining the two sets of data it is possible to obtain absolute values for the rate constants of (2) with tetrachloroethylene and pentachloroethane.

EXPERIMENTAL

Throughout the present work all analysis of reaction products was carried out by gas chromatography. A katharometer was used as detector and hydrogen as the carrier gas. Since the total quantity of chloride products required for analysis was between 0·02 and 0·5 cm^3 vapour at s.t.p. it was possible to carry out chlorinations with pressures of chlorine between 1 and 5 mm Hg in a reaction vessel of about 50 ml. By using a large excess of the mixture to be chlorinated secondary chlorination could be kept to a minimum.

The reaction vessel was of Pyrex and was thermostatted by vapour or liquid baths. Chlorine was generally added first to the evacuated reaction vessel and followed by the rest of the reaction mixture which had previously been prepared in a mixing vessel fitted with a small convection heater. The reaction was normally initiated by light from a 250 W tungsten filament projection lamp but some thermal runs were carried out at the higher temperatures. When the chains were likely to be short (with chloroform at room temperature for instance) pressures of chlorine up to 10 cm were used but only 1-5 mm of this was allowed to react, the remainder being removed before analysis by allowing the reaction mixture to expand into an evacuated tube containing copper bronze. Otherwise, illumination was continued until a high percentage of the chlorine had reacted and the reaction products then distilled straightway into the evacuated sampling U-tube of the gas chromatography apparatus. Self-heating of the reaction sometimes occurred above 300°C. This was eliminated by adding a large excess of nitrogen to the mixture.

The temperature range accessible in the experiments was usually 0-320°C but when propane was one of the competitors decomposition of the isopropyl chloride and to a lesser extent of the n-propyl chloride rendered runs above 300°C unreliable. The lower temperature was set by the increasing involatility of the higher chloromethanes, difficulties arising from short chain lengths, and, with propane as one of the reactants, great differences in the reactivities of the two competitors.

MATERIALS

Chlorine from a cylinder was purified by several trap-to-trap distillations from −80 to −186°C.

Methane from a cylinder was passed in a stream of hydrogen over reduced copper oxide at 500°C and condensed at −186°C. Higher hydrocarbons were removed by prechlorinating about 10 % of the sample. The methane was finally freed from chlorides and hydrogen chloride by two distillations from −186°C to a pump-down liquid oxygen trap.

Propane was obtained from a cylinder and contained about 0·1 % of propylene and 0·6 % of isobutane.

Methyl chloride was initially obtained from a cylinder. This sample contained no higher chlorides. Later methyl chloride was prepared by the reaction of concentrated hydrochloric acid on methanol. This sample contained traces of dimethyl ether but no methylene chloride.

Methylene chloride was obtained by distillation of a commercial sample. It contained 0·002 % of ethyl and propyl chlorides and 0·01 % of chloroform. The trace of chloroform was unimportant as more than 1 % of the methylene chloride was usually chlorinated in any experiment.

Chloroform was also obtained by distilling a commercial sample. It contained about 0·002 % each of three unidentified impurities.

RESULTS

Details of the experiments on each mixture studied are given below. The best Arrhenius parameters obtained by the method of least squares are summarized in table 1 along with the standard deviations of the results. The absolute Arrhenius parameters derived from the relative values given in table 1 are recorded in table 2.

TABLE 1.—RELATIVE ARRHENIUS PARAMETERS

$$\text{Standard reactions, } Cl + R_aH = HCl + R_b \qquad (2a)$$

$$Cl + R_aH = HCl + R_b \qquad (2b)$$

competitors		$E_{2a}-E_{2b}$ cal mole^{-1}	A_{2a}/A_{2b}
R_aH	R_bH		
CH_2Cl_2	pri-C_3H_8	2025 ± 90*	0·32 ± 0·03*
CH_2Cl_2	sec-C_3H_8	2290 ± 90	0·38 ± 0·04
CH_4	$CHCl_3$	515 ± 35	3·5 ± 0·15
$CHCl_3$	CH_3Cl	265 ± 20	0·26 ± 0·01
CH_4	CH_2Cl_2	875 ± 40	1·00 ± 0·05
CH_3Cl	pri-C_3H_8	2400 ± 50	0·39 ± 0·04

* standard deviations.

TABLE 2.—ABSOLUTE ARRHENIUS PARAMETERS

$$\text{Standard reaction, } Cl + RH = HCl + R. \qquad (2)$$

substance	competitor(s)	E_2 cal mole^{-1}	$10^{-13} \times A_2$	$10^{-10} \times k_2$ at 333°K
			cm³ mole^{-1} sec^{-1}	
CH_4	standard	3850	2·4	7·0
CH_3Cl	$CH_4 + CHCl_3$	3070 ± 60*	2·6 ± 0·2*	24 ± 2*
	pri-C_3H_8	3400 ± 100	3·9 ± 0·6	23 ± 4
CH_2Cl_2	CH_4	2975 ± 40	2·4 ± 0·1	26 ± 1
	pri-, sec-C_3H_8	3000 ± 130	3·0 ± 0·6	32 ± 6
$CHCl_3$	CH_4	3340 ± 40	0·69 ± 0·03	4·5 ± 0·2

* cumulative standard deviations.

METHYLENE CHLORIDE + PROPANE

Mixtures of methylene chloride and propane ranging in molar composition from 2 : 1 to 20 : 1 were chlorinated at 10, 42, 76, 156, 220, and 290°C. The products were analyzed on a 1·5 m column containing 10 % of dinonyl phthalate on firebrick at 40°C.

42 successful runs were carried out. The standard deviations of $k_2(CH_2Cl_2)/k_2(\text{pri-}C_3H_8)$ and $k_2(CH_2Cl_2)/k_2(\text{sec-}C_3H_8)$ from the best Arrhenius plots were 15 %.

METHANE + CHLOROFORM

Approximately equimolar mixtures were chlorinated at 13, 42, 88, 156, 220, 290 and 320°C. The products were analyzed on a 1·5 m column containing 14 % of dibutyl phthalate + 5 % of polyethylene glycol 400 on firebrick. The column temperature was raised during analysis from about −20 to about 50°C in order to elute both methyl chloride and carbon tetrachloride as conveniently shaped peaks for area measurement. On this column, carbon tetrachloride was eluted before the very much larger quantity of chloroform always present in the reacted mixture.

In the experiments at 13°C the relative yield of carbon tetrachloride to methyl chloride increased with chlorine pressure when the amount of chlorine consumed was kept constant. This indicated that the chains were very short. Accordingly, runs were carried out at much higher than normal chlorine pressures. Values of the right-hand side of (A) ($R_aH = CH_4$) were accordingly plotted against $[Cl_2]^{-\frac{1}{2}}$. The experimental points fell on the expected straight line (see appendix) which was extrapolated to zero abscissa to give the true value of $k_2(CH_4)/k_2(CHCl_3)$. This value was in good agreement with the value predicted from the experiments at higher temperatures when no chloride dependence was noted.

Sixty successful experiments were carried out. The standard deviation of the rate constant ratio from the best Arrhenius plot was 9 %.

CHLOROFORM + METHYL CHLORIDE

Mixtures of chloroform and methyl chloride ranging in molar composition from 1 : 2 to 10 : 1 were chlorinated at −33, 0, 10, 42, 100, 110, 156, 290 and 320°C. The reaction products were analyzed on a 1·5 m column containing 18 % of dibutyl phthalate + 2 % of polyethylene glycol 400 on firebrick. With this column at 40°C, carbon tetrachloride was eluted midway between methylene chloride and chloroform.

Rather surprisingly, no chlorine dependence was noted in this series even at −33°C. For this reason the results are somewhat suspect. If the yield of CCl_4 had in fact been low due to removal of CCl_3 radicals, our value for $E_2(CH_3Cl)$ would be too low. Nevertheless, the standard deviation of the 50 values of the rate constant ratio from the best Arrhenius plot was only 5 %, the lowest value obtained in any series.

METHYLENE CHLORIDE + METHANE

Approximately equimolar mixtures were chlorinated at 0, 20, 42, 83, 156, 220 and 290°C. The products were analyzed on the column employed for the chloroform + methane experiments. Twenty-six successful experiments were carried out. The standard deviation of the rate constant ratio from the best Arrhenius plot was 6 %.

METHYL CHLORIDE + PROPANE

Mixtures of methyl chloride and propane ranging in molar composition from 10 : 1 to 200 : 1 were chlorinated at −2, 25, 42, 80, 100, 110, 156, 190, 223 and 325°C. Analysis was carried out on the column used for the chloroform + methane experiments. At 325°C the propyl chlorides showed significant decomposition and the results obtained at this temperature were not included in the final least-squares analysis. At the lowest temperature, difficulty was experienced due to the great difference in reactivity of the two substances since traces of butyl chlorides formed from the isobutane present in the propane interfered with the methylene chloride peak. To avoid this, it was necessary to work with very high methyl chloride to propane ratios and at the limit of sensitivity of the chromatography apparatus. The spread of values at the lowest temperature was thus considerably greater than that at the higher temperatures. The values for −2°C were therefore given only half the weight of the rest in the least-squares treatment.

For the experiments with methyl chloride and propane a modified apparatus was used in which all greased taps with which the reactants or products had previously come in contact were replaced by teflon + stainless steel valves (made by F. J. Hone Ltd., Eldon Park, London, S.E.25). It was hoped thereby to reduce the random error of the results. Forty successful experiments were carried out giving a standard deviation of the rate constant ratio from the best Arrhenius plot of 7 %. In view of the experimental difficulties encountered in this series, the standard deviation of 7 % compares very favourably with the 15 % found for the comparable methylene chloride-propane experiments.

CALIBRATIONS

The katharometer was calibrated using known mixtures both in the original apparatus with greased taps and in the modified apparatus with stainless steel valves.

The standard deviation of the calibration factors in the original apparatus was about 7 %. This was reduced to 2-3 % by changing to greaseless valves. Using hydrogen as the carrier gas and a filament current of 180 mA, the area calibration factors were as follows:

methyl chloride 0·77; ethyl chloride 0·92; propyl chlorides 0·89; methylene chloride 1·00 (standard); chloroform 1·11; carbon tetrachloride 1·28. Values obtained with the original apparatus were in good agreement except with carbon tetrachloride for which a lower sensitivity was obtained. This was almost certainly due to solution in tap grease.

DISCUSSION

Previous work on saturated hydrocarbons [1, 9, 10] had established the absolute Arrhenius parameters of reaction (2) for methane by direct competitive chlorination of methane and hydrogen, and for propane by two further competitive chlorinations of methane against ethane and ethane against propane. In the present work the chloromethanes have been chlorinated competitively against methane and propane and any absolute values which are calculated will embody the errors in the assumed parameters for methane. If one includes the possible error in the activation energy for chlorine atom attack on hydrogen, E for methane may be in error by up to 250 cal mole^{-1}. However, for the evaluation of relative Arrhenius parameters and in order to check the internal consistency of the results, it is more convenient to regard the methane values as accurate, taking

$$k_2\,(\text{methane}) = 2{\cdot}4\times10^{13}\exp\,[-3850/\boldsymbol{RT}]\ \text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}.$$

The absolute Arrhenius equations for propane, including the standard deviations of E and A then become

$$k_2\,(\text{pri-propane}) = (10{\cdot}0\pm1{\cdot}0)\times10^{13}\exp\,[-1000\pm60/\boldsymbol{RT}],$$
$$k_2\,(\text{sec-propane}) = (7{\cdot}2\pm0{\cdot}8)\times10^{13}\exp\,[-680\pm60/\boldsymbol{RT}],$$

the units of E being cal mole^{-1} and of k cm^3 mole^{-1} sec^{-1}.

The Arrhenius parameters for the chloromethanes are then readily derived from the values given in table 1. They are given in table 2 along with the cumulative standard deviations.

The experiments just described along with those on methane, ethane and propane from part 1 enable two circuits of competitive chlorinations to be set up:

(i) methane, ethane, propane, methylene chloride, methane; and

(ii) methane, ethane, propane, methyl chloride, chloroform, methane,

in which every adjacent pair of substances has been chlorinated in competition. The two series provide an excellent internal check for consistency of the derived Arrhenius parameters. The consistency of the results is most clearly established by comparing the rate constants determined by two different paths for methyl chloride and methylene chloride. The rate constants calculated for the middle of the experimental temperature range are given in the last column of table 2 and agree well within the experimental error. Although there is only a single value for chloroform, this value is confirmed since it is involved in the calculation of one of the values for methyl chloride.

The comparison of Arrhenius parameters provides a more critical test. For methylene chloride the agreement of the two pairs of values derived respectively by competition with methane and propane agree excellently, the differences being within the standard deviations. The two sets of Arrhenius parameters for methyl chloride are just within the 95 % probability limits of the two sets of data. The probability is therefore high that one of the values includes a systematic rather than random error. Such an error could have arisen in the chloroform + methyl chloride series for, as has already been noted, no chlorine dependence of the relative rate constants was observed at the low temperatures. Had a proportion of the CCl_3 radicals been removed from the system without forming carbon tetrachloride the apparent activation energy difference $E(CHCl_3) - E(CH_3Cl)$ would have been too large. Consequently the absolute value of $E(CH_3Cl)$ would have been too low. This then suggests that the higher value of $E(CH_3Cl) = 3400$ cal mole^{-1} is the more likely to be correct.

Previously, Pritchard, Pyke and Trotman-Dickenson [9] had obtained for reaction (2) with methyl chloride,

$$k_2 \text{ (methyl chloride)} = 5 \times 10^{13} \exp\left[-3400/\boldsymbol{R}T\right] \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1},$$

using a rather difficult competitive technique in which methane and methyl chloride were chlorinated simultaneously, the change in concentration of the two substances being determined. Although they did not claim high accuracy for this value, the evidence is nevertheless somewhat in favour of the higher of the two pairs of values given in table 2. In the absence of further experimental data, however, we prefer to take intermediate values weighted slightly in favour of the higher set:

$$k_2 \text{ (methyl chloride)} = (3{\cdot}4 \pm 0{\cdot}5) \times 10^{13} \exp\left[-3300 \pm 100/\boldsymbol{R}T\right] \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

The relative values recently obtained by Goldfinger, Huybrechts and Martens [7] by competitive chlorination of methane and the chloromethanes against tetrachloroethylene are in rough agreement with those reported here. The experiments were not, however, carried out over a sufficient temperature range for accurate activation energy data to be obtained. Nevertheless, it is clear that within the limits of the experiments their activation energy differences agree with those calculated from our own results. The best comparison of the two sets of data is between rate constants calculated for a temperature near the middle of their range (say, 420°K). By adjusting the absolute scale of Goldfinger, Huybrechts and Martens's results so as to give the best agreement with our own the following values are obtained for $\log k_2$:

	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$
present work	11·36	11·83	11·86	11·07
Goldfinger *et al.*	11·6	11·8	11·6	11·2$_5$
difference	−0·2$_4$	+0·0$_3$	+0·2$_6$	−0·1$_8$

The agreement is not as good as might have been hoped but is probably within the error of the two sets of experiments. In spite of the slight uncertainty as to how to fix the absolute scale, the correlation of the two sets of data is of considerable value in that it enables absolute Arrhenius parameters to be calculated for reaction (2) with tetrachloroethylene and pentachloroethane:

$$k_2(C_2Cl_4) = 16 \times 10^{13} \exp\left(0/\boldsymbol{R}T\right] \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1},$$

$$k_2(C_2HCl_5) = 0{\cdot}5 \times 10^{13} \exp\left[-3400/\boldsymbol{R}T\right] \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

The value of zero for $E_2(C_2Cl_4)$ is of considerable interest as it provides good confirmation of the correctness of the activation energy taken for the reaction with hydrogen. The Arrhenius parameters for pentachloroethane are interesting in being very close to those for chloroform.

In previous papers,[11-13] attempts have been made to calculate absolute *A* factors for halogen atom reactions. These calculations have assumed (i) that the $>$C——H——X bonds in the activated complexes (X = F, Cl, or Br) are linear and 0·18 Å longer than normal single bonds, and (ii) that the vibrational modes peculiar to the activated complex, namely, the symmetrical stretching and the bending of the C——H——X bonds, have the same force constants as the similar vibrations in the H——H——Cl complex, these force constants having been chosen [14] to give agreement between the experimental and calculated values of the *A* factors for the hydrogen chlorine reaction.

These assumptions, particularly the second, represent a great oversimplification of the actual situation but nevertheless they lead to remarkable agreement between the calculated and experimental *A* factors for some thirty halogen-atom reactions.[13]

The largest discrepancy between the two values is for $Cl+CH_4$ where the calculated value is some 4·5 times too large. It was therefore of particular interest to find out whether this discrepancy was to be observed in the chloromethanes. The relevant data are given in table 3. The substitution of hydrogen atoms by Cl clearly reduces the discrepancy. The agreement for methylene chloride and chloroform is well within the probable error in the calculations. It appears then that the vibrations in the complexes CH_3——H——Cl and CH_2Cl——H——Cl are somewhat stiffer than assumed in the calculations.

TABLE 3.—EXPERIMENTAL AND CALCULATED A FACTORS

substance	$10^{-13}\times A_{\text{exp.}}$ per H atom cm³ mole⁻¹ sec⁻¹	$10^{-13}\times A_{\text{calc.}}$ per H atom cm³ mole⁻¹ sec⁻¹	$A_{\text{calc}}/A_{\text{exp.}}$
CH_4	0·60	2·7	4·5
CH_3Cl	1·10	3·7	3·3
CH_2Cl_2	1·35	1·5	1·1
$CHCl_3$	0·69	0·9	1·3

As with all the halogen atom reactions studied, the *A* factors are close to the collision frequencies. This arises since the decrease in the rotational and translational entropies of activation as RH becomes larger are almost exactly counteracted by the increase in the vibrational entropies of activation.

The activation energies for the four methanes do not fall continuously as might have been expected but show a minimum at methylene chloride. The rise from methylene chloride to chloroform may arise from the effect of the continual decrease in zero point energy in going from methane to chloroform.

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APPENDIX

The dependence upon chlorine pressure of the relative rates of formation of CH_3Cl and CCl_4 in the competitive chlorination of CH_4 and $CHCl_3$ when the chains are short may be derived as follows.

It is assumed that all chains initiated by dissociation of chlorine are terminated by recombination of CCl_3 radicals and that the important reactions are therefore:

$$Cl_2 = 2Cl \tag{1}$$

$$Cl + CH_4 = HCl + CH_3 \tag{2m}$$

$$Cl + CHCl_3 = HCl + CCl_3 \tag{2c}$$

$$CH_3 + Cl_2 = CH_3Cl + Cl \tag{3m}$$

$$CCl_3 + Cl_2 = CCl_4 + Cl \tag{3c}$$

$$2CCl_3 = C_2Cl_6. \tag{8}$$

Under steady illumination the rate of reaction (1) can be written as $k_1[Cl_2]$. Assuming a stationary state has been set up, we have

$$[CCl_3] = \{k_1[Cl_2]/k_8\}^{\frac{1}{2}};$$

and, denoting rates of formation by R,

$$\begin{aligned} R_{CH_3Cl} &= k_{3m}[CH_3][Cl_2] = k_{2m}[CH_4][Cl] \\ R_{CCl_4} &= k_{3c}[CCl_3][Cl_2] \\ &= k_{2c}[CHCl_3][Cl]\{1+k_8[CCl_3]/k_{3c}[Cl_2]\}^{-1} \\ &= k_{2c}[CHCl_3][Cl]\{1+(k_1k_8/k_{3c}^2)^{\frac{1}{2}}[Cl_2]^{-\frac{1}{2}}\}^{-1}\ . \end{aligned}$$

Hence

$$\frac{R_{CH_3Cl}/[CH_4]}{R_{CCl_4}/[CHCl_3]} = \frac{k_{2m}}{k_{2c}}\left\{1+\left(\frac{k_1k_8}{k_{3c}^2}\right)^{\frac{1}{2}}[Cl_2]^{-\frac{1}{2}}\right\}. \tag{B}$$

Thus, the fractional rate of formation of methyl chloride divided by the fractiona. rate of formation of carbon tetrachloride should be a linear function of $[Cl_2]^{-\frac{1}{2}}$l Extrapolation of a plot of the l.h.s. of eqn. (B) against $[Cl_2]^{\frac{1}{2}}$ will then give k_{2m}/k_{2c} as the intercept.

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THE COMPETITIVE CHLORINATION OF PROPANE AND OLEFINS

A.K.E. Hagopian, J.H. Knox and (in part) Miss E.A. Thompson
Department of Chemistry, University of Edinburgh

Summary

By chlorinating mixtures of propane and olefins (ethylene, propene and isobutene) we have shown that there is a strong heterogeneous component in the chlorination of the olefins. The heterogeneous reaction can be somewhat reduced by choosing a suitable reaction vessel surface but cannot be completely eliminated. However in favourable cases it can be allowed for and the ratios of the rate constants for chlorine atom attack on propane and olefins can be determined. The absolute rate constants for addition of chlorine atoms to olefins can then be derived using the known value of the rate constant for $Cl + C_3H_8 = C_3H_7 + HCl$.

The competitive method of studying chlorination reactions has been used successfully to determine the absolute rate constants for chlorine atom abstraction reactions (reaction 2) ($^{1-6}$). It was the aim of the present work to determine the rate constants for addition of chlorine atoms to simple olefins by competitive chlorination of olefins and propane, k_2 being known for propane (^{3}). The expected reactions in a competition between a hydrocarbon RH, an olefin A and chlorine atoms when the ACl radical is stable (i.e. below about 150°C) (^{7}) are :

$$Cl + RH = R + HCl \quad (2)$$

$$R + Cl_2 = RCl + Cl \quad (3)$$

$$Cl + A = ACl \quad (2')$$

$$ACl + Cl_2 = ACl_2 + Cl . \quad (3')$$

To a good approximation when the percentage consumptions of A and RH differ by less than 30% the rate constant ratio $k_{2'}/k_2 = R$, where R is the concentration ratio

$$R = [ACl_2]\,[RH]_m/[RCl]\,[A]_m$$

$[ACl_2]$ and $[RCl]$ are the yields of the two chloride products which we determine by gas chromatography, and $[RH]_m$ and $[A]_m$ are the mean concentrations of hydrocarbon and olefin during the reaction.

An essential test of the simple mechanism is that the concentration ratio R is independent of the concentration of hydrocarbon, chlorine or any additive which does not react with R or ACl. If R does depend upon any of these factors the mechanism is more complex than supposed and $R \neq k_{2'}/k_2$.

EXPERIMENTAL

Experiments were carried out in a 50 ml Pyrex reaction vessel which was thermostatted at 35 °C. The reaction vessel was illuminated when desired by light from a 250 w tungsten filament projection lamp placed about 20 cm from the reaction vessel. The light was filtered and roughly focussed by means of a spherical 1 litre flask containing copper sulphate solution. When the reaction vessel was not illuminated it could be kept in complete darkness by a light tight jacket. The rest of the high vacuum apparatus was of conventional design except that all taps which came in contact with chlorine or the reaction products were metal valves with teflon seats and glands (manufactured by F. J. Hone Ltd., 19 Eldon Park, London S. E. 25). Solution of reactants and products in tap grease was thereby avoided.

Reaction products were analysed by gas chromatography using hydrogen as carrier gas and a katharometer as detector.

Reactants were taken from cylinders and purified by trap to trap distillation. They were degassed under high vacuum. The purity thus attained was certainly not sufficient for overall kinetic studies and it is likely that the reaction chains were terminated by first order removal of free radicals.

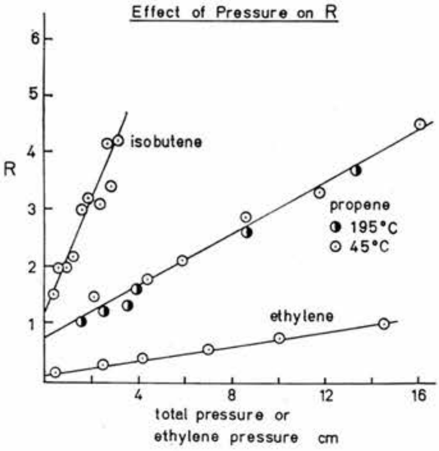

Fig. 1 — The effect of hydrocarbon pressure on the parameter R for mixtures of propane with ethylene, propene and isobutene at 35 °C (except for propene/propane mixtures). Chlorine pressure = 1.5 mm Hg. Surface = clean Pyrex.

RESULTS

Figures 1 and 2 show that the ratio R is not independent of hydrocarbon concentration as required by the simple mechanism : R increases linearly with total hydrocarbon pressure for propene/propane and isobutene/propane mixtures and linearly with ethylene pressure (propane pressure has no influence) for ethylene/propane mixtures.

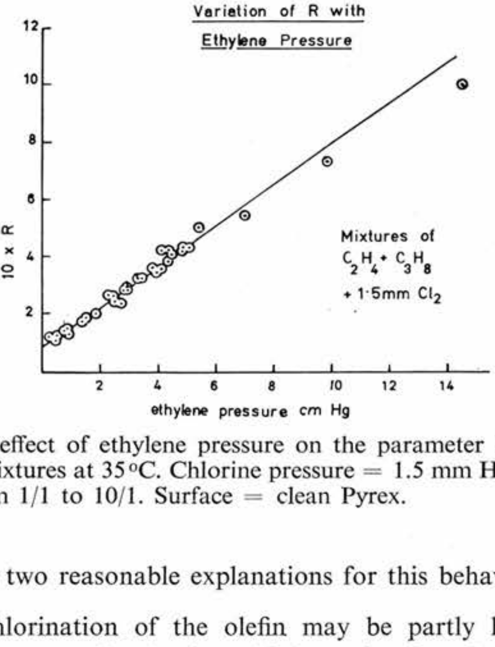

Fig. 2 — The effect of ethylene pressure on the parameter R for ethylene/propane mixtures at 35 °C. Chlorine pressure = 1.5 mm Hg. Composition varied from 1/1 to 10/1. Surface = clean Pyrex.

There are two reasonable explanations for this behaviour :

1) The chlorination of the olefin may be partly heterogeneous, the heterogeneous reaction having a higher order than the homogeneous free radical chlorination.

2) If the chlorination of the olefin is homogeneous the dependence of R upon hydrocarbon concentration can be explained by supposing that the ACl radical is initially formed in an activated state as proposed by Ayscough, Cocker and Dainton (8). The ACl* then decomposes into A + Cl unless deactivated by collision. Reaction (2′) must then be replaced by four reactions :

$$\begin{aligned} A + Cl &= ACl^* && (2'') \\ ACl^* &= A + Cl && (a) \\ ACl^* + Cl_2 &= ACl + Cl_2 && \\ \text{or}\quad & ACl_2 + Cl && (c) \\ ACl^* + M &= ACl + M && (d) \end{aligned}$$

where M represents any molecule other than Cl_2 which can deactivate the ACl* radicals. The olefin itself would be expected to be the most potent deactivator but deactivation by other molecules might be observable if this scheme held. The ratio R is now given by the more complex expression

$$\mathrm{R} = \frac{k_2''}{k_2} \cdot \left\{ \frac{k_c[\mathrm{Cl_2}] + k_d[\mathrm{M}]}{k_a + k_c[\mathrm{Cl_2}] + k_d[\mathrm{M}]} \right\}$$

At low concentrations of M and Cl_2, R will be proportional to [M]; at sufficiently high pressure R will become independent of reactant pressures and then gives the true value of k_2''/k_2.

For propene and isobutene the first explanation accounts for the observations; for ethylene the situation is more complex. There are certainly heterogeneous effects but they cannot account for the observations and there may be a contribution from an activated molecule scheme. Experiments are now in progress to test this hypothesis.

Experiments to elucidate the heterogeneous effects were carried out with propene/propane mixtures at 35°C in Pyrex reaction vessels with various coatings. In order to eliminate any dark reaction which might occur outside the reaction vessel the following procedure was adopted. Chlorine at a pressure of a few mm Hg was added to the evacuated reaction vessel in the dark. This was followed by 5-10 cm of a roughly equimolar propene/propane mixture. The reaction was allowed to proceed in the dark for a measured time. The remaining molecular chlorine was then destroyed by illuminating the mixture for 30 mins. If the dark reaction is assumed to be first order in chlorine and to produce only 1,2 dichloropropane, the rate of formations of dichloropropane during the dark period may be written Rate $= k_{\mathrm{het}}[\mathrm{Cl_2}]$ where k_{het} may depend upon both the hydrocarbon pressure and the nature of the surface. It can then be readily shown that

$$\ln(1 + \mathrm{R}') = \ln(1 + \mathrm{R}_0') + k_{\mathrm{het}} t_d$$

where t_d is the duration of the dark period, R′ is the ratio $[\mathrm{ACl_2}]/[\mathrm{RCl}]$ at the end of the experiment, and R_o' the ratio of chloride products which would be obtained if there were no period of dark reaction. Figures 3-5 show that plots of $\ln(1 + \mathrm{R}')$ against t_d are indeed straight lines as predicted.

Figure 3 shows plots of $\log_{10}(1 + \mathrm{R}')$ against t_d for a number of reaction vessel surfaces. The rate of the dark reaction varies widely with the nature of the surface but it cannot be reduced to zero. It is therefore possible that some homogeneous dark reaction occurs. In subsequent work a urea-formaldehyde resin surface prepared in situ was used since it had low activity and gave reproducible results.

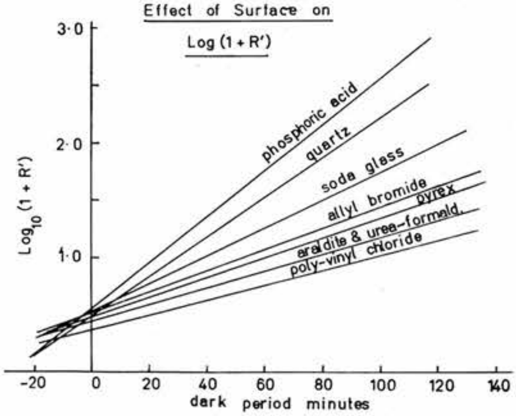

Fig. 3 — The effect of surface on the dark reaction at 35 °C for propene/propane mixtures. Approximate mixture composition : 15 mm Hg propane, 15 mm Hg propene, 1.5 mm Hg chlorine.

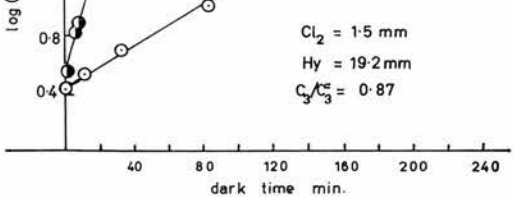

Fig. 4 — The effect of surface/volume ratio on the dark reaction at 35 °C for propene/propane mixtures. Surface = urea formaldehyde resin.

The effect of change in surface to volume ratio is shown in figure 4. The effect is what might be expected for a heterogeneous reaction and there is no evidence for any homogeneous dark reaction. The flattening of the curve for the packed reaction vessel at values of Log (1 + R′) above 2.2 may be explained by a slight light leak into the reaction vessel or by a very slow heterogeneous chlorination of propane.

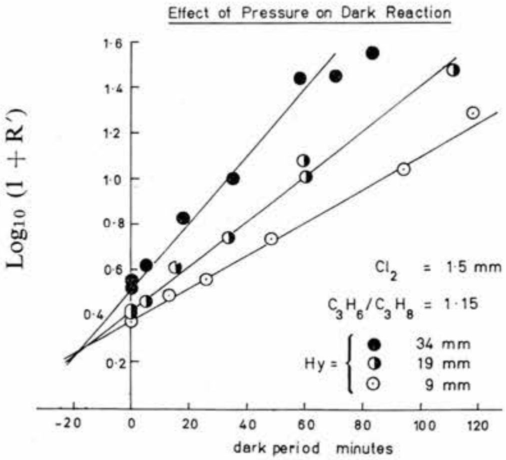

Fig. 5 — The effect of hydrocarbon pressure on dark reaction at 35 °C for propene/propane mixtures. Surface = urea formaldehyde resin.

The effect of change of total pressure on the heterogeneous reaction at a constant chlorine pressure of 1.5 mm Hg is shown in figure 5. k_{het} increases approximately linearly with total hydrocarbon pressure. The three lines intersect at approximately —20 mins. Had the light source been of such intensity that the homogeneous reaction could be considered to be instantaneous, all values of R_o' should have been the same. However under our conditions the homogeneous reaction took a finite time and inevitably some heterogeneous reaction must have taken place concurrently. Thus the lines in figure 5 would be expected to intersect, as observed, at a negative time somewhat less than the duration of illumination.

From the geometry of figure 5 it can be seen that the intercepts R_o' must increase with pressure. It is just from such intercepts that the ratio R (plotted in figure 1) is calculated.

It seems that for propene/propane mixtures the increase in R with pressure can be adequately explained by the occurrence of concurrent heterogeneous and homogeneous reactions. The rate of the heterogeneous reaction decreases with pressure of hydrocarbon and it is likely that at very low pressures of hydrocarbon its rate will be negligible. Thus the intercept of lines in figures 1 and 2 on the y axis will give the true value of $k_{2'}/k_2$. Likewise the intersection of the three lines in figure 5 should give the same value. The values of $k_{2'}$ obtained in this way for propene, making use of the known value of k_2 for propane, is given in the table.

TABLE 1

Rate constants for addition of Cl *to olefins*

Olefin	Temperature	$\mathrm{Log}_{10}k_{2'}$ (1)	Reference
C_2Cl_4	110-210 °C	9.20	5,4.
$C_2H_2Cl_2$	30-65 °C	9.43	9
sec C_3H_8	35 °C	10.36	3
C_2H_4(2)	35 °C	9.3 ± 0.1	this work
C_3H_6	35 °C	$10.2_5 \pm 0.1$	this work
iC_4H_8	35 °C	10.4 ± 0.1	this work

(1) The units of k are $\mathrm{l.mole^{-1}\,sec^{-1}}$.

(2) See text for discussion of reliability of value of $k_{2'}$.

The results obtained with isobutene, although less extensive, are similar and indicate that the reaction has a strong heterogeneous component. The rate of this reaction is so high that considerable difficulty was experienced in obtaining reproducible results. The heterogeneous chlorination of isobutene differs from that of propene in that it produces $CH_2Cl.C(CH_3){=}CH_2$ in amounts comparable with the yield of dichloroisobutane. Only very small quantities of allyl chloride are formed in the heterogeneous chlorination of propene.

CONCLUSIONS

We believe that with propene and isobutene the values of the intercepts in figure 1 and of the intersection of lines in figure 5 can be used to calculate true values of $k_{2'}/k_2$ and hence absolute values of $k_{2'}$.

For ethylene the intercept in figure 2 appears to give too low a value for $k_{2'}$. The value obtained is an order of magnitude lower than that for propene or isobutene; it is approximately equal to the value obtained for C_2Cl_4 by Goldfinger et al (5) and somewhat lower than that obtained by Ayscough et al. (9) for cis-dichloroethylene. Rough transition state calculations similar to those previously carried out for alkanes (10) indicate that the A factor for Cl atom attachment to ethylene should be five to ten times that for attachment to chlorinated ethylenes containing two or more Cl atoms. Since the activation energy for $Cl + C_2H_4$ is not likely to be greater than that for $Cl + C_2Cl_4$ it is probable that the rate constant for the former reaction is at least five times greater than for the latter.

Dr. G. Martens (Brussels) said :

1. We have now been able to measure the rate constant of $C_2H_4 + Cl$; a constant value has been found $\log k_2 = 10.2 \pm 0.1$ between 310 and 400°K competing ethylene either with methyl chloride or with ethane.

2. In both cases the absence of wall effects has been checked by a careful analysis following the reaction order up to approximately 30%. I believe that careful checks of the reaction mechanism, as done in this paper, are of particular interest even if the mechanism is believed to be known.

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[17]

THE GASEOUS PRODUCTS FROM THE OXIDATION OF PROPANE AT 318°C

THE GASEOUS PRODUCTS FROM THE OXIDATION OF PROPANE AT 318°C

BY JOHN H. KNOX
Dept. of Chemistry, University of Edinburgh

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The gaseous products of the oxidation of propane at 318°C have been determined by gas chromatography and particular attention has been paid to the relative yields in the early stages. The initial percentage conversion of propane is 75 % to propylene, 5 % to ethylene and 10-20 % to carbon monoxide. These values are almost independent of oxygen pressure over a twenty-fold range. It is concluded that the oxidation in the initial stages occurs mainly by an HO_2 radical chain (reactions (1) and (2)). The yield of propylene in oxygen-rich mixtures reaches a maximum which is independent of oxygen pressure and nearly independent of added propylene pressure. It is concluded from this that an equilibrium is reached and that a change of mechanism occurs, the HO_2 radical chain giving way to a more complex multi-radical reaction in the later stages.

A previous paper [1] described the general features of the low-temperature oxidation of ethane and propane at 318°C. In the present paper a more detailed account is given of the gaseous products of the oxidation of propane.

Earlier work on the oxidation of propane [2-4] concentrated mainly on the products, particularly the oxygenated products, from the later stages of the reaction. This was partly because the methods of analysis then available required rather large quantities of material and were not generally suitable for the determination of small percentage impurities in gas samples, and partly because it was believed that the oxygenated products were the key to the reaction mechanism. With the advent of gas chromatography it has become possible to determine accurately small traces of impurities in gas samples and therefore to determine with precision the yields of different products from the very early stages of a reaction.

Gas chromatography was applied by Falconer and Knox [5] in a study of the high-temperature oxidation of propane and by Yokely and Ferguson [6] to the cool-flame oxidation of propane. The high-temperature study [5] showed that an important reaction in the early stages was the conversion of propane to propylene by an HO_2 radical chain. We were therefore interested to discover whether this was a characteristic high-temperature reaction only or whether it occurred at all temperatures above 300°C; whether, in fact, the well-established negative temperature coefficient and the associated phenomenon of cool flames could be explained in terms of a change from a " low-temperature " mechanism to an HO_2 " high-temperature " mechanism.

The results which follow show that even at 318°C the main initial reaction in the oxidation of propane is still best represented by the HO_2 chain defined in reactions (1) and (2):

$$C_3H_7 + O_2 = C_3H_6 + HO_2 \tag{1}$$

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2. \tag{2}$$

EXPERIMENTAL

The oxidations were carried out in a 500-ml spherical reaction vessel which had been aged by carrying out a large number of oxidations. It was housed in an electric furnace thermostatted at 318°C. Variation from this temperature over the reaction vessel was less than 2°C and time variation was undetectable. The reaction mixture was made up in a 1-l. bulb and admitted to the reaction vessel through capillary tubing. For analysis the reaction vessel was connected to a 28-ml detachable trap maintained at room temperature. Approximately 0·2 mmoles were taken for each analysis.

On transfer to the gas-analysis apparatus, the trap was cooled in liquid oxygen. The permanent gases were transferred by a Toepler pump to a calibrated gas-burette and finally to the pick-up U-tube of the chromatography apparatus. The mixture, containing O_2, CO and CH_4, was analyzed on a 360-cm column containing activated charcoal at room temperature. The C_2—C_4 fraction was then taken off by warming the trap to -78°C, measured, and analyzed on a 360-cm column of activated alumina at room temperature, a low flow-rate being used for elution of ethane and ethylene and a higher flow-rate for the elution of propane, propylene and isobutane (an impurity in the propane). Calibration for each gas was carried out using peak-heights. Detection throughout was by katharometer and the carrier gas was hydrogen. The minimum detectable quantities of each gas, which gave about 1 % full-scale deflection, were (in μmoles): oxygen 0·01; carbon monoxide 0·02; methane 0·1; ethane 0·005; ethylene 0·005; propane 0·01; and propylene 0·02. Carbon dioxide which would appear in the second fraction was unfortunately not determined as it is irreversibly adsorbed on alumina. However, the results of Chernyak, Antonovskii, Revzin and Shtern [3] show that the yield of carbon dioxide at 350°C is initially only 1/10th that of carbon monoxide and towards the end of the reaction about 1/4.

MATERIALS

Oxygen was obtained from B.O.G. cylinders and was used without purification apart from passage through a trap cooled in liquid oxygen to remove water and other condensable impurities.

Propane was a gift sample by I.C.I. Ltd. It was subjected to several trap-to-trap distillations. Analysis by gas chromatography showed the impurities to be: ethane 0·18 %; propylene 0·23 %; and isobutane about 0·6 %.

Propylene was prepared by dehydration of isopropanol and contained no impurities detectable by gas chromatography.

RESULTS

Analyses were carried out at various stages in the oxidation of the following mixtures:

mixture	C_3H_8, mm Hg	O_2, mm Hg	C_3H_6, mm Hg	total, mm Hg	$\frac{\text{hydrocarbon}}{\text{oxygen}}$
A	100	10·2	0·0	110·2	9·8
B	83	27·5	0·0	110·5	3·0
C	55	55	0·0	110	1·00
D	44	83	0·0	127	0·53
E	40	83	4·1	127	0·53

The analytical results are shown graphically in fig. 1-6. The most striking feature is that the variation of the % conversion to the different products never varies by a factor of more than two even when the [hydrocarbon]/[oxygen] ratio alters by a factor of nearly 20.

Fig. 1 shows that the disappearance of oxygen for all the mixtures studied is approximately linear with pressure rise and that the proportionality factor does not depend significantly on the initial oxygen pressure. Fig. 1 therefore provides a justification for taking pressure rise in oxidations as a measure of the extent of reaction. To a close approximation for all the mixtures studied the decrease in oxygen pressure ($-\Delta[O_2]$) is twice the pressure increase (Δp):

$$-\Delta[O_2]/\Delta p = 2{\cdot}0.$$

It is also noted that the oxygen is not completely consumed by the end of the reaction and that the residual oxygen increases more rapidly than the oxygen initially present (broken line in fig. 1). This finding is in agreement with kinetic results which show that there exists an oxygen pressure below which chain branching no longer takes place.

Consumption of propane is illustrated in fig. 2. The rate of consumption of propane relative to pressure rise decreases as the reaction proceeds. The pressure rise does not therefore give a good measure of the consumption of hydrocarbon. The initial rates of consumption of C_3H_8 cannot be established with high accuracy owing to the scatter of the points but they appear to be nearly equal for mixtures B, C and D. In the absence of more exact data it is assumed that the initial rates for mixtures A, B, C and D are identical and are given by the parallel lines in fig. 2. These have been drawn with gradients

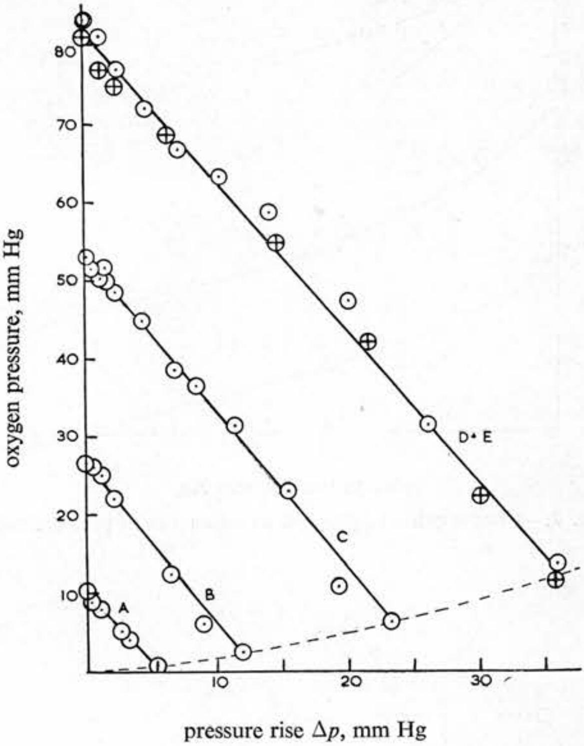


FIG. 1.—Consumption of oxygen as a function of pressure rise.
Top line : ⊙ mixture D, ⊕ mixture E.

$$-\Delta[C_3H_8]/\Delta p = 1{\cdot}4,$$

giving

$$\Delta[C_3H_8]/\Delta[O_2] = 0{\cdot}7.$$

Propane is thus consumed somewhat more slowly than oxygen in the early stages. In the later stages of the reaction the difference is much greater and with mixtures D and E in the last 30 % of reaction :

$$-\Delta[C_3H_8]/\Delta p = 0{\cdot}4,$$

$$\Delta[C_3H_8]/\Delta[O_2] = 0{\cdot}2.$$

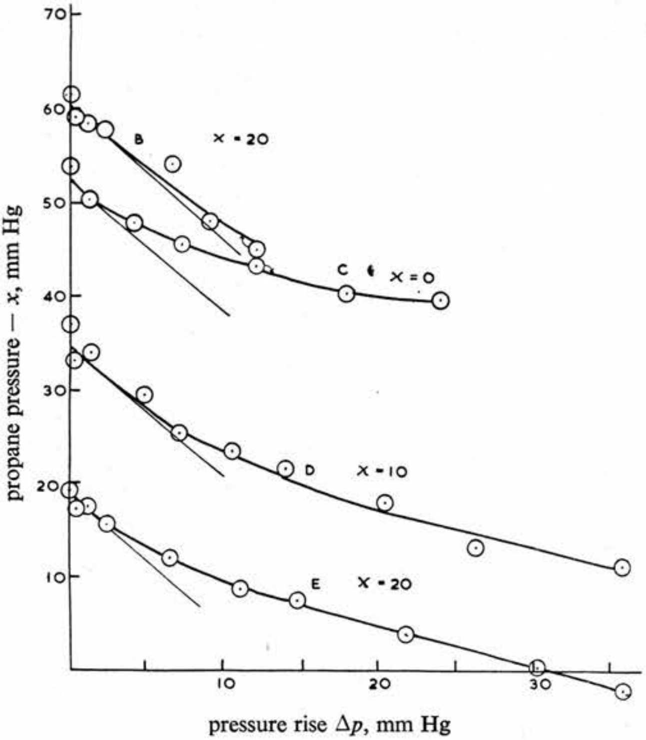


FIG. 2.—Consumption of propane as a function of pressure rise.

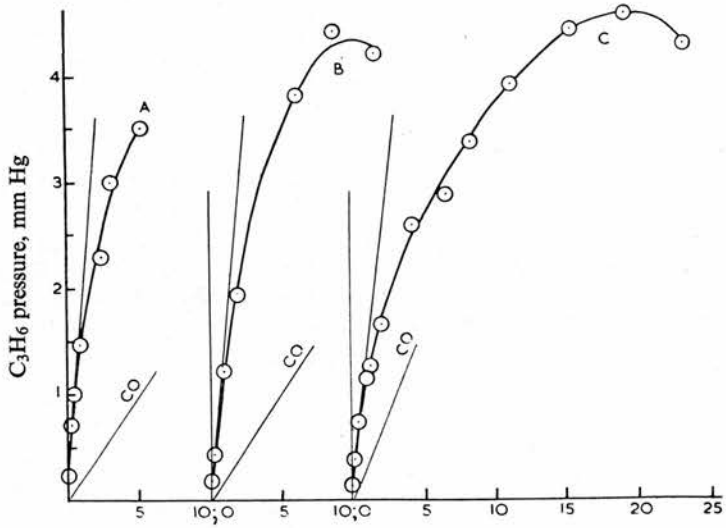


FIG. 3.—Formation of propylene as a function of pressure rise showing initial rates for propylene and carbon monoxide.

This final ratio corresponds to the complete combustion of propane to CO_2 and water. One must, however, bear in mind that oxygenated intermediates are

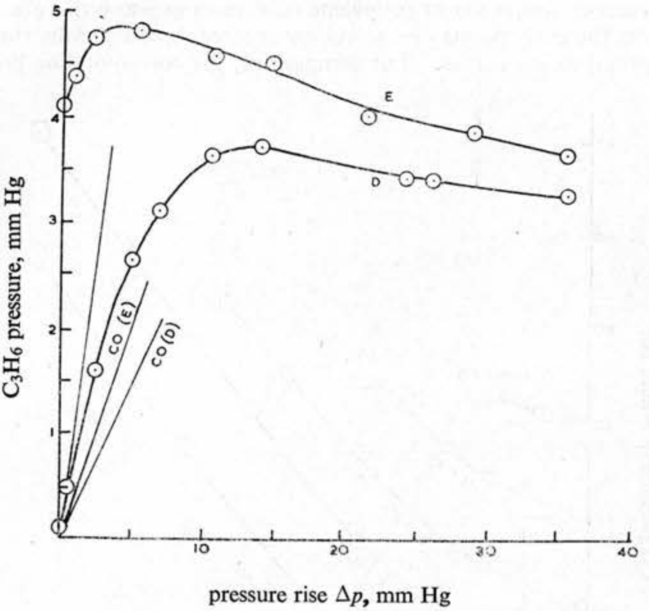


FIG. 4.—Effect of added propylene on formation of propylene as a function of pressure rise.

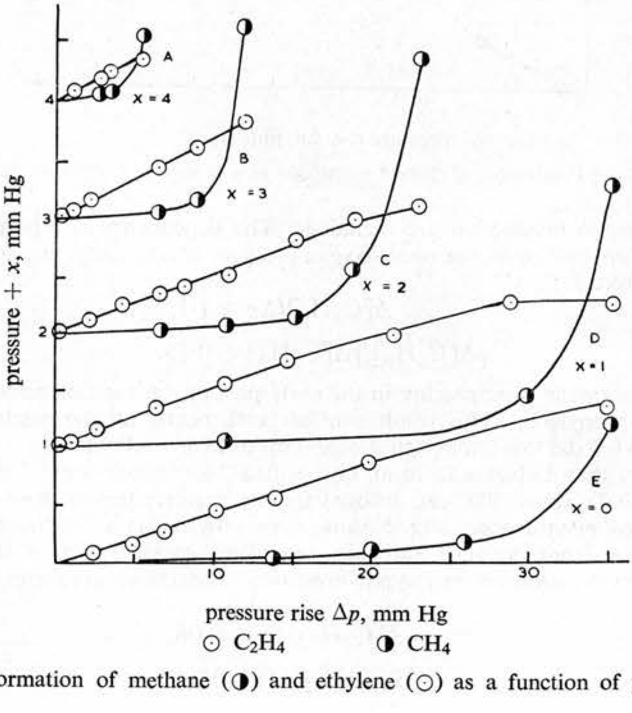


FIG. 5.—Formation of methane (◑) and ethylene (⊙) as a function of pressure rise.

probably being oxidized rapidly at this stage and that combustion of C_3H_8 to CO_2 and water will not represent the reaction actually occurring.

The main initial product of the reaction is propylene as seen from fig. 3 and 4. The initial rates of formation of propylene relative to pressure rise are accurately obtained from the early points on the curves and are represented by the fine lines drawn tangential to the curves. For comparison, the corresponding lines for the carbon monoxide production are included. The dependence of the initial conversion to propylene upon the total oxygen pressure is very slight and for all mixtures apart from E:

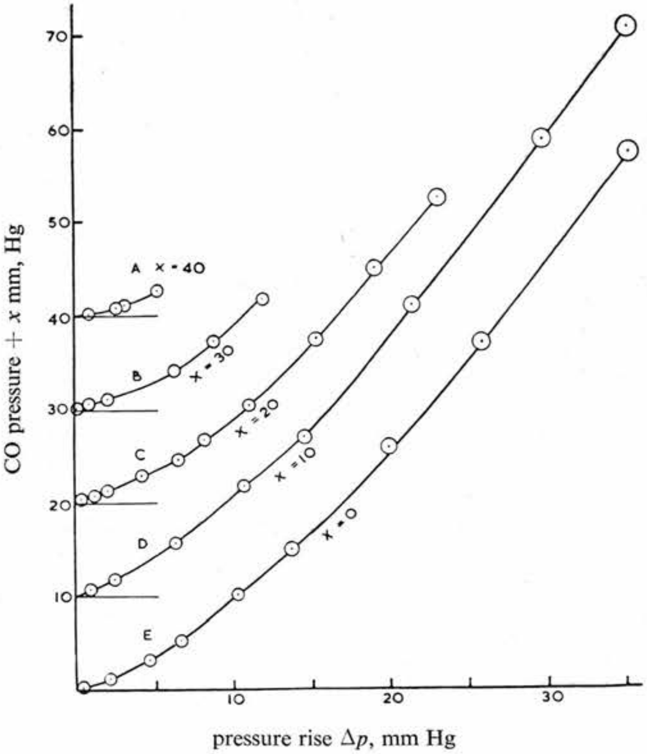


FIG. 6.—Formation of carbon monoxide as a function of pressure rise.

$$\Delta[C_3H_6]/\Delta p \doteqdot 1{\cdot}1,$$

$$-\Delta[C_3H_6]/[\Delta[C_3H_8] \doteqdot 0{\cdot}75.$$

75 % of the propane disappearing in the early part of the reaction appears in the products as propylene. This result conflicts with nearly all the mechanisms so far advanced for the low-temperature oxidation of hydrocarbons, and it eliminates the possibility that a change from an unspecified " low-temperature " mechanism to an HO_2 chain above 400° can account for the negative temperature coefficient and associated phenomena. Fig. 5 shows that ethylene is a significant product of the reaction from the start and, like propylene, its yield relative to pressure rise shows no dependence on oxygen pressure. The initial gradients are represented by

$$\Delta[C_2H_4]/\Delta p \doteqdot 0{\cdot}06,$$

$$\Delta[C_3H_6]/\Delta[C_2H_4] \doteqdot 18.$$

Carbon monoxide, although a major reaction product in the later stages, is not formed in quantity in the early stages. Its initial rate of formation relative to pressure rise increases slightly with oxygen pressure from 0·15 with the 9·8/1 mixture to 0·30 with the 1/2 mixture. Carbon monoxide is formed initially much more slowly than propylene, but later in the reaction much faster (fig. 6). Towards the end of the reaction in the 1/2 mixture it is formed roughly equimolecularly as the oxygen is consumed. Presumably the formation of water and carbon dioxide accounts for the remainder of the oxygen consumed in the later stages.

The yield of methane is shown in fig. 5. It is formed only towards the end of the reaction and is almost certainly derived from methyl radicals which are normally oxidized.

The main features of the early stages in the reaction may therefore be represented by the equation

$$140O_2+100C_3H_8 = 75C_3H_6+5C_2H_4+10\text{-}20CO+\text{other products},$$

and one might conclude that the initial reaction of a molecule of propane results in the formation of either one molecule of propylene, or one molecule of ethylene, or one molecule of carbon monoxide.

DISCUSSION

Detailed measurement of the initial rates of formation of the different gaseous products relative to pressure rise gives the values in table 1. Only the yield of carbon monoxide is significantly dependent upon oxygen pressure and even then the increase is by a factor of only two when the oxygen pressure increases by a factor of 20. The reactions forming propylene, ethylene and carbon monoxide must therefore have almost the same kinetic dependence upon oxygen pressure.

TABLE 1.—INITIAL YIELDS OF GASEOUS PRODUCTS FROM THE OXIDATION OF PROPANE AT 318°C RELATIVE TO PRESSURE RISE (IN mm PRODUCT PER mm RISE OF PRESSURE)

mixture	A	B	C	D	E
[hydrocarbon]/[oxygen]	9·8	3·0	1·0	0·53	0·53 (10 % C_3H_6)
oxygen cons.	1·8	2·15	2·1	2·0	1·9
propane cons.*	1·4	1·4	1·4	1·4	1·1
propylene	1·25	1·1	1·0	0·95	0·4
ethylene	0·075	0·07	0·06	0·04	0·055
carbon monoxide	0·15	0·18	0·30	0·27	0·36
$[C_3H_6]/[C_2H_4]$	17	16	20	23	7
$[C_3H_6]+[C_2H_4]+[CO]$	1·47	1·35	1·35	1·26	0·81
$[C_3H_6]/[CO]$	8·4	6·1	3·3	3·5	1·1
$[O_2]-([C_3H_6]+[C_2H_4])$	0·5	1·0	1·05	1·0	1·1

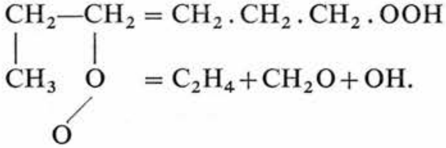
* all values except that for mixture E assumed to be 1·4.

Even in the later stages, oxygen pressure has little effect on the relative yields and therefore reactions of free radicals with oxygen cannot be rate determining in the oxidation. This suggests that they are very fast compared with the reactions in which radicals attack the hydrocarbon. In addition, no important competitive reactions can be occurring where one reaction requires oxygen and another does not. Ethylene, for example, cannot arise from the pyrolysis of the propyl radical if propylene arises from its reaction with oxygen.

Since oxygen is consumed at least as fast as propane and since propylene is the major initial product, the formation of propylene must require at least one molecule of oxygen. The only possible scheme which satisfies this condition is one involving reactions (1) and (2). The reaction forming ethylene must have the same oxygen dependence and must therefore be either

$$\text{pri } \mathrm{C_3H_7 + O_2 = CH_3OO + C_2H_4}, \tag{3}$$

or a reaction of the C_3H_7OO radical such as



$$\begin{array}{ll} \mathrm{CH_2{-}CH_2} & = \mathrm{CH_2\,.\,CH_2\,.\,CH_2\,.\,OOH} \\ |\qquad\ \ | & \\ \mathrm{CH_3}\quad \mathrm{O} & = \mathrm{C_2H_4 + CH_2O + OH.} \\ \qquad / & \\ \quad \mathrm{O} & \end{array} \tag{4}$$

This reaction is similar to the reactions postulated by Bailey and Norrish[7] to account for the formation of ring ethers in the cool-flame combustion of hexane. Ethylene is formed at a roughly constant rate throughout the reaction and it is unlikely that any other mode of formation becomes important in the later stages of the reaction.

The early formation of carbon monoxide is difficult to explain, but in the later stages it is clearly formed by extensive degradation of the propane molecule. The rough correspondence between the carbon monoxide formed and the oxygen consumed suggests that a reaction such as

$$\mathrm{CHO + O_2 = CO + HO_2} \tag{5}$$

may be the major source of carbon monoxide. During the later stages of reaction, a notable feature of the results is the rapid fall-off in the production of propylene. In the high-temperature oxidation, replacement of propane by propylene greatly increased the initial rate of formation of carbon monoxide and it was thought that the initial rate observed in the present work might be due to the oxidation of the propylene already formed by the time that the first analysis was made. However, fig. 5 and 6 show that the replacement of propane by propylene had little effect on the initial rate of formation of carbon monoxide and virtually no effect on its later production. The initial carbon monoxide must therefore arise predominantly from the oxidation of the C_3H_7 radical not from propylene. Since its relative yield is only slightly dependent upon oxygen pressure and independent of the actual rate of reaction it must arise from a sequence of reactions, none of which is more than first order in the reaction products (free radicals or stable molecules). Comparison of the figures for the relative rate of propane consumption and the relative rate of formation of $C_3H_6+C_2H_4+CO$ suggest that in all oxidations except that of mixture E a propane molecule can give rise initially to only one molecule of CO. The initial formation of CO probably follows a skeleton reaction

$$\mathrm{C_3H_7OO} \rightarrow \rightarrow n\mathrm{CO} + ?$$

where $n \doteqdot 1{\cdot}0$. In view of the kinetics of the reaction there are few possibilities. (i) CO may be formed as a result of a surface oxidation of either C_3H_7OO or one of its decomposition products such as an aldehyde. (ii) CO may be formed as a result of a series of gas-phase reactions involving the progressive stripping of some free radical. (iii) CO may be formed by the oxidation of a stable product, such as an aldehyde, derived from the decomposition of the peroxy radical.

Possibility (iii) may be discounted for a number of reasons. The reaction of oxygen with any likely intermediate would almost certainly be slow and would in any case be a branching reaction if it occurred in the gas phase. Now it is highly probable that any branching agent formed in the early stages is removed at the walls of the reaction vessel,[1] as indicated by the very slow initial acceleration of the oxidation of propane. If the branching agent is then the source of CO it is most likely that the CO is formed at the surface as proposed in (i) above. But again this is unlikely since the observed yield of CO would require that 10-20 % of the propane is initially converted to a branching agent which is then destroyed. The kinetic experiments previously described [1] are against this unless the chain length for oxidation is very short indeed. However, this does not discount the possibility that some other early product diffuses to the walls and produces CO there. The importance of such a source of CO could be established by carrying out experiments (*a*) in the presence of a large excess of inert gas when diffusion to the walls is prevented or (*b*) by analyzing the products formed in the vicinity of the wall by using a highly sensitive analytical technique.

The second possibility has the disadvantage that one is immediately faced with the necessity of postulating somewhat implausible radical reactions such as (7) in the sequence below:

$$C_3H_7OO = CH_3CHO + CH_3O, \qquad (6)$$

$$CH_3O + O_2 = CHO + H_2O_2, \qquad (7)$$

$$CHO + O_2 = CO + HO_2. \qquad (8)$$

These conclusions regarding the formation of carbon monoxide both in the initial and later stages contrast with the views of Tipper [8] who suggests that it arises mainly from the decomposition of RCH_2CO radicals formed as a result of radical attack on aldehydes. Although such a reaction must certainly be a source in the later stages it cannot account for the early formation of CO because it is at least second order in primary reaction products.

From the analysis of products from the oxidation of pure propane (mixtures A-D), it might be concluded that the early stages of the oxidation involved mainly the conversion of propane to propylene and the later stages the additional oxidation of propylene. This can be represented by the simplified scheme:

$$C_3H_8 + X \overset{k_a}{\rightarrow} \rightarrow C_3H_6 + Y,$$

$$C_3H_6 + X \overset{k_b}{\rightarrow} \rightarrow \text{other products} + Z,$$

X, Y and Z being free radicals. A scheme of this sort would give rise to an increase in the propylene yield from zero at the start of the reaction to an equilibrium value of

$$[C_3H_6] = k_a[C_3H_8]/k_b.$$

A mixture initially with this equilibrium composition would be expected to be oxidized without change in the $[C_3H_6]/[C_3H_8]$ ratio. The experiments with mixture E show that even when a substantial amount of propylene is initially present the early reaction is still the production of more propylene. It is only later that the $[C_3H_6]/[C_3H_8]$ ratio begins to decline towards its equilibrium value. The radical which removes propane in the early stages must therefore be considerably less reactive with respect of propylene than the radical or radicals which remove it in the later stages. These radicals must attack propylene about 8 times as fast as they attack propane.

It is now clear that the change from the low-temperature (L.T.) type of oxidation to the high-temperature (H.T.) type does not involve the sudden appearance of an HO_2 radical chain about 400°C. If we define the high-temperature mechanism as basically an HO_2 radical chain modified as required by introduction of pyrolysis reactions, and the low-temperature mechanism as that of the later stages of the reaction below 350°C, then both mechanisms operate at all temperatures from 300-500°C. In the early stage of the reaction the H.T. mechanism operates and in the later stage the L.T. mechanism.

Falconer and Knox arrived at a similar conclusion in their study of the high-temperature reaction when they observed that the propylene yield reached a stationary value, and it was suggested that the later stages of the reaction occurred by the low-temperature type of mechanism. If the same reaction is responsible for the equilibrium between propane and propylene at 320°C and 435-475°C then the relative Arrhenius parameters for this reaction with propane and propylene can be shown to be

$$\begin{aligned} k_a/k_b &= k_{C_3H_8}/k_{C_3H_6} \\ &= 150 \exp\left[-8{,}500 \pm 500 \text{ cal mole}^{-1}/\boldsymbol{RT}\right]. \end{aligned}$$

Such a high activation-energy difference and high A factor ratio almost certainly indicates that a mixture of radicals, not a single radical, is attacking the two hydrocarbons and that the composition of the mixture changes as the temperature is raised. However, the invariance of the equilibrium concentration of propylene at any one temperature as the oxygen pressure is altered is evidence that the composition of this radical mixture does not depend upon oxygen.

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THE SLOW OXIDATION OF ETHANE AND ETHYLENE IN THE GAS PHASE

Part I. GENERAL FEATURES AT 362°C
Part II. DETAILED ANALYTICAL FEATURES

by John H. Knox and Clifford H. J. Wells
Department of Chemistry, University of Edinburgh

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THE SLOW OXIDATION OF ETHANE AND ETHYLENE IN THE GAS PHASE.

Part I. GENERAL FEATURES AT 362°C

by J.H. KNOX and C.H.J. WELLS
Department of Chemistry, University of Edinburgh.

Summary

The general kinetic and analytical features of the oxidation of ethane and ethylene at 362° are described. In the early stages of the oxidation of ethane 80% of the hydrocarbon consumed gives ethylene. In the intermediate stages the ethylene is itself oxidised. In the initial stages of the oxidation of pure ethylene over 80% of the hydrocarbon consumed gives formaldehyde, and in the intermediate stages the formaldehyde is oxidised to carbon monoxide. The main molecular stages in the oxidation are therefore:- ethane → ethylene → formaldehyde → carbon monoxide, with water also being formed at the appropriate stages.

The kinetics of the ethane oxidation are similar to those of the propane oxidation and the autocatalysis of the reaction is probably due to the oxidation of formaldehyde. The slow start of the acceleration is in part

due to the fact that the branching intermediate is not an initial product of the reaction.

The general nature of hydrocarbon oxidation reactions is discussed. It is concluded that the main reaction of alkyl radicals with oxygen at 300-400° is usually an abstraction reaction

$$C_nH_{2n+1} \;+\; O_2 \;=\; C_nH_{2n} \;+\; HO_2$$

However there is strong evidence that the HO_2 radical is unable to abstract H from ethane or most other hydrocarbons, and it is proposed that a key reaction in alkane oxidation is the conversion of HO_2 to OH. The reaction $2HO_2 = 2OH + O_2$ is suggested.

THE SLOW OXIDATION OF ETHANE AND ETHYLENE IN THE GAS PHASE

PART I - GENERAL FEATURES

By J.H. KNOX and C.H.J. WELLS

Department of Chemistry, University of Edinburgh.

Although the gas phase oxidation of fuels has been studied intensively for about 70 years we are still uncertain about many of the detailed steps and even some of the major steps in the process. Fortunately there is general agreement about the main experimental facts. The reactions are usually autocatalytic and numerous intermediate products can be identified; the rates of oxidation of most fuels show a negative temperature coefficient between 300 and 400°C with the associated phenomenon of cool flames; the overall rates of oxidation of single fuels are very sensitive to their structure but their relative rates of oxidation in mixtures are much less so. It is universally agreed that these facts demand a free radical chain mechanism for their explanation.

To date three distinct types of chain mechanism have been proposed for the oxidation of alkanes (and more generally saturated fuels). They may briefly be termed the peroxide[1-3], the aldehyde[4,5] and the olefin mechanisms.[6,7] All accept that the primary product from free radical attack on an alkane is an alkyl radical; they differ primarily in the mode of oxidation of the alkyl radical. With ethyl for example the theories give:-

Peroxide $C_2H_5 + O_2 = C_2H_5OO$ (1)
$C_2H_5OO + C_2H_6 = C_2H_5OOH + C_2H_5$ (2)
Aldehyde $C_2H_5 + O_2 = CH_3CHO + OH$ (3)
Olefin $C_2H_5 + O_2 = C_2H_4 + HO_2$ (4)

The first two mechanisms were proposed before complete analysis of the oxidation products could be made, particularly in the early stages of the reaction when secondary reactions are minimal, and they were supported by the evidence of peroxides and aldehydes in the reaction products. Recent work on the oxidation of propane[8], isobutane[9] and now ethane has however shown that in the early stages of alkane oxidations the major initial product is an olefin with the same number of carbon atoms as the alkane. As this reaction accounts for about 80% of the alkane disappearing, the peroxide and aldehyde theories cannot account for more than about 20% of the oxidation at most. The evidence now presented shows that for ethane at least reactions (2) and (3) are unimportant above about 320°.

Apart from the olefin, hydrogen peroxide and water are the only important initial products and in the early stages their combined yield is close to that of the olefin. The peroxide yield is usually about 30% that of the water.[10,11] For ethane the overall initial reactions thus appear to be

$$C_2H_6 + O_2 = C_2H_4 + H_2O_2 \qquad (5)$$

and

$$C_2H_6 + \tfrac{1}{2}O_2 = C_2H_4 + H_2O \qquad (6)$$

Some and possibly all of the water could arise by heterogeneous decomposition of the peroxide.

Hydrogen peroxide could arise from two reactions

$$2\ HO_2 = H_2O_2 + O_2 \qquad (7)$$

$$HO_2 + C_2H_5 = H_2O_2 + C_2H_5 \qquad (8)$$

Reaction (7) has been clearly established by Baldwin and co-workers[12] as important in the oxidation of hydrogen at 500° in boric acid coated vessels. At this temperature the peroxide quickly dissociates and the reaction proceeds by means of a "degenerate chain" in which free radical and molecular intermediates alternate as active species. Recent work by Sampson[13] on the oxidation of ethane at 600° has shown convincingly that a similar mechanism applies there. The degenerate chain for both systems can be written

$$\begin{array}{rcll} OH + C_2H_6\ (H_2) & = & H_2O + C_2H_5\ (H) & (9)\\ C_2H_5\ (H + M) + O_2 & = & C_2H_4\ (M) + HO_2 & (4)\\ 2\ HO_2 & = & H_2O_2 + O_2 & (7)\\ H_2O_2 + M' & = & 2\ OH + M' & (10) \end{array}$$

(the reactants and products in brackets apply to the hydrogen/oxygen reaction). It is an experimental fact that the overall rates of such reactions are close to the independently measurable rate of homogeneous pyrolysis of the hydrogen peroxide present. At 300° however such mechanisms cannot apply since the rate of pyrolysis of the peroxide is much too low[14]. Thus reaction (7) cannot be the main remover of HO_2 since the overall oxidations must be chain reactions. Reaction (9) first proposed by Gray[6] therefore appears inevitable, but there are serious objections to it. The recent re-determination of the thermochemistry of HO_2 by Foner and Hudson[15] closely brackets D[H-OOH] as 89 ± 2 kcal: therefore most reactions of HO_2 with alkanes will be endothermic and are likely to have activation energies at least 5 kcal greater than their endothermicities. The reactivity of HO_2 might therefore be expected to be similar to that of the bromine atom (D[H-Br] = 87 kcal). Competitive oxidation[16,17] studies have shown that the species responsible for removal of hydrocarbons in mixed oxidations has a selectivity between that of Cl and CH_3O and much less than that of Br. For example Knox, Smith and Trotman-Dickenson[16] found that the relative rates of oxidation of propane and ethane in mixtures of the two hydrocarbons differed by a factor of 2.3. The relative rates of attack of Cl[18], CH_3O[14] and Br[18] on these hydrocarbons are 2.0, 3.0 and 10 at 350°C. On the basis of these experiments taken alone, OH is the most likely attacking radical. Although direct data on the selectivity of OH is lacking there is good evidence for the unreactivity of HO_2 from the work of Baldwin and Mayor[12] on the hydrogen-oxygen reaction and from the work of Enikolopyan[20] and co-workers on the methane oxidation. The dependence of the rate of slow oxidation of hydrogen on the hydrogen mole fraction at 500° requires the introduction of a "regeneration reaction."

$$HO_2 + H_2 = H_2O_2 + H \qquad (11)$$

Although the HO_2 concentration must be much higher than the OH concentration this reaction never accounts for more than 5% of the hydrogen consumption. From the known rate of the reaction as a whole and the assumptions that reactions (7) and (11) have steric factors of unity, E_{11} is calculated to be about 27 kcal. Even if reaction (11) had a steric factor of 10^{-3}, as is the case for methyl radicals, the activation energy would be about 17 kcal.

In the oxidation of methane, Enikolopyan et al showed that the formaldehyde concentration passed through a maximum during the reaction. This maximum increased with temperature with an activation energy of about 8 kcal. According to their mechanism[20] which gives an excellent account of the experimental results this activation energy if given by

$$E_F = \tfrac{1}{2}\left\{E(HO_2+CH_4) + E(OH + CH_4) - E(HO_2 + CH_2O) \right.$$
$$\left. - E(OH + CH_2O)\right\}$$

Since the activation energies of the two OH radical reactions are likely to be low the difference in the activation energies of the HO_2 radical reactions must be close to 16 kcal and thus $E(HO_2 + CH_4) > 16$ kcal. These values for $E(HO_2 + H_2)$ and $E(HO_2 + CH_4)$ compare with 20 and 18 kcal for the corresponding reactions of bromine atoms[18]. It is therefore likely that $E(HO_2 + C_3H_8) > 13$ kcal. It is most unlikely that the competitive experiments can be explained on the basis of HO_2 as the radical attacking the hydrocarbons. Since the formation of HO_2 along with the olefin in reaction (4) seems unavoidable, a key reaction in hydrocarbon oxidation appears to be the conversion of HO_2 to OH. There are few reactions which achieve this while still allowing an olefin and hydrogen peroxide + water as the major initial products. The most plausible reaction is

$$2\ HO_2 = [HOO\text{-}OOH] = 2\ OH + O_2 \qquad (12)$$

This reaction is analogous to those of alkyl peroxy radicals to give alkoxy radicals + oxygen[21-22], but whereas the latter are almost certainly exothermic since they occur at room temperature, reaction (12) is about 8 kcal endothermic. The difficulty of the endothermicity can be overcome if it is supposed that the hydrogen tetroxide is a true intermediate which decomposes preferentially to OH and O_2 rather than to HO_2. The decomposition into three fragments rather than two might be expected to have an A factor higher by between 10^2 and 10^3, which could compensate for the adverse activation energy[23]. The full implications of such a reaction on the mechanism of the hydrogen oxygen reaction are considered later.

The present work was started before many of the points raised above were clear and the initial aim was to discover whether ethane, the simplest hydrocarbon showing all the characteristics of higher alkane combustion[24], was oxidised initially to ethylene, acetaldehyde or ethyl hydroperoxide above 320°. It was also hoped that by carrying out detailed analysis of the reaction products under a variety of reaction conditions we could establish the main products of oxidation of ethyl between 300 and 400°C. These aims have been successfully achieved and we have shown that ethylene indeed accounts for about 80% of the initial products with formaldehyde as a minor product. During the later stages of the oxidation the pressure of ethylene reaches a maximum at about the point of maximum reaction rate and then declines. The concurrent study of the oxidation of ethylene has shown that its main initial oxidation product is formaldehyde ($>80\%$) with ethylene oxide as a minor product. The main molecular stages of the oxidation of ethane are thus

$$\text{Ethane} \longrightarrow \underset{+\ \text{water}}{\text{Ethylene}} \longrightarrow \text{Formaldehyde} \longrightarrow \underset{+\ \text{water}}{\text{Carbon monoxide}}$$

The results agree with earlier observations of Gray[6] and of Steacie and Plewes[25] as regards the production of ethylene and with those of Bone and Hill[26] who established the main oxygenated products. They also fall into line with the work of Sampson[13] on the ethane oxidation at 600°C and that of Dingledy and Calvert[22] on the oxidation of ethyl radicals at room temperature.

Experimental

Materials. Oxygen was taken directly from B.O.G. cylinders and dried by bubbling through liquid oxygen. It contained 0.3% nitrogen. Ethane, supplied by B.O.G. contained 1.5% ethylene which was removed by passing the gas through a column of charcoal saturated with bromine. Any bromine carried over from this column was absorbed by N:N-dimethyl-p-toluidine supported on firebrick. The ethane was finally dried by passage through a trap at -80°C and collected at -183°C. It was finally subjected to several trap to trap distillations, first and last fractions being rejected. Ethylene, supplied by B.O.G., contained 1.5% carbon dioxide as the only detectable impurity.

Apparatus. The reaction was carried out under static conditions in a 500 ml. Pyrex reaction vessel 5.5 cm. diameter housed in an electric furnace whose temperature was constant and uniform to about 1 degree. Reaction mixtures were made up in a mixing vessel to the required composition. The reaction was followed by measurement of pressure change with a Pyrex-glass spoon gauge fitted with an all-glass link system which moved a small mirror. A light spot reflected by the mirror moved 5.30 cm. on a scale for each cm. Hg pressure difference.

Analysis. The analysis of reaction products was carried out wherever possible by gas chromatography. Eluted components were identified by comparison of their retention times with those of pure substances and where possible by their infra-red spectra. Infra-red identification required about 10^{-5} moles of sample. Formaldehyde and hydrogen peroxide were analysed colorimetrically. The sampling system consisted of two 25 ml. traps which could be simultaneously connected to the reaction vessel. Both sampling vessels and the connecting tubing were heated to prevent condensation of water vapour. The sample in one of the traps was analysed for formaldehyde or hydrogen peroxide and that in the other by gas chromatography for the remaining products. The sharing ratios between the two sampling vessels and the reaction vessel were known and absolute measurement of the quantities of the various products present in the sample volumes enabled their pressures in the reaction vessel to be determined. Calibration of the gas chromatograph was accordingly carried out on an absolute rather than a relative basis.

The formaldehyde was determined by the chromotropic acid method of Bricker and Johnston[27] and the hydrogen peroxide by the titanium sulphate method of Egerton et al.[28]

No analysis was made for other peroxides which on the basis of the work of Cartlidge and Tipper[29] and our own carbon balances were assumed to be absent. Formic and acetic acids[26] were probably formed in small quantities but they were not detected by gas chromatography. Their limits of detection would have been considerably higher than those of the other condensables apart from water. Since hydrogen peroxide analysed as water, the yields of water given throughout the paper refer in fact to (water + hydrogen peroxide).

Gas Chromatographic Analysis. The contents of the trap for gas chromatographic analysis were divided into three fractions a) gases uncondensed at -183°C, b) products involatile at -183° but volatile at -80° and c) the remaining products termed "the condensables." The quantities of a) and b) were separately measured in a calibrated gas burette fitted to a Toepler pump, and aliquots were transferred to the sampling U-tube of the gas chromatography apparatus. From the gas chromatograms subsequently obtained the proportions of each component were obtained and hence their partial pressures in the reaction vessel. Absolute determination of the amounts of components present in the aliquots agreed well with the total quantities of sample indicating that no component in fractions a) or b) was missed. The condensables were completely transferred to the U-tube of the chromatography apparatus and an absolute quantitative analysis carried out.

The columns employed for the analysis of the three fractions are given in Table 1. Detection was by katharometer and the carrier gas was hydrogen.

The analysis of fractions a) and b) presented no problems. The low temperature column used for the separation of ethylene, carbon dioxide and ethane was ideal in this application since ethylene was eluted before ethane and trace quantities could readily be determined. Acetylene was eluted before ethylene and none could be detected in the oxidation products of ethylene.

The analysis of fraction c) was complicated for several reasons. 1) Owing to the slight volatility of ethylene oxide and acetaldehyde at -80° small quantities of these substances were usually present in fraction b) and it was always necessary to analyse an aliquot of this fraction on column 4. 2) Since acetaldehyde and ethylene oxide were not separated on column 3, the first peak containing these components was trapped in a spiral packed with glass beads and cooled to -183°. After their elution the trap was by-passed for the rest of the analysis. The contents of the spiral were then analysed on column 4.

3) Water was eluted from column 3 long after ethanol. To obtain analysis in a reasonable time and with reasonable sensitivity the second half of column 3 was disconnected after the elution of the alcohols and the water eluted from the first half of the column only.

4) Acetaldehyde is known to condense with hydrogen peroxide[30] and the gas chromatographic determination of acetaldehyde in the presence of hydrogen peroxide would be expected to be low. Tests in which solutions of acetaldehyde in 30% hydrogen peroxide were analysed on column 4 showed that only about 1/7th of the acetaldehyde was eluted as such. However by coating the walls of the sampling vessel with barium hydroxide about 95% of the aldehyde was recovered. When the coated sampling vessel was used for oxidation products the yield of acetaldehyde rose by only 30%. Thus the heating and cooling of the sample must have been so rapid that no appreciable reaction of aldehyde with peroxide could take place.

Results

Detailed kinetic experiments were carried out at 362°. Analytical experiments were carried out on seven ethane-oxygen mixtures between 318 and 386°, one ethane-ethylene-oxygen mixture at 362° and three ethylene-oxygen mixtures at 318 and 362°. Details are given in Table 2.

A. Kinetic Features

The oxidations of both ethane and ethylene are autocatalytic as found by Bone and Hill[26] and by Harding and Norrish[31]. Typical pressure-time curves are shown in figure 1a.

In the oxidation of ethane the pressure rise, Δp, is proportional, except in the last stages of reaction, to the amount of water formed and to the consumption of oxygen (figures 1b and 1c). The proportionality constants (except for the ethane-ethylene-oxygen mixture) are independent of composition at any temperature. Thus pressure rise can be used as a genuine measure of the extent of reaction for the greater part of the reaction and can be used as a basis for kinetic measurements. The proportionality between pressure rise and water production is independent of temperature as well as composition.

$$d[H_2O]/d\Delta p = 2.6$$

but that between oxygen consumption and pressure rise falls with rise of temperature

$$d[O_2]/d\Delta p = 3.0 \text{ at } 318^\circ \text{ and } 2.6 \text{ at } 362^\circ$$

Initially ethane is consumed at about twice the rate of pressure rise (figure 1d) but later because of oxidation of the initial products the rate of consumption falls. In figure 1d the broken lines have been drawn with an initial gradient

$$d[C_2H_6]/d\,\Delta p = 2.0$$

The initial gradients are similar to those obtained for the oxidation of propane at 318°[8].

The pressure time curves for ethane (figure 1a) are sigmoid and at low temperatures and pressures the reaction exhibits an induction period during which little pressure change or reaction occurs. Generally it is believed that oxidation reactions accelerate exponentially during the initial stages, that is

$$\Delta p = A\,e^{\phi t} \text{ or } d\,\Delta p/dt = \phi\,\Delta p$$

However the plot of reaction rate against pressure rise (figure 2a) shows that the acceleration is not uniform but gradually increases from nearly zero to a maximum value which is held almost until the maximum rate of reaction is achieved. Thereafter the reaction slows down at a rate which is greater the less oxygen is present. The period of increasing acceleration, ringed in figure 2a, was also noted with propane[7] and found to be highly susceptible to the addition of inert gases. During this period some reactive species is efficiently removed on the walls of the reaction vessel. Later the walls are less effective judged by the same criterion. This may be because the walls become acclimatised during the reaction or because the mechanism of the reaction changes.

The maximum acceleration constant, measured from the straight parts of plots like that in figure 2a, increases rapidly with ethane pressure at 362° with an order much higher than unity (figure 2b). The dependence is similar to that found with isobutane at 318°[32] but contrasts with that found for ethane and propane at this temperature when ϕ increased linearly with hydrocarbon pressure above a certain limiting pressure[7,32]. With increasing oxygen pressure ϕ increases linearly at first but becomes independent of oxygen pressure when it exceeds the ethane pressure. This behaviour has been noted with other hydrocarbons[7,33]. Inert gas (carbon dioxide) has a very slight catalytic effect on the reaction. This contrasts with the marked effect noted with propane on the early part of the reaction and indicates that diffusion controlled processes are important in the early stages only.

Replacement of part of the ethane by ethylene (figure

2c) increases the maximum acceleration constant considerably and ethylene is thus a promoter of the reaction as is propylene in the oxidation of propane[7]. The effect of ethylene partly explains the maintenance of the acceleration constant in spite of the consumption of the reactants since ethylene accumulates during the reaction. Replacement of ethane by ethylene oxide has no effect on ϕ and the addition of ethylene oxide has the same effect as the addition of an equal amount of ethane. Ethylene oxide is therefore neither a promoter nor a branching agent. It has very much the same reactivity as ethane in the oxidising mixture.

Acetaldehyde is a known catalyst of gas phase oxidations and is often suggested as a degenerate branching agent. Its addition to a mixture of ethane and oxygen (figure 2d) considerably reduces the induction period but even a 4% addition (based on the ethane pressure) does not eliminate the period of autocatalysis. Approximately 1% (2 mm. pressure) is required to reduce the induction period substantially but this is about ten times the maximum quantity of acetaldehyde found by analysis at 362°. It therefore seems unlikely that acetaldehyde is an important branching agent in the oxidation of ethane.

The oxidation of ethylene differs from that of ethane in starting with a pressure decrease at 362° and below. The pressure decrease is more pronounced the lower the temperature, and has often been noted with other olefins[34-36]. Pressure change cannot therefore be used as a measure of the extent of reaction and there is no simple way of studying the kinetics of the reaction except by an analytical method. There is even some doubt as to whether the reactions are truly autocatalytic at the lowest temperatures.

B. GENERAL ANALYTICAL FEATURES

In order to elucidate the reactions occurring at various stages in the oxidation it is necessary to carry out detailed analyses and it is desirable to plot the yields of the products against some measure of the extent of reaction rather than against time. The lines for true initial products then start from the origin at a finite angle to the X-axis whereas those of secondary products start tangential to the X-axis.

There are several possible measures of the extent of reaction. Pressure rise is the simplest but may be in error in the earliest stages either because of small temperature fluctuations or because of uncertainty in the mechanism in a region where pressure change cannot be accurately correlated with consumption of reactants. Furthermore it can only be used for alkane oxidations since the olefin oxidations start with pressure decreases. The consumption of hydrocarbon or oxygen is the only true measure of the extent of reaction but analytical techniques at present available are not sufficiently accurate to measure very small consumptions. The yield of some major product such as water is satisfactory if it is known to follow the consumption of one or other of the major reactants. In presenting the overall results and those for the final stages this parameter is the most convenient, but is not ideal for the presentation of the results for the initial stages firstly because the analysis of traces of water by gas chromatography is difficult and secondly because water is not a major initial product of the oxidation of ethylene. For this region the quantity of carbon found by analysis in the products is undoubtedly the best measure of extent of reaction, provided that the carbon balances are close to 100%. Generally throughout the work this was the case. Only for the ethane + ethylene + oxygen mixture (6EA11) was there a systematic discrepancy and for this reason the nature of the reaction in the initial stages could not be satisfactorily examined. This measure of the extent of reaction is unfortunately not applicable to the final stages of the reaction since they involve mostly the oxidation of products and the total carbon in the products is therefore nearly constant even when oxidation continues to occur.

The general analytical features of all mixtures were similar and are illustrated in outline for equimolar ethane-oxygen and ethylene-oxygen mixtures at 362° (mixtures 6E11 and 6A11) in figures 3a and 3b. Ethane and ethylene give the same oxidation products although in different proportions, and their oxidations are closely interrelated. The data for acetaldehyde are not included in the figure since the maximum concentration recorded at 362° was 0.2 mm.

Ethylene and an equivalent amount of water + hydrogen peroxide are the chief initial products of the oxidation of ethane; and formaldehyde alone is the chief initial product of the oxidation of ethylene. The yields of both ethylene and formaldehyde pass through maxima indicating their consumption in the later stages of the oxidations. Since carbon monoxide and water are the main oxidation products of formaldehyde[37,38] the molecular stages in the oxidation of ethane must be:

$$C_2H_6 \xrightarrow[a]{+O_2} C_2H_4 \xrightarrow[b]{+O_2} 2\ CH_2O \xrightarrow[c]{+2O_2} 2\ CO$$

with water and hydrogen peroxide being formed in appropriate amounts in stages a and c. The initial yield of hydrogen peroxide from both ethane and ethylene oxidations was about 30% that of the (water + peroxide). As the yield of peroxide did not fall off until near the end of the reaction, it seems likely that heterogeneous decomposition was not of major importance, and that the figure of 30% represents the true proportion of peroxide actually formed in the reaction.

Minor initial products were formaldehyde from the oxidation of ethane, and ethylene oxide from the oxidation of ethylene. Methanol as shown in part II was not an initial product of either oxidation; it was formed in greater yield in the oxidation of ethane and therefore cannot be a secondary product formed through the agency of ethylene. Its most likely free radical precursor is methoxy. Ethylene oxide appears to be formed only by oxidation of ethylene and not as an initial product from the ethane oxidation in agreement with Sampson's work at 600°C[13].

Methane and ethanol appear towards the end of both oxidations, and ethane appears at the end of the oxidation of ethylene. These products suggest the prior formation of methyl, C_2H_5O and ethyl. Certain deductions may be made at this stage about the reactions involving these radicals.

Methoxy- If methanol is derived from methoxy and if methoxy is an initial product of the oxidation it must be largely oxidised to formaldehyde in the early stages. Only when a good hydrogen donor such as formaldehyde, has accumulated can abstraction compete with oxidation. The precursor of methanol is unlikely to be hydroxymethyl since it has a lower heat of formation[39] and its abstraction reactions would mostly be endothermic. Oxidation would probably be the preferred reaction.

C_2H_5O. Ethanol is formed in the last stages of the oxidations at 362° when the oxygen concentration is low. This suggests that a competition may take place between oxidation of and abstraction by C_2H_5O. However the likely oxidation products are acetaldehyde and ethylene oxide.[11] Since both are formed in relatively small proportions, too small to be regarded as substitutes for ethanol, it seems that the C_2H_5O radical is peculiar to the final stages of the reaction.

Methyl. The most likely source of methyl is the decomposition of the ethoxy radical which has an activation energy of about 17 kcals.[39] There are no obvious sources of methyl radicals amongst the other species likely to be present in the oxidising mixtures. The formation of ethanol and methane may therefore be closely connected. Both may derive from the ethoxy radical.

Ethyl. The formation of ethyl in the ethylene oxidation strongly suggests that reaction (4) is reversible and that when the oxygen concentration is low the equilibrium

$$C_2H_4 + HO_2 = C_2H_5 + O_2$$

is sufficiently displaced to the right that abstraction by ethyl can take place from substances with weak C-H bonds such as formaldehyde and methanol.

Discussion

Detailed discussion of the reaction mechanism is left until after full presentation of the analytical results in part II. It is however convenient to discuss the general features of the reaction at this stage.

The analytical data so far presented strongly suggest that the main reactions removing ethane are

$$C_2H_6 + X = C_2H_5 + XH \qquad (13)$$

$$C_2H_5 + O_2 = C_2H_4 + O_2 \qquad (4)$$

with about 5% of the reaction occurring by

$$C_2H_5 + O_2 = CH_2O + CH_3O \qquad (14)$$

$$CH_3O + O_2 = CH_2O + HO_2 \qquad (15)$$

The oxidation of ethylene produces formaldehyde and a small proportion of ethylene oxide. HO_2 will be formed both in the oxidation of ethane by (4) and in the oxidation of ethylene through the concurrent oxidation of formaldehyde by reaction (16)

$$CHO + O_2 = CO + HO_2 \qquad (16)$$

Because it is a relatively unreactive radical it is likely to be present in rather high concentration. The major reaction of ethylene is therefore likely to be addition to HO_2

$$C_2H_4 + HO_2 = CH_2.CH_2.OOH \qquad (17)$$

$$CH_2CH_2OOH \quad = \quad CH_2O \quad + \quad CH_2OH \qquad (18)$$

$$CH_2OH \; + \; O_2 = \quad CH_2O \quad + \quad HO_2 \qquad (19)$$

followed by decomposition of the peroxy radical and finally oxidation of the hydroxymethyl radical. The formation of ethylene oxide is readily explained by the "planting" of an O atom by HO_2 on to the ethylene molecule

$$HO_2 \quad + \quad C_2H_4 \quad = \quad C_2H_4O \quad + \quad OH \qquad (20)$$

It is unlikely to be formed via 3 membered ring transition states from C_2H_3OO or C_2H_4OOH.

In the ethane oxidation the further oxidation of the ethylene initially formed is therefore the main source of formaldehyde. Near the point of maximum reaction rate the ethylene and formaldehyde concentrations are stationary and therefore both formaldehyde and ethylene must be undergoing oxidation at nearly the same rate as the ethane (slightly less because not all the ethane yields ethylene and not all the ethylene yields formaldehyde as initial products). The relative ease of oxidation of ethane, ethylene and formaldehyde must therefore be roughly in inverse proportion to their concentrations at this point in the reaction. The relative reactivities are then:- ethane - 1.0, ethylene - 5, and formaldehyde - 10. <u>If</u> a single radical is responsible for the attack on these three substances then these figures represent relative rate constants (see for example ref. 40).

The identity of the degenerate branching intermediate in oxidation reactions has been a subject of much controversy. It is now becoming gradually accepted that hydroperoxides are probably important below about 300° while aldehydes are more important above this temperature.[29] In the oxidation of ethane there are few possibilities. Acetaldehyde is only a trace product and the low catalytic activity of added acetaldehyde rules it out as the major autocatalyst at 362°. Ethylene oxide was suggested by Harding and Norrish[31] as a possible autocatalyst in the ethylene oxidation above 400° but it is certainly not a catalyst in the ethane oxidation at 362° as shown by its negligible effect on the acceleration constant when added in quite substantial quantity. Hydrogen peroxide is known to have little catalytic effect on oxidations[41-43] even when it is probably pyrolysing homogeneously at a considerable rate. Methanol does not itself oxidise below about 400°[44]. Thus formaldehyde which oxidises above 270°[45] remains the only reasonable possibility. It is unfortunate that the catalytic effect of formaldehyde was not investigated in the present study. Since formaldehyde is formed mainly from ethylene and not directly from ethane the slow start of the ethane oxidation can be partly explained. The failure of acetaldehyde to remove the autocatalysis even when in considerable concentration is likewise explained since the reaction can only proceed at maximum rate when both ethylene and formaldehyde have accumulated. This requires a substantial amount of reaction, considerably more than that induced by the oxidation of the added acetaldehyde. In working out the kinetics of such a reaction where the degenerate branching intermediate is essentially a secondary product the usual assumption that the maximum reaction rate can be achieved with insignificant consumption of the fuel is quite untenable. In the oxidation of ethylene this situation does not arise and it is significant that Harding and Norrish could completely remove the induction period and autocatalysis of the reaction by the addition of sufficient formaldehyde to the mixture.

We therefore conclude that the oxidation of ethane and possibly other alkanes is not a simple degenerately branching chain reaction as originally described by Semenov[46] but one in which the branching intermediate is a secondary product of the oxidation. This fact probably accounts for the promoting effect of olefins on the oxidation of alkanes. The kinetics of this type of reaction are obviously going to be more complicated than those of a simple degenerately branching chain reaction and it is possible that the apparent exponential acceleration over quite a considerable part of the reaction results simply from the balancing of a number of compensatory factors.

The high order of acceleration constant with respect to ethane concentration probably reflects this complexity since the build up of formaldehyde results from two consecutive processes. The independence of the acceleration constant on oxygen pressure in fuel weak mixtures is in line with the analytical data presented later that oxygen concentration has little effect on the relative yields of important products. It therefore appears to have little kinetic role in oxidations and its major role is to add or abstract it from radicals in processes which are not rate determining.

We have so far avoided any discussion of the nature of the species X in reaction (13). The relative reactivities of the C-H bonds in ethane and formaldehyde are approximately 1:7 as deduced from the concentrations of the two species when the formaldehyde concentration is a maximum. If we assume that the same radical attacks formaldehyde as ethane and that the A factors per C-H bond are equal the activation energy for attack of X on ethane is about 2 kcal greater than for attack on formaldehyde. This is a small difference when it is taken with the relative bond strengths in ethane and formaldehyde and suggests that X, if a single species, is much less selective than HO_2 might be expected to be. In their interpretation of the oxidation of methane Enikolopyan and co-workers[19] suggested that activation energy difference for HO_2 attack on methane and formaldehyde is somewhat less than 16 kcal. In the ethane oxidation it therefore seems more likely that the ethane is removed predominantly by OH radical attack and the formaldehyde by HO_2 radical attack. Thus a conversion of HO_2 to OH is required on the basis of internal evidence.

Further support for this is found in the contrasting effects of inert gas on the induction period and the main part of the reaction. Reaction (12) which we have proposed for the conversion of HO_2 to OH is second order in HO_2 and will therefore only occur when the concentration of HO_2 is rather high. In the absence of mutual reaction of HO_2

radicals by (7) or (12) the radicals will tend to diffuse to the walls of the reaction vessel possibly attacking a small number of C_2H_6 molecules on the way. Thus we might expect a diffusion controlled chain reaction in the initial stages which becomes a gas phase terminated chain reaction in the later stages when the rate of reaction has risen sufficiently.

The time of diffusion of HO_2 to the walls in the present reaction vessel is about 0.5 sec. (see ref. 46) and the rate constant of reaction (8) is probably given approximately by

$$\begin{aligned} k_8 &= 10^9 \exp\left[-13{,}000/RT\right] \text{mole}^{-1}\text{l.sec}^{-1} \\ &= 10^{+4.5} \text{ mole}^{-1}\text{l.sec}^{-1} \text{ at } 635^\circ K \end{aligned}$$

The chain length with an ethane concentration of 200 mm. (5.10^{-3} mole $l.^{-1}$ at 635°K) is then about 90.

As the reaction accelerates the concentration of HO_2 rises and eventually mutual reaction will occur. The chain length will then decrease due to reaction (7). When the chains are fully terminated in the gas phase inert gas will have no effect.

The importance of HO_2 attack on ethane may be assessed as follows. Let us assume that HO_2 is involved only in reactions (7) and (8). Baldwin[12] considers that $k_7 = 10^{10}$ mole^{-1}l. sec^{-1}, which is slightly less than the collision number. The maximum rate of removal of ethane in the 1:1 mixture at 362°C in 0.3 mm sec^{-1}. Denoting reaction rates by R_7, R_8 etc. we then have

$$0.3 \text{ mm sec}^{-1} = R_8 = k_8(HO_2)(RH)$$
$$R_7 = k_7(HO_2)^2$$
$$R_7/R_8 = k_7R_8/(k_8(RH))^2$$

with $k_8 = 10^{+4.5}$, $k_7 = 10^{10}$, $R_8 = 10^{-5}$ and $(RH) = 5.10^{-3}$ (units being mole l^{-1} and sec.) we obtain $R_7/R_8 = 3$. Recombination of HO_2 would therefore be expected to compete strongly with abstraction of HO_2 from ethane. The evidence is therefore that HO_2 chains cannot account for the observed rate of removal of ethane if they are in fact properly terminated by reaction (7). If on the other hand the mutual reaction of HO_2 radicals occurs to some extent by reaction (12) then for every HO_2 which terminates the reaction by (7) there will be a number of OH radicals which will remove ethane. On the basis of the initial yield of H_2O_2 and water, k_{12}/k_7 cannot be greater than 2 or 3. Thus the chains are likely to be extremely short and for the reaction to show autocatalysis a strong branching reaction must be introduced. In an earlier paper[7] it was deduced that alkane oxidations proceeded by chains which provided only a very few molecules of branching agent per chain; it was thought at the time that this was due to the small proportion of chain steps forming branching agent rather than to the shortness of the chains. It now appears that the second alternative may be correct for the main stages of the reaction although the first may be true during the induction period. There is indirect evidence that oxidation chains may be much shorter than generally thought. When hydrogen peroxide is added to methane-oxygen[42] and formaldehyde-oxygen[41] mixtures it has very little catalytic effect even at temperatures where it should be decomposing at a substantial rate. This can only be explained by supposing that the internal sources of new radicals produces them faster than the added material. Since the rate of generation of OH by hydrogen peroxide is in some cases a quite large fraction of the reaction rate the chains must in fact be very short.[47]

We therefore conclude that the oxidations start as wall terminated chain reactions in which HO_2 is the chain carrier and where the chain length may be about 100 units, but that at quite a low percentage conversion, when the reaction rate is only just becoming measurable, wall reaction of HO_2 radicals is replaced by mutual reaction in the gas phase. We feel that the evidence is strong that a high proportion of the HO_2 radicals reacting in this way produce hydroxyl and oxygen directly not hydrogen peroxide as is generally supposed.

In proposing the conversion of HO_2 to OH by reaction (12) it is necessary to consider the effect of its introduction into the scheme for the hydrogen oxygen reaction. Baldwin and co-workers[12] have shown that the slow oxidation in boric acid coated vessels proceeds by a degenerate chain reaction comprising reactions (9), (4), (7) and (10) which in Baldwin's notation are numbered (i), (iv), (x) and (vii). For the sake of those familiar with this notation we shall use it in the following discussion. This scheme predicts that the overall rate of slow oxidation at pressures above the second explosion limit is close to the independently measurable rate of homogeneous decomposition of hydrogen peroxide, which is thought to occur by the reactions[14]

$$H_2O_2 + M' = 2OH + M' \qquad (vii)$$

$$OH + H_2O_2 = H_2O + HO_2 \qquad (xv)$$

$$2HO_2 = H_2O_2 + O_2 \qquad (x)$$

Thus the observed rate of pyrolysis of the peroxide is twice the rate of reaction (vii). The introduction of the further reaction (12) or (xa)

$$2HO_2 = 2OH + O_2 \qquad (12)(xa)$$

which effectively short-circuits reaction (x) and (vii) would make the observed rate of pyrolysis $2(k_{xa}+k_x)/k_x$ times that of (vii). However this simply introduces an error into the derived value of k_{vii} and does not affect the conclusion that the rate of slow oxidation of hydrogen should be close to the experimentally observable rate of pyrolysis of the hydrogen peroxide present. Thus the addition of (xa) to Baldwin's scheme does not affect the conclusions regarding the rate of the slow reaction. This is not true for the second explosion limit. Neglecting quadratic branching the second explosion limit results from the introduction of the branching reactions

$$H + O_2 = OH + O \qquad (ii)$$

$$O + H_2 = OH + H \qquad (iii)$$

and explosion occurs when (iv) just fails to balance (ii) and (iii). The limit pressure is $[M] = 2k_{ii}/k_{iv}$ and the explosion develops with extreme rapidity with an isothermal time constant $t = 1/k_{ii}[O_2]$[48] which at 500° would be about 3×10^{-5} sec. Under these conditions the lifetime of H_2O_2

is several seconds and reaction (x) can be regarded as a chain terminating reaction. In KCl coated vessels it is generally accepted that chain termination occurs by removal of HO_2 at the walls of the reaction vessel before they react mutually by (x). Thus in either case at the second limit all HO_2 radicals are effectively "dead." This interpretation is confirmed by the observation that when quadratic branching is allowed for, the second limit in boric acid coated vessels is close to that in a KCl coated vessel. If reaction (xa) is introduced the explosion limit in boric acid vessels should be higher than in KCl coated vessels by a factor of $(k_{xa} + k_x)/k_x$. In order to explain the hydrocarbon oxidation results the ratio would need to be at least three. The maximum value for the ratio according to Baldwin would be about 1.25.[49] Thus reaction (xa) as it stands is inadmissible as one might also argue from its endothermicity. Both difficulties can be circumvented if an unstable peroxide H_2O_4 is postulated and if reaction (xa) is written

$$2HO_2 = HOO\text{-}OOH \qquad (xa')$$

$$HOO\text{-}OOH = 2OH + O_2 \qquad (viia)$$

For (xa') to be effectively chain terminating at the second explosion limit the peroxide H_2O_4 must have a lifetime of at least 10^{-4} sec. at 500°. This would imply an activation energy for decomposition of about 30 kcal. if the reaction were unimolecular. There is some evidence for the existence of a compound which may be H_2O_4 although its properties do not meet the above requirements. Nekrasov, Skorokhodov, Kobozev and co-workers[50] have shown that identical products are obtained either by freezing the products of a silent discharge through water vapour at -196° or by reaction of H atoms with liquid ozone. The initial product appears to be the HO_2 radical and measurements of the e.s.r. spectrum of the solid product at -196° reveals a free radical concentration of about 0.4%. Since up to 60% reaction can occur in the ozone reaction the major component of the product is not a free radical. On warming the solid it melts at between -60 and -70° and then decomposes to equimolar quantities of H_2O_2 and O_2 between -55 and -40° giving out 35 kcal per mole of oxygen liberated. It is suggested that the reaction occurring is

$$H_2O_4 \;=\; H_2O_2 \;+\; O_2 \qquad H \;=\; -35 \text{ kcal}$$

From known thermochemical data[51] the heat of formation of H_2O_4 in solution must be about -12 kcal and its heat of dissociation to HO_2 about +6 kcal. The lifetime of the superoxide at -70° should be of the order of 1 sec. The observed lifetime of about 100 sec. at -50° requires an activation energy for decomposition of 15 kcal if the reaction is unimolecular. There is clearly a serious discrepancy between the experimental data from frozen peroxy radical condensates and the requirements of the theory of hydrocarbon oxidation.

TABLE 1

Gas Chromatographic Columns

Column	Fraction	Container	Length cm.	Support	Liquid phase	Temp. (Flow rate ml.min.$^{-1}$)	Substances analysed
1	a	Glass U	150	Linde Molecular sieve 5A + activated Charcoal		18°C (30)	O_2, (N_2), CO, CH_4
2	b	Copper coil	300	Celite 60-80 mesh	20% 140-160°C. Petroleum	-80°C (30)	(C_2H_2) CO_2, C_2H_4 C_2H_6
3	c	Glass U	150	Celite 60-80 mesh	20% polyethylene glycol 400	47°C (70)	Condensables*
4	d	Copper coil	150	same as column 3		0°C (70)	CH_5CHO, C_2H_4O

* Condensables in order of elution were $CH_3CHO + C_2H_4O$, CH_3OH, C_2H_5OH and H_2O

TABLE 2

Mixtures studied

Mixture a)	Components	Molar composition	Total pressure mm.Hg.	Temp. °C	Notes
2E31	ethane + oxygen	3:1	296	318	
2E11	" "	1:1	442	318	
4E11	" "	1:1	442	340	b
6E31	" "	3:1	296	362	
6E11	" "	1:1	442	362	c
6E12	" "	1:2	442	362	
8E11	" "	1:1	442	386	b
6EA11	ethane + ethylene + oxygen	6.3:1:7.3	442	362	
2A11	ethylene + oxygen	1:1	442	318	
6A11	" "	1:1	441	362	
6A12	" "	1:2	333	362	b

Notes a - The first number in the code gives the approximate oxidation temperature in tens of degrees above 300°; the letters E and A denote ethane and ethylene respectively; the final two figures give the hydrocarbon to oxygen ratio.

b - reaction products analysed only in the initial stages.

c - reaction studied with and without the addition of 1% acetaldehyde.

Captions to Figures

Figure 1. (a) Pressure time curves for various mixtures. (b) Yield of water, (c) oxygen pressure and (d) ethane pressure as functions of pressure rise. For key to mixture compositions and temperatures see Table 2.

Figure 2. (a) Rate versus pressure rise curve for 355 mm. ethane + 90 mm. oxygen at 362°. $\phi = 0.35\ \text{min}^{-1}$ (b) Variation of ϕ with reactant pressure at 362°.

7.7 cm. oxygen, ethane varied; 15.3 cm. oxygen, ethane varied; 25.6 cm. ethane, oxygen varied; 21.8 cm. ethane, 7.7 cm. oxygen, carbon dioxide varied. (c) Variation of ϕ, mixture 6E11.

ethylene substituted for ethane

ethylene oxide substituted for ethane

ethylene oxide added.

ethane added, (from figure 2b)

(d) Effect of added acetaldehyde on pressure time curves. Pressures of added acetaldehyde are marked on lines, Mixture 6E11.

Figure 3. (a) Product development in the oxidation of ethane, mixture 6E11.

(b) Product development in the oxidation of ethylene, mixture 6A11.

EO = ethylene oxide, M = methane, EA = ethanol.

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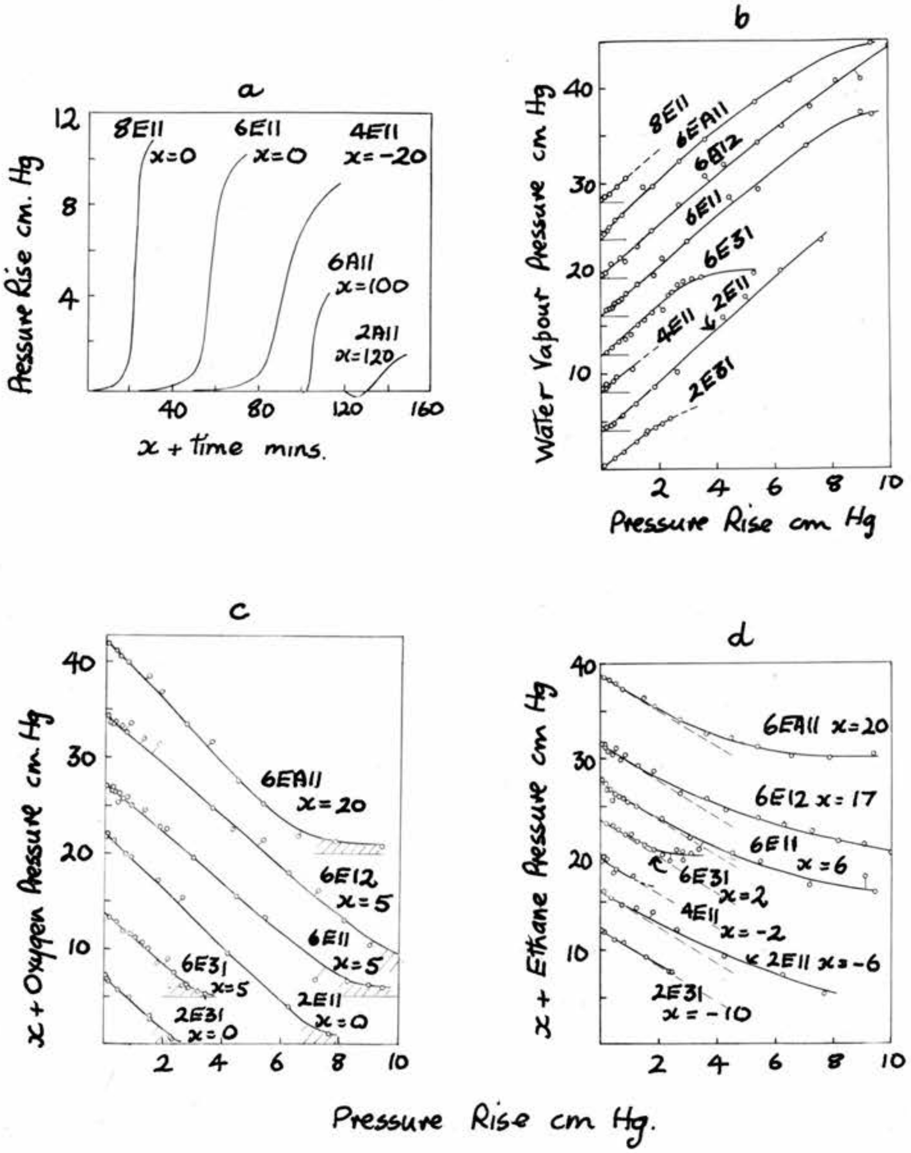
Figure 1.



a
12
8
4
40
80
120
160
Pressure Rise cm. Hg
x + time mins.
8E11 x=0
6E11 x=0
4E11 x=-20
6A11 x=100
2A11 x=120
b
40
30
20
10
2
4
6
8
10
Water Vapour Pressure cm Hg
Pressure Rise cm Hg
8E11
6EA11
6E12
6E11
6E31
4E11
2E11
2E31
c
40
30
20
10
2
4
6
8
10
x + Oxygen Pressure cm Hg
6EA11 x = 20
6E12 x = 5
6E11 x = 5
6E31 x=5
2E11 x = 0
2E31 x = 0
d
40
30
20
10
2
4
6
8
10
x + Ethane Pressure cm Hg
6EA11 x=20
6E12 x = 17
6E11 x = 6
6E31 x = 2
4E11 x = -2
2E11 x = -6
2E31 x = -10
Pressure Rise cm Hg.

Figure 2

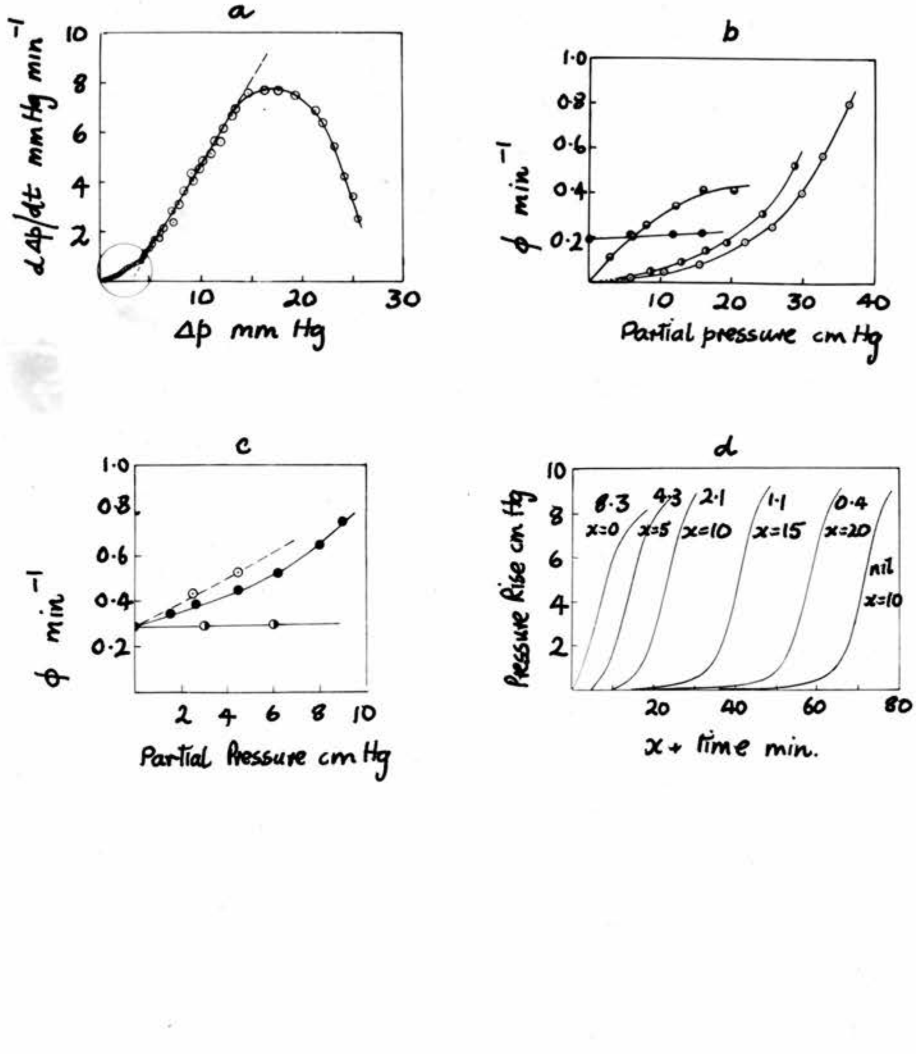
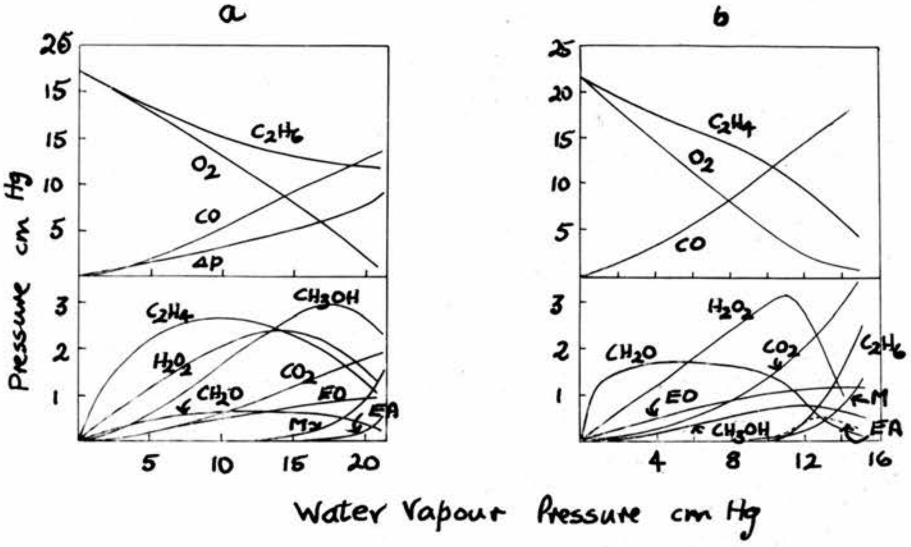

a
dΔp/dt mmHg min⁻¹
10
8
6
4
2
10
20
30
Δp mm Hg
b
1·0
0·8
0·6
0·4
0·2
ϕ min⁻¹
10
20
30
40
Partial pressure cm Hg
c
1·0
0·8
0·6
0·4
0·2
ϕ min⁻¹
2
4
6
8
10
Partial Pressure cm Hg
d
10
8
6
4
2
Pressure Rise cm Hg
8·3
x=0
4·3
x=5
2·1
x=10
1·1
x=15
0·4
x=20
nil
x=10
20
40
60
80
x + time min.

Figure 3



EO = Ethylene Oxide
M = Methane
EA = Ethanol

[19]

THE SLOW OXIDATION OF ETHANE AND ETHYLENE IN THE GAS PHASE

Part II. DETAILED ANALYTICAL FEATURES

By John H. Knox and Clifford H. J. Wells,
Department of Chemistry, University of Edinburgh.

SUMMARY

It is established by detailed analysis of the initial stages of the oxidations of ethane that water, ethylene and formaldehyde are the only significant initial products at 362° and that acetaldehyde is an additional initial product at 318°. Methanol, ethanol, ethylene oxide, carbon monoxide and carbon dioxide are secondary products. As oxygen has no effect on the relative yields of initial products they are produced by reactions of the same kinetics. Between 362 and 318° there is a profound change in the distribution of initial products. It is proposed that the equilibrium (1) is established

$$C_2H_5 + O_2 = C_2H_5OO \qquad (1)$$

and that ethylene is formed by direct H atom abstraction from ethyl while formaldehyde is formed from the ethyl peroxy radical.

The initial products from the oxidation of ethylene are ethylene oxide, formaldehyde and acetaldehyde. The secondary products are the same as from ethane. Various possible mechanisms are discussed for their formation. It is concluded that HO_2 is the main radical attacking ethylene. The end products of the oxidations are methane, ethane (from ethylene) and ethanol.

PART I$^{(1)}$ described the general kinetic and analytical features of the oxidation of ethane and ethylene at 362°. The oxidation of ethane is autocatalytic producing ethylene as the major initial product. The degenerate branching agent is probably formaldehyde which is formed mainly as a secondary product from ethylene. There is some question as to which radical is the main propagator in the reaction. HO_2 is probably too unreactive to abstract hydrogen from ethane although it can probably add to ethylene and abstract from formaldehyde. We have suggested in Part I that OH radicals may be formed by mutual reaction of HO_2 radicals and may in fact be the main radicals attacking the ethane.

The detailed analytical results presented here substantiate these conclusions and point to certain other unexpected features of the oxidations. In particular it seems that an equilibrium

$$C_2H_5 + O_2 \rightleftharpoons C_2H_5OO \qquad (1)$$

must be established and that ethylene is formed by hydrogen abstraction from ethyl by oxygen whereas formaldehyde is produced via a four membered ring transition state of low entropy from the ethyl peroxy radical.

Experimental. The details of the apparatus and analytical procedure have been fully described in Part I. Details of the temperatures and compositions of mixtures are given in Table I.

Results. When more than one product can arise from a common free radical the relative kinetics of their formation can be obtained by studying the effect of reactant concentrations on the product ratios.(2) In particular if products are formed in reactions of identical kinetics their relative yields are unaffected by changes in reactant concentrations, and relative Arrhenius parameters can be obtained by measuring product ratios over a temperature range. For such studies to be convincing it is essential to determine the product distribution in the early stages of the oxidation when secondary reactions are minimal and to cover reasonably wide ranges of temperature and composition. Since the initial products from the oxidation of

alkenes must

alkanes must arise from the reactions of alkyl radicals with oxygen rather than the parent hydrocarbon, alkane concentration should have no effect on the initial product yields. We have accordingly investigated only the effect of oxygen pressure on the product yields.

In order to distinguish clearly between initial and secondary products we have plotted the yields of products against the total carbon content of the reaction products measured as a hypothetical C_1 gas pressure. The results for the initial and intermediate stages of the oxidation of ethane are presented in figures 1a-1d and 2a-2d, and for the oxidation of ethylene in figures 3a-3d and 4a,4b. The figures for the ethylene containing mixtures also show curves for the 1:1 ethane:oxygen mixture at 362° for comparison.

Water, ethylene and formaldehyde (figures 1a, b and c) are the initial products from the oxidation of ethane between 318 and 362°. Acetaldehyde (figure 1d) is a minor initial product at 318° and probably a trace initial product at the higher temperatures. Carbon monoxide, methanol ethanol and ethylene oxide (figures 2a, 2b, 1d and 2c) are secondary products. Carbon dioxide is a minor product and at the lowest temperature may be an initial product formed in surface reactions (figure 2d). At the higher temperatures it is a secondary product.

In the oxidation of ethylene at 318 and 362° formaldehyde and ethylene oxide are the main initial products (figures 3a and 3b). Acetaldehyde is a minor initial product (figure 1d). The yield curves for water and carbon monoxide (figures 3c and 3d) almost coincide and both rise sharply convex to the X-axis. It is therefore difficult to establish the initial gradients but it is likely that neither are initial products. They are probably formed by the oxidation of formaldehyde

$$CH_2O + \tfrac{1}{2}O_2 = CO + H_2O \qquad (2)$$

Methanol, carbon dioxide and ethanol (figures 4a, 4b and 1d) are secondary products.

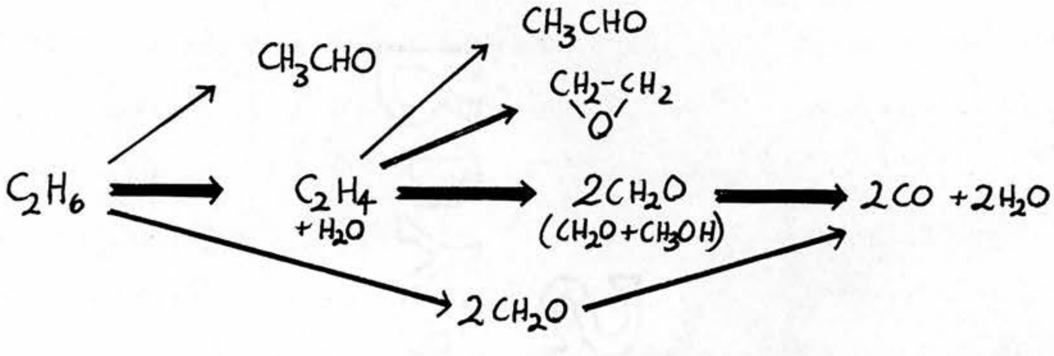
The initial fractional yields derived by measurement of the initial gradients of the lines in figures 1-4 are given in Table I. The key features of the experimental results derivable from both the figures and Table I are:-

(1) The yields of ethylene and formaldehyde produced from ethane rise to maximum values and eventually decline; the yield of formaldehyde in the oxidation of ethylene passes through a maximum. Thus formaldehyde and ethylene are intermediate products in the oxidation of ethane between 318 and 386° and formaldehyde is an intermediate in the oxidation of ethylene.

(2) There is no dependence of the initial yields of ethylene and formaldehyde from ethane on the oxygen pressure at either 318 or 362°.

(3) There is a profound change in the distribution of products in the ethane oxidation as the temperature falls from 362 to 318°. The yields of formaldehyde and acetaldehyde increase greatly between 362 and 318° while the yield of ethylene falls. In the intermediate stages of the oxidation the yield of methanol shows similar features and its formation may be linked with that of formaldehyde. In the oxidation of ethylene a similar but lesser effect is noted in the yields of ethylene oxide and acetaldehyde relative to formaldehyde. The activation energy differences associated with these changes in product distribution are about 35 kcal for the ethane oxidation and about 10 kcal for the ethylene oxidation.

These observations suggest that the main molecular stages in the ethane oxidation can be represented by the scheme below: the thickness of any line indicates qualitatively the fraction of the reaction proceeding by that path; the products written inside brackets are alternatives formed in the intermediate stages of the oxidation.



Certain minor features of the yield curves bear out this scheme. We have already noted that the yield of methanol in the intermediate stages of the oxidation follows the yield of formaldehyde in the initial stages when the temperature is altered. The yield curves for formaldehyde at the higher temperatures start with a positive gradient indicating that formaldehyde is an initial product but instead of remaining constant or decreasing the gradients of the curves increase slightly before they flatten off. This is due to an increase in the rate of formaldehyde production due to the oxidation of ethylene. When the yields of ethylene and formaldehyde are constant the major reaction is effectively a straight through run from ethane to carbon monoxide. The yield curves show that 70% of the carbon consumed appears as CO and 70% of the hydrogen consumed appears as water.

The development of the products in the final stages of the oxidations are shown in figures 4c and 4d for the ethane and ethylene oxidations respectively. In the oxidation of ethane at 362° methane and ethanol appear in the final stages. They arise only when the oxygen concentration is low but there is no simple relationship between the pressures of methane, ethanol, and oxygen and quantitative interpretation is not possible. At 318° ethanol although not an initial reaction product appears like methanol in the intermediate stages and there is no upward trend of the yield curve at the end of the oxidation as might have been expected by comparison with the curves for 362°. There therefore appears to be two mechanisms forming ethanol, one for the intermediate stages which increases in importance as the temperature falls and one for the final stages which decreases in importance as the temperature falls. Since the yield of methane falls with temperature there may be a connection, between the reactions forming the two products in the final stages of the reaction as was suggested in Part I.

In the last stages of the oxidation of ethylene, ethane appears in addition to methane and ethanol. The yields of all three final products rise with rise of temperature. The formation of ethane in the ethylene oxidation suggests that the main reaction proposed for the oxidation of ethyl can be reversed.

$$C_2H_4 + HO_2 = C_2H_5 + O_2 \qquad (3)$$

Discussion - Ethane

The absence of dependence of the initial formaldehyde/ethylene ratio on oxygen pressure (varied fourfold at 362° and threefold at 318°) indicates that both products are formed by reactions with the same dependence on oxygen concentration. Since ethylene can hardly be formed other than by reaction (4), formaldehyde

$$C_2H_5 + O_2 = C_2H_4 + HO_2 \qquad (4)$$

must be formed in a reaction which for kinetic purposes can be written

$$C_2H_5 + O_2 = CH_2O + CH_3O \qquad (5)$$

followed by the oxidation of methoxy since methanol is not an initial product of the reaction

$$CH_3O + O_2 = CH_2O + HO_2 \qquad (6)$$

There is evidence for reaction (6) in the work of Hanst and Calvert(3) who found that the yield of methanol formed in the pyrolysis of dimethyl peroxide was greatly reduced by the addition of oxygen at about 200°C. It may also occur in the oxidation of methanol(4) although here the predominant radical is probably CH_2OH not CH_3O. The formation of methanol later in the reaction must then be dependent upon the formation of a good hydrogen donor. Even at room temperature(5) there is evidence that methanol can arise by reaction.(7)

$$CH_3O \quad + \quad CH_2O \quad = \quad CH_3OH \quad + \quad CHO \qquad (7)$$

Since formaldehyde is certainly formed and consumed in the intermediate stages of the ethane oxidation this reaction seems most likely as the source of methanol. The analogous reaction (8) may also occur, but, being less exothermic(6)

$$CH_2OH \quad + \quad CH_2O \quad = \quad CH_3OH \quad + CHO \qquad (8)$$

than (7), oxidation is the more likely fate of hydroxymethyl. These suggested reactions for the formation of methanol agree with the view of Fisher and Tipper(7) on the role of formaldehyde as a hydrogen donor in the oxidation of methane. The increase in the yield of methanol in the ethane oxidation as the temperature falls agrees with this set of reactions. The fraction of ethyl radicals giving rise to methoxy by reaction (5) rises as the temperature falls and so does the concentration of formaldehyde in the intermediate stages of the reaction: thus the rate of (7) should increase so as to give a higher proportional yield of methanol.

Acetaldehyde is only a trace product at the higher temperatures but is readily detectable as an initial product at 318°. It is the only initial product whose fractional yield depends upon the oxygen pressure to any extent, the initial yield being roughly proportional to the oxygen pressure. The formation of acetaldehyde by a reaction of higher order in oxygen than formaldehyde seems to demand a reaction scheme such as

$$C_2H_5 + O_2 = C_2H_5OO \quad (1)$$

$$C_2H_5OO = CH_2O + CH_3O \quad (9)$$

$$C_2H_5OO + O_2 \doteq CH_3CHO + OH + O_2 \quad (10)$$

Reaction (9) requires a four membered ring transition state of low entropy but the direct decomposition of C_2H_5OO to give acetaldehyde and hydroxyl as originally proposed by Norrish(8) requires an even more unlikely transition state. It is therefore conceivable that the formation of acetaldehyde from the ethyl peroxy radical can only occur by the formation of a 6 membered ring which includes a second oxygen molecule.

Ethanol is not an initial product of the reaction but it is formed in approximately the same yield as acetaldehyde and so might be an alternative product to acetaldehyde formed by a mechanism similar to that proposed for methanol. However the yield of acetaldehyde depends upon the oxygen concentration while that of ethanol does not. We accordingly feel that ethanol cannot be regarded as a substitute product for acetaldehyde. It seems more likely that it arises from the addition of OH to ethylene followed by abstraction by the CH_2CH_2OH radical

$$CH_2CH_2 + OH = CH_2CH_2OH \qquad (11)$$

$$CH_2CH_2OH + CH_2O = CH_3CH_2OH + CH_2O \qquad (12)$$

which cannot otherwise be oxidised or decompose. The low yield of ethanol in the intermediate stages of the reaction is then in accord with the view that the OH concentration is much lower than the HO_2 concentration.

Ethylene oxide is not an initial product from ethane and therefore reaction (13) does not occur

$$C_2H_5OO = \overline{CH_2\text{-}O\text{-}CH_2} + OH \qquad (13)$$

The striking increase in the aldehyde/ethylene ratio as the temperature falls from 362 to 318° is the most surprising feature of the results and requires an apparent activation energy difference $E_4 - E_5 = 35$ kcal, along with an exceptionally low A factor ratio A_5/A_4. The most likely explanation of the observations is that the equilibrium (1) is established, and that whereas ethylene is formed by a direct abstraction by oxygen from ethyl, formaldehyde is eventually formed as a result of the decomposition of the peroxy radical by reaction (9). Provided that the equilibrium (1) is not disturbed by these two reactions it is not difficult to show that the apparent activation energy difference and A factor ratio are

$$E_4 - E_5 = E_4 - \Delta H_1 - E_9 \qquad A_4/A_5 = A_4\exp[-\Delta S_1/R]/A_9$$

This scheme may be represented as follows

$$C_2H_4 + HO_2 \xleftarrow{(4)} C_2H_5 + O_2 \underset{(-1)}{\overset{(1)}{\rightleftarrows}} C_2H_5OO \xrightarrow{(9)} CH_2O + CH_3O$$

Assessment of the feasability of this scheme requires the independent estimation of the apparent activation energy difference and apparent A factor ratio.

Direct evidence on the bond strengths of alkyl peroxy radicals is lacking, the only well established peroxy bond strength being that in HO_2, D(H-OO) = 45 kcal.(9) An upper limit may be set to D(R-OO) on the basis of the reactions of RO_2 radicals. It is well established that the peroxy radicals CH_3OO,(5) C_2H_5OO(10) and C_4H_9OO(11) disproportionate at room temperature to give the appropriate alkoxy radicals. Since these reactions can hardly be endothermic the maximum R-OO bond strengths can be evaluated from known thermochemical data on the alkyl and alkoxy radicals.(6) This type of calculation gives 30 kcal. A value of ΔH_1 = -25 kcal, might therefore be taken as reasonable. The discovery of substantial quantities of ethane in the end stages of the oxidation of ethylene indicates that even in the presence of moderate concentrations of oxygen ethyl radicals can abstract hydrogen atoms from suitable H donors in preference to being oxidised. The direct abstraction reaction (4) may therefore have a moderate activation energy of up to 10 kcal. Reaction (9) is quite exothermic and although it necessarily passes through a transition state of low entropy it may still have a near zero activation energy. Thus an overall activation energy difference $E_4 - E_5$ of about 35 kcal is not impossible.

To calculate the apparent A factor ratio we require estimates of the entropy change in reaction (1) and the entropy of activation in reactions (4) and (9).

The C_2H_5OO radical is in many ways similar to the n-butane molecule. The translational and rotational entropies will be very similar. Only the entropy contribution from internal degrees of freedom, vibrations and internal rotations will be significantly different in the two molecules. Pitzer[12] has shown that the entropies of straight chain molecules may be divided into components for the vibrations and internal rotations of the chain, and components for the vibrations and internal rotations of the C-H bonds and CH_3 groups. The entropies for the chain processes in the two molecules should be similar, but those due to the vibrations of the C-H bonds and the internal rotations of the CH_3 groups in the C_2H_5OO radical will be exactly half those in the n-butane molecule. With additional allowances for the change in symmetry number and electronic degeneracy the entropy of the peroxy radical can thus be calculated. The entropy of the ethyl radical can be taken as close to that of ethane(13) again with allowance made for change in symmetry number and electronic degeneracy. Calculating in this way the entropy loss in the formation of the C_2H_5OO radical from C_2H_5 and O_2 can be shown to be about 32 cal $deg^{-1} mole^{-1}$ between 300 and 400° for standard pressures of 1 atm.

The entropy loss on forming the transition state in reaction (9) may also be estimated. Since the transition state will be a four membered ring all free rotations and low frequency chain vibrations will be lost. There are two internal rotations (one for the chain and one for the CH_3 group) and three low frequency chain vibrations. The entropy loss will then be about 25 cal deg^{-1} $mole^{-1}$ and A_9 will be approximately $10^{10}\exp[-25/1.99] = 10^{7.5}$. The A factor for reaction (4) will be close to the collision frequency and might be set at 10^{10} atm^{-1} sec^{-1}. The ratio of the rates of formation of ethylene and formaldehyde can therefore be estimated as

$$R_4/R_9 = R_4/R_5 = \{A_4\exp[-\Delta S_1/R]/A_9\} \times \exp[(-E_4 + \Delta H_1 + E_9)/RT]$$
$$= 10^{9.5} \exp[(-E_4 + E_5)/RT]$$

Since the experimental ratio is about 3 at 600°K a maximum activation energy difference of about 25 kcal is obtained since larger entropy contributions in reactions(1) and (9) would be difficult to accept. This compares with the experimental value of 35 kcal and shows that the unexpected temperature dependence of the aldehyde/ethylene yield is still not fully explained.

The further point must also be borne in mind that for the equilibrium (1) to be insignificantly disturbed, reaction (9) must be considerably slower than (-1). If (-1) is ten times as fast as (9) we can write

$$10^{7\cdot 5} = 0\cdot 1\ A_{-1}\ \exp[-25000/1\cdot 99 \times 600]$$

whence $A_{-1} = 10^{17.5}$ an unacceptably high value. Recently Dingledy and Calvert(10) have measured the rate of reaction (1) and obtained the value $k_1 = 10^{12.6}\text{cm}^3\text{mole}^{-1}\text{sec}^{-1} = 10^8$ $\text{atm}^{-1}\text{sec}^{-1}$. If $\Delta S_1 = 32$ cal $\text{deg}^{-1}\text{mole}^{-1}$ we obtain $A_{-1} = 10^{15}$ sec^{-1}. The A factor for the decomposition of the ethyl peroxy radical is therefore likely to be high but hardly high enough to allow reaction (9) to be slower than (-1). If the suggestion that equilibrium between ethyl and ethyl peroxy is the correct explanation of the observed temperature dependence of the aldehyde/ethylene ratio then the entropy loss in reaction (9) must be larger than 25 cal $\text{deg}^{-1}\text{mole}^{-1}$. It is difficult to see how this can be the case.

The appearance of methane and ethanol at the close of the oxidations of ethane and ethylene is not explained by any simple mechanism. The ethyl radical cannot pyrolyse and the ethyl peroxy radical could only give rise to methyl and formic acid, by an extremely improbable reaction. Furthermore the final yield of methane is so large that substantial quantities of formic acid should have been observed, and in addition the yield of methane declines with temperature whereas the yield of products typically derived from the peroxy radical apparently increase with fall in temperature. The most probable sources of methyl are then the CH_3CO and CH_3CH_2O radicals. The former would be produced by radical attack on acetaldehyde. Although acetaldehyde is obviously attacked during the oxidations at 318°C the proportion of acetaldehyde formed is never sufficient to account for all the methane observed even at 318° where the aldehyde yield is highest. At 362° only a very small fraction of the methane could arise in this way. The most likely precursor is therefore CH_2CH_2O if a mechanism for the formation of this radical can be found.

Ethanol, quite apart from methane, could arise from the abstraction reactions of three radicals, CH_3CHOH, CH_2CH_2OH or CH_3CH_2O. The first of these radicals is known from the work of Cullis and Newitt[14] to oxidise to to acetaldehyde and HO_2 at temperatures above 270°. At 362° the observed yield of acetaldehyde is always too small to account for the formation of ethanol as an alternative product. The CH_2CH_2OH radical probably formed by addition of OH to ethylene is a very plausible precursor of ethanol as it can neither be oxidised nor can it pyrolyse without rearrangement. As we have already noted it appears to give a good explanation of the formation of ethanol in the intermediate stages of the reaction and there seems no reason why this radical should be formed only at the end of the ethane and ethylene oxidations at 362°. Thus the ethoxy radical seems to be the most likely precursor of ethanol formed at the close of the oxidations. The ethoxy radical cannot be formed in a simple way from ethyl or ethyl peroxy. A conceivable mode of formation is via ethyl hydroperoxide which itself might be formed by reaction (14).

$$C_2H_5OO + CH_2O = C_2H_5OOH + CHO \qquad (14)$$

However this being a typical product formed from ethyl peroxy rather than ethyl it would be expected that the formation of ethanol at the end of the reaction would be encouraged by a reduction in temperature which is not the case. Other possible sources of ethoxy are radical/radical reactions. Three possibilities are

$$2C_2H_5OO = 2C_2H_5O + O_2 \qquad (15)$$

$$C_2H_5OO + HO_2 = C_2H_5O + O_2 + OH \qquad (16)$$

$$C_2H_5 + HO_2 = C_2H_5O + OH \qquad (17)$$

The first two reactions would occur throughout the oxidation and the absence of ethanol in the intermediate stages of the oxidation at 362° could only be explained by assuming oxidation of the ethoxy radicals. Since there is no obvious alternative product produced in sufficient yield (acetaldehyde or ethylene oxide) it appears that (17) is the only reasonable possibility. The concentration of ethyl will rise as the reaction proceeds due to the reversal of the equilibrium (1) so the early formation of ethoxy and thence ethanol from this reaction is not expected. The effect of temperature is also explained: as the temperature is reduced the equilibrium (1) moves further to the right hand side and the concentration of ethyl decreases as shown in Table 2. In addition the overall oxidation is slower and the radical concentrations lower. Thus the rate of (17) is strongly temperature dependent.

Table 2

Equilibrium constant for the reaction

$C_2H_5 + O_2 = C_2H_5OO$; $\Delta H = -25$ kcal mole^{-1}, $\Delta S^o = -32$ cal deg^{-1} mole^{-1}

Temperature ^oK		500	600	650	700	750	800
$Log_{10}K_p = (\Delta S^o - \Delta H/T)/4.6$		-3.7	-2.2	-1.5	-0.9	+0.3	+0.3
$\frac{[EtOO]}{[Et]}$	$[O_2]$ = 10 mm Hg	100	2.0	0.4	0.10	0.025	0.007
	$[O_2]$ = 100 mm Hg	1000	20	4	1.0	0.25	0.07

The formation of ethane at the end of the oxidation of ethylene is also explained on the basis of the increasing stability of the ethyl radical as the temperature is raised, particularly if reaction (4) requires a significant activation energy. In agreement with this view the yield of ethane increases with temperature from 318 to 362°.

Ethylene

There are several ways of explaining the formation of formaldehyde as the major product from the oxidation of ethylene above 320°C. The simplest suggestion already made by Cullis, Fish and Turner$^{(15)}$ is the direct addition of an oxygen molecule across the double bond to give a four membered ring peroxide which then decomposes (reactions 18 and 19).

$$C_2H_4 + O_2 = \overline{CH_2\text{-}O\text{-}O\text{-}CH_2} \qquad (18)$$

$$\overline{CH_2OOCH_2} = 2\ CH_2O \qquad (19)$$

These reactions could explain the initial pressure decrease observed in this and other olefin oxidations if the ring peroxide has some stability. However, the fact that the oxidations of ethane and ethylene are closely interlinked and that ethylene oxide is also an initial product of the ethylene oxidation makes it extremely unlikely that the major part of the oxidation of ethylene proceeds by a molecular rather than a free radical process. The direct addition of oxygen if it occurs at all, which we doubt, must be a minor reaction. A more likely cause of the pressure decrease is a partial polymerisation also suggested by Cullis et al. which might occur by the series of free radical steps initiated by the addition of HO_2 to ethylene

$$C_2H_4 \xrightarrow{+HO_2} HOOC_2H_4 \xrightarrow{+O_2} HOOC_2H_4OO \xrightarrow{+C_2H_4} HOOC_2H_4OOC_2H_4$$

$$\xrightarrow{+RH} HOO(C_2H_4OO)_nH \xrightarrow{\text{Pyrolysis}} 2n\ CH_2O \ + \ H_2O_2$$

Since the observed pressure decreases are small compared with the amount of oxidation at any stage the reactions responsible must always be of minor importance and it is most unlikely that this type of polymerisation reaction is the main source of formaldehyde in the oxidation.

There are at least three plausible chain mechanisms which can explain the formation of formaldehyde although none of them explains the initial pressure decrease at low temperatures. The first mechanism proposed by Harding and Norrish[16] was based on analytical and kinetic evidence. The chain propagation reactions were

$$C_2H_4 + OH = C_2H_5O \qquad (20)$$

$$C_2H_5O = CH_3 + CH_2O \qquad (21)$$

$$CH_3 + OH = CH_2O + OH \qquad (22)$$

The radical formed in (20) would be expected to be CH_2CH_2OH and an isomerisation to CH_3CH_2O would be required before reaction (21) could occur. This would require some 20-30 kcal activation energy, and it might be argued that the formation of ethanol should be observed in the initial stages. A rather more serious objection to the scheme comes from the oxidation of higher olefins where rapidly accumulating evidence indicates that the initial reaction can generally be represented by

$$R^aR^bC{=}CR^cR^d + O_2 = R^aR^bC{=}O + O{=}CR^cR^d \qquad (23)$$

If reactions (21) - (23) held generally then in the oxidation of 2-methyl-but-2-ene reaction (23) would produce either ethyl or iso-propyl radicals. Above 320° these radicals are oxidised predominantly to the olefins and therefore ethylene and propylene would be expected to be major products contrary to observation. Likewise with but-2-ene ethylene should be an important product at temperatures above 320° contrary to the observations of Porter and Norrish[17] and Skirrow.[18] Skirrow and co-workers have overcome this disadvantage of the original scheme by proposing that the radical formed in (20) is further oxidised

$$CH_2CH_2 + OH = CH_2CH_2OH \qquad (20)$$

$$CH_2CH_2OH + O_2 = OOCH_2CH_2OH \qquad (23)$$

$$OOCH_2CH_2OH = CH_2O + CH_3O + OH \qquad (24)$$

The formation of ethylene oxide can then be accommodated within the scheme by incorporating reaction (25)

$$CH_2CH_2OH + O_2 = \overline{CH_2OCH_2} + HO_2 \qquad (25)$$

This scheme has two disadvantages when considered in connection with the oxidation of ethane. Firstly reaction (25) requires a strained low entropy transition state and would hardly be expected to compete effectively with the addition of oxygen to CH_2CH_2OH. Secondly in the oxidation of ethane the radical in the highest concentration is almost certainly HO_2 since any OH radicals even if they are mainly responsible for removing ethane will quickly be converted to HO_2 by reactions (26) and (4)

$$OH + C_2H_6 = H_2O + C_2H_5 \qquad (26)$$

$$C_2H_5 + O_2 = C_2H_4 + HO_2 \qquad (4)$$

Likewise in the oxidation of ethylene itself, after the initial stages, OH whenever formed will be rapidly converted to HO_2 via the reaction with formaldehyde. In both oxidations HO_2 is very likely to be the predominant radical and since the additions of HO_2 and OH to ethylene will both be exothermic their activation energies are both likely to be small. Thus the major part of the attack on ethylene will be carried on by HO_2. Accordingly we prefer a third mechanism for the olefin oxidations in general, involving the reactions (27) to (30)

$$CH_2CH_2 + HO_2 = CH_2CH_2OOH \tag{27}$$

$$CH_2CH_2OOH = CH_2O + CH_2OH \tag{28}$$

$$CH_2OH + O_2 = CH_2O + HO_2 \tag{29}$$

Reaction (28) is analogous to the decomposition of the ethyl peroxy radical into CH_3O and CH_2O and involves a four membered ring transition state. The formation of ethylene oxide can occur by the direct reaction of HO_2 with ethylene

$$C_2H_4 + HO_2 = \overline{CH_2OCH_2} + OH \tag{30}$$

This scheme has the advantage of accounting for the formation of rather small amounts of methanol in the ethylene oxidation. The CH_2OH radical formed in (38) has a lower heat of formation than CH_3O(6) and therefore abstracts with greater difficulty. Even in the presence of formaldehyde in quite high concentration there is a high probability that it will be oxidised.

The fact that the yield of ethylene oxide increases as the temperature falls indicates that reaction (27) has a higher activation energy than (30). While reaction (30) involves a ring transition state it is very exothermic and may have a near zero activation energy while reaction (27) might reasonably be expected to have a small positive activation energy.

There appears to be a further way in which HO_2 can add to ethylene which accounts for the formation of ethane in the last stages of the ethylene oxidation

$$CH_2CH_2 + HO_2 = CH_3CH_2 + O_2 \qquad (-4)$$

This reaction must occur throughout the oxidation but normally the ethyl radicals are oxidised back to ethylene. However a small proportion will give rise to formaldehyde and methanol and this may indeed be the source of the methanol in the ethylene oxidation rather than abstraction by CH_2OH.

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Captions to Figures Part II.

Figure 1. Development of products from the oxidation of ethane. a) water, b) ethylene, c) formaldehyde, d) acetaldehyde O, ethanol O. For convenience most of the curves in this and later figures are displaced vertically. For mixture code see Table I.

Figure 2. Development of products from the oxidation of ethane. a) carbon monoxide, b) methanol, c) ethylene oxide, d) carbon dioxide.

Figure 3. Development of products from oxidation of ethylene. a) formaldehyde, b) ethylene oxide, c) carbon monoxide, d) water.

Figure 4. Development of products a) methanol from ethylene, b) carbon dioxide from ethylene, c) end products from ethane, d) end products from ethylene.

TABLE I

Initial Products from the Oxidation of Ethane and Ethylene

Mixtures Code[(a)]	Pressures of Hydro-carbon	Pressures of Oxygen	Initial Product Yields in Mole per 100 moles hydrocarbon consumed: Water	Ethylene	Formaldehyde	Acetaldehyde	Methanol[(b)]
2E31	222	74	80±10	50±10	60±5	1.8±0.2	60±10
2E11	221	221	80±5	55±10	60±5	4.5±0.5	60±10
4E11	221	221	90±5	70±5	17±2	-	-
6E31	222	74	90±5	90±5	12±1	0.2	20±5
6E11	221	221	90±5	90±5	12±1	0.2	30±5
6E12	148	296	90±5	90±5	12±1	0.2	20±5
8E11	221	221	95±5	95±5	11±1	-	-
			Water or Carbon monoxide		Formaldehyde	Ethylene oxide	Acetaldehyde
2A11	221	221	20		150±10	17±2	1.6±0.1
6A11	221	221	20		170±10	8±1	0.8±0.1
6A12	111	222	20		170±10	8±1	0.5±0.1

a) Mixture code. First figure refers to reaction temperature in tens of degrees above 300°C:- 2 = 318°; 4 = 340°; 6 = 362°; 8 = 386°. Letter gives hydrocarbon:- E = ethane; A = ethylene. Last two figures give (Hydrocarbon)/(oxygen) ratio.

b) The figures for methanol are the maximum proportional yields in the intermediate stages of the reaction. Methanol is not an initial product.

Figure 1

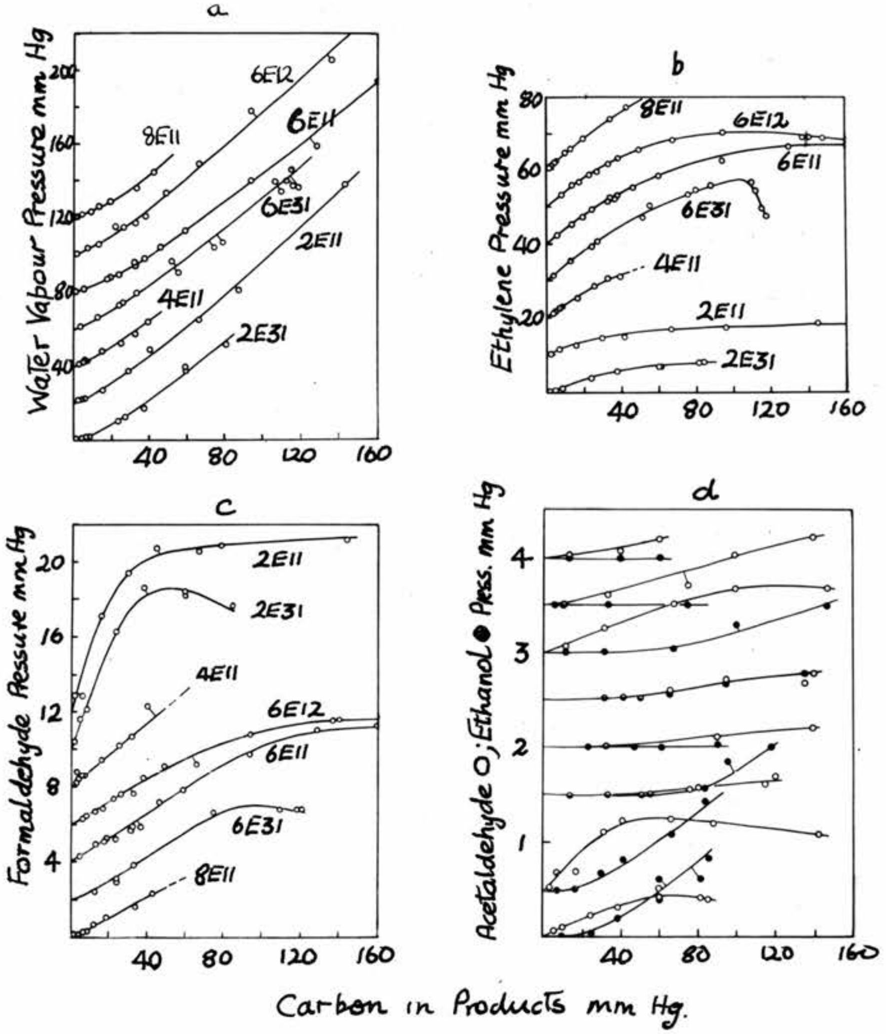
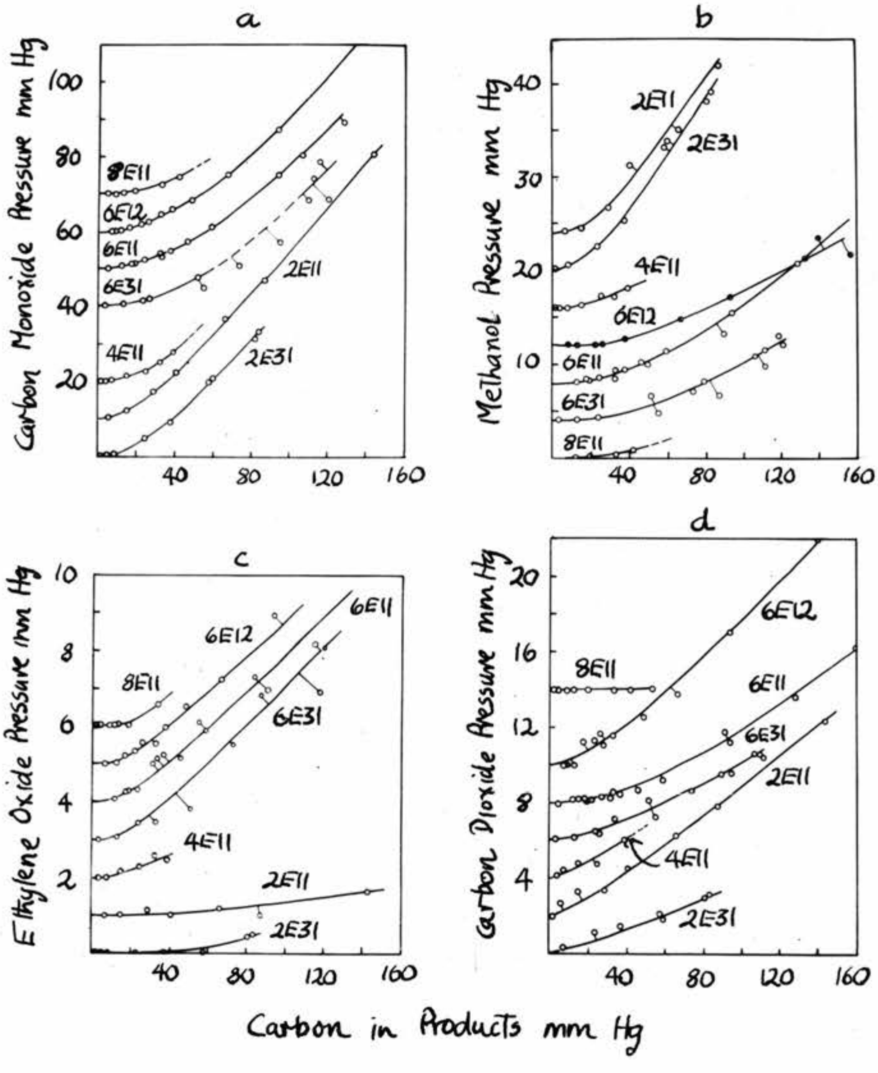

a
Water Vapour Pressure mm Hg
200
160
120
80
40
8E11
6E12
6E11
6E31
2E11
4E11
2E31
40
80
120
160
b
Ethylene Pressure mm Hg
80
60
40
20
8E11
6E12
6E11
6E31
4E11
2E11
2E31
40
80
120
160
c
Formaldehyde Pressure mm Hg
20
16
12
8
4
2E11
2E31
4E11
6E12
6E11
6E31
8E11
40
80
120
160
d
Acetaldehyde ○; Ethanol ● Press. mm Hg
4
3
2
1
40
80
120
160
Carbon in Products mm Hg.

Figure 2.



a
Carbon Monoxide Pressure mm Hg
100
80
60
40
20
8E11
6E12
6E11
6E31
4E11
2E11
2E31
40
80
120
160
b
Methanol Pressure mm Hg
40
30
20
10
2E11
2E31
4E11
6E12
6E11
6E31
8E11
40
80
120
160
c
Ethylene Oxide Pressure mm Hg
10
8
6
4
2
8E11
6E12
6E11
6E31
4E11
2E11
2E31
40
80
120
160
d
Carbon Dioxide Pressure mm Hg
20
16
12
8
4
8E11
6E12
6E11
6E31
2E11
4E11
2E31
40
80
120
160
Carbon in Products mm Hg

FIGURE 3

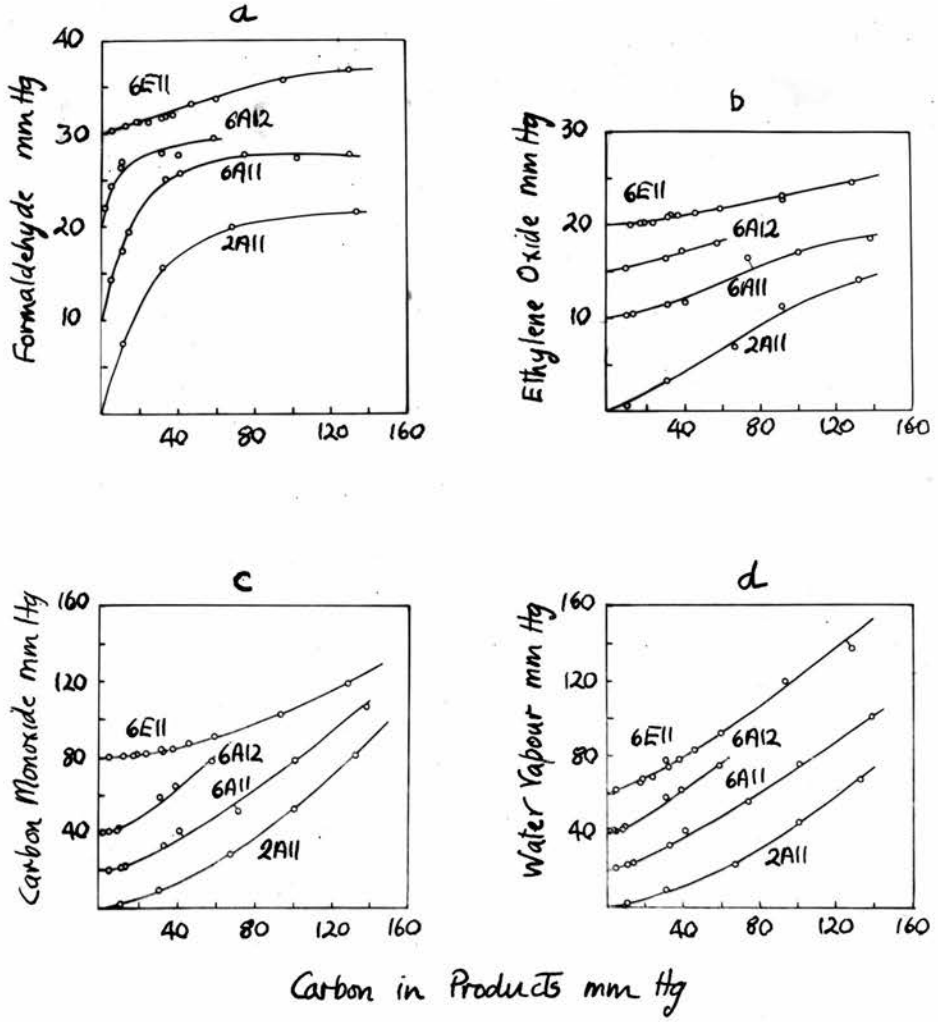
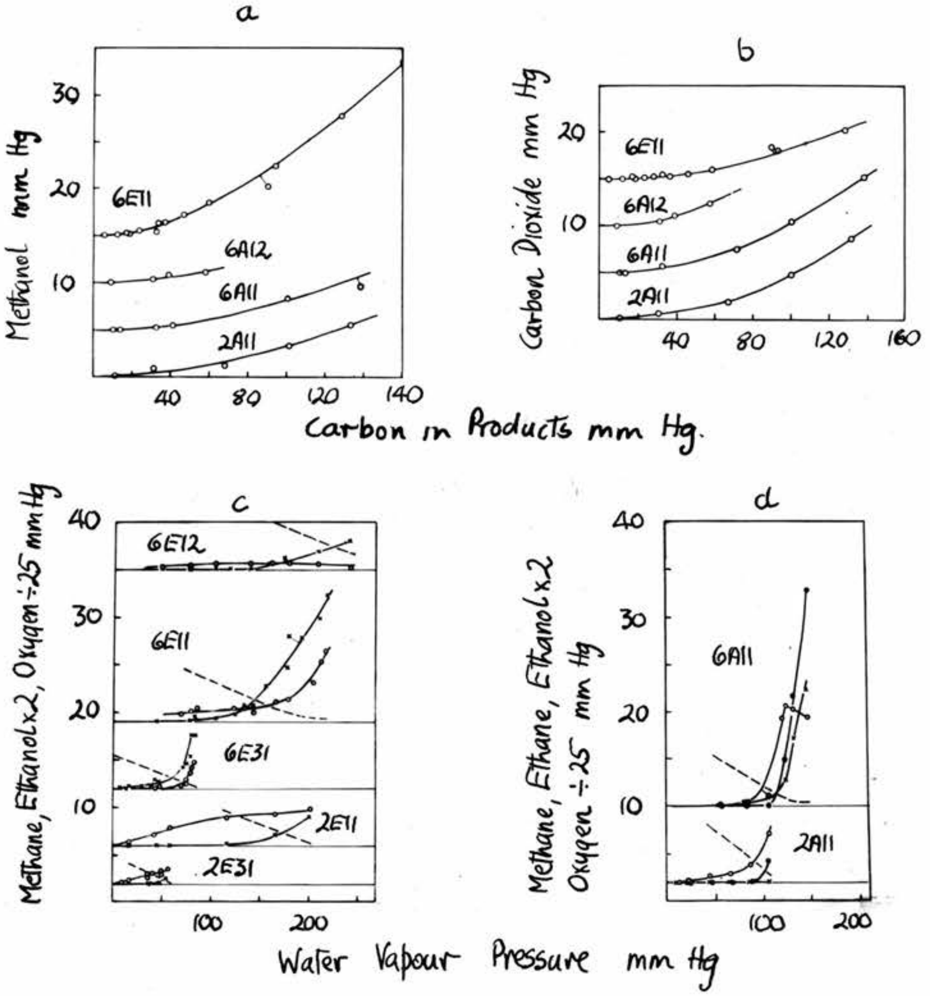

a
Formaldehyde mm Hg
40
30
20
10
6E11
6A12
6A11
2A11
40
80
120
160
b
Ethylene Oxide mm Hg
30
20
10
6E11
6A12
6A11
2A11
40
80
120
160
c
Carbon Monoxide mm Hg
160
120
80
40
6E11
6A12
6A11
2A11
40
80
120
160
d
Water Vapour mm Hg
160
120
80
40
6E11
6A12
6A11
2A11
40
80
120
160
Carbon in Products mm Hg

Figure 4



x Methane
O Ethanol
● Ethane
--- Oxygen

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[20]

SOME FEATURES OF THE OXIDATION OF PROPANE AND ETHANE AT 318°C

SOME FEATURES OF THE OXIDATION OF PROPANE AND ETHANE AT 318°C

BY JOHN H. KNOX
Dept. of Chemistry, University of Edinburgh

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Analytical and kinetic evidence is presented, including data on the duration of the induction period τ, the acceleration constant ϕ, and the maximum rate of pressure rise $\rho_{\max}$. Interpretation of the measurements of τ is shown to be extremely difficult and even that of $\rho_{\max}$ sometimes open to question. It is concluded that the most useful parameter is ϕ. Theoretical relations for the dependence of ϕ on reactant concentrations are shown to be obeyed by the oxidations of ethane and propane, and from them it is concluded that the lifetimes of the branching intermediates in these oxidations are approximately 2 and 1 min respectively. The results also indicate that only very few molecules of these intermediates are formed by each complete reaction chain. This conclusion agrees with the analytical data which show that the main chain reaction removing propane is similar to that occurring at high temperatures (i.e. an HO_2 radical chain forming propylene as its major product) and one which does not itself form any branching intermediate. The propylene so formed is, however, itself oxidized and reaches a maximum concentration. This secondary oxidation adds to the complexity of the reaction and causes additional acceleration.

The slow oxidations of many organic compounds, particularly hydrocarbons, between 250 and 500°C are examples of degenerately branching chain reactions.[1] That is, they are reactions which proceed by way of straight free-radical chains which produce reactive intermediates capable of initiating new chains long after the original chains have terminated.

The oxidations proceed with a pressure rise Δp, which gives a reasonable measure of the disappearance of the reactants, particularly the oxygen [2-5] which is consumed at approximately twice the rate of pressure rise.[6, 7] They are normally characterized by an induction period during which the rate of reaction is very small, followed by a period of exponential acceleration during which the equations

$$\Delta p = A \exp(\phi t), \qquad \text{or} \qquad \rho = \mathrm{d}(\Delta p)/\mathrm{d}t = \phi \Delta p,$$

are approximately obeyed. A and ϕ are constants, the latter being termed the acceleration constant or net branching factor of the reaction. ϕ is readily determined by plotting either log Δp against t,[4, 8] or ρ against Δp (cp. ref. (9)). The latter method has many advantages, the chief being that ϕ can be determined at any stage in the reaction as the gradient of the line. It need not be constant from the start of the reaction.

A typical such plot is shown in fig. 1 for the oxidation of a propane + oxygen mixture in the 500 ml spherical reaction vessel used in all the experiments described. The vessel was of Pyrex glass and uncoated but had been aged by carrying out a large number of oxidations. During the induction period (inset) lasting 58 min the rate and acceleration of the reaction increase slowly from values close to zero. Between A and B the reaction accelerates exponentially ($\phi = 1{\cdot}50\ \text{min}^{-1}$) for about 1·5 min. After B the acceleration falls and becomes zero at the point of maximum rate. Thereafter the reaction decelerates at an almost constant rate until all the oxygen is consumed. The steepness of the deceleration is greater the less oxygen is present and may be almost vertical when oxygen weak mixtures are used.

The three parameters which are most readily measured for any such oxidation are the duration of the induction period τ, the acceleration constant ϕ, and the maximum rate of pressure rise $\rho_{\max}$. The dependence of ϕ on reaction conditions has not been widely investigated probably since it is often believed that its dependence is similar [10] to that of $\rho_{\max}$. However, this is not strictly true and the differences in the behaviour of these two parameters may give useful data about the reaction mechanism.

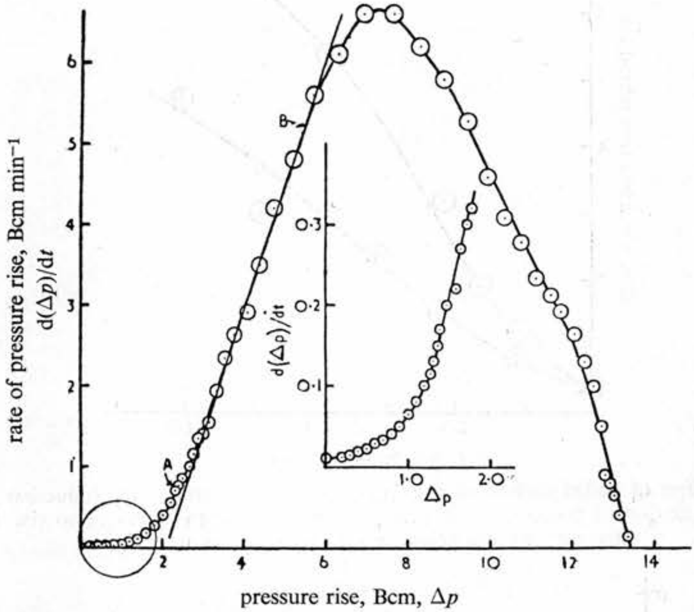

FIG. 1.—Typical rate against pressure-rise plot. *Inset*: an enlargement of the circled portion of the curve. 1 Bourdon cm (Bcm) = 0·215 cm Hg; mixture: 68 mm propane + 68 mm oxygen at 318°C.

THE INDUCTION PERIOD

The duration of the induction period in oxidations at low temperatures (250-350°C) is extremely sensitive to variables such as the state of the reaction vessel surface and the reactant concentrations,[11] and unlike the other two parameters it is often considerably reduced by the addition of inert gases.[11, 12] These effects have been taken to indicate that diffusion of some species to the walls of the reaction vessel is important in retarding the reaction during the induction period. Similar results are obtained with propane (fig. 2) where $1/\tau$, a measure of the rate of reaction during the induction period, increases regularly, although not linearly, with inert gas pressure. Carbon dioxide, as might be expected, is more effective than nitrogen. Fig. 3 shows that addition of inert gas has two distinct effects upon the early part of the reaction: it increases the initial rate of reaction, and it removes the initial period of slow acceleration by increasing the initial acceleration. It does not affect the latter part of the reaction. Any diffusion-controlled process is therefore important only during the induction period of the reaction.

Since the average time for the diffusion of a small molecule to the walls of a 10-cm diam. spherical vessel under the present conditions [1] is about 2 sec, this must be the approximate duration of the diffusion-controlled process. The process could be either the removal of a free radical or of a more stable molecular intermediate. If the former, the duration of the chains during the induction period must be about 2 sec. Unless chain-termination reactions later develop which involve some reaction product, their duration in the later part of the reaction must be much greater than this, say, at least 20 sec. If, on the other hand, some

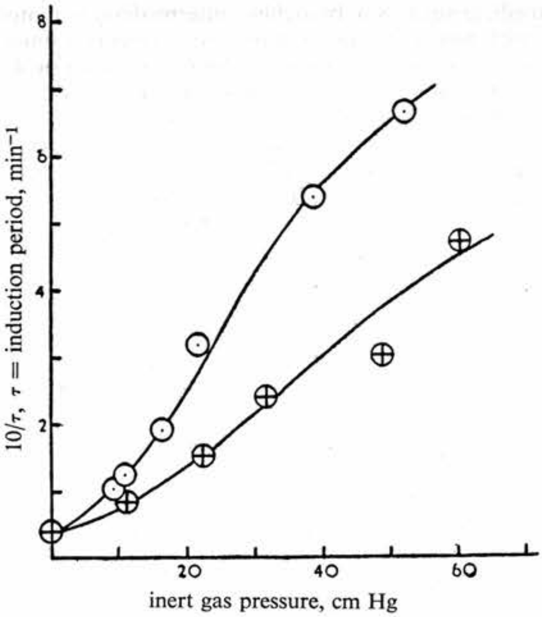

FIG. 2.—Effect of added carbon dioxide (⊙) and nitrogen (⊕) on the induction period τ of the oxidation of propane. τ is taken as the time for the pressure to rise 1 Bcm. Mixture: 88 mm propane + 82 mm oxygen at 318°C.

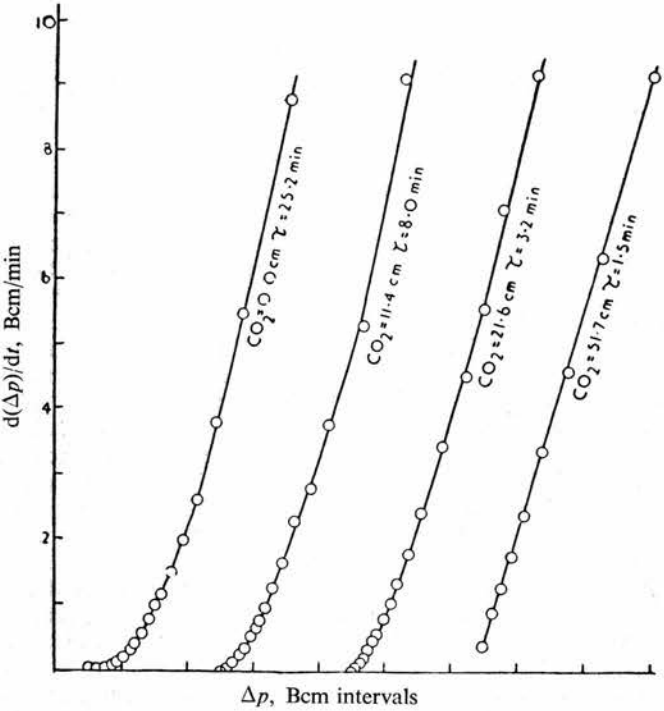

FIG. 3.—Effect of added carbon dioxide on the rate against pressure-rise curves for propane; mixture as for fig. 2.

important intermediate such as a branching intermediate is removed at the walls then its lifetime with respect to any homogeneous reactions must be some 20 sec or more. In view of the high reactivity of the free radicals probably involved in oxidations and the likelihood that the chains are not excessively long, it is most unlikely that the diffusion process involves a free radical as had been originally suggested by Neumann.[12] It is much more likely that either the branching intermediate or one of its immediate precursors is destroyed at the walls during the induction period. Its lifetime then agrees with that deducted later.

The facts that the acceleration of the reaction continuously increases during the induction period and that diffusion is not rate-determining during the later part of the reaction suggest either that the walls must become poisoned by the end of the induction period or that the reaction mechanism changes radically by that point so that the efficient destruction of a particular intermediate is no longer important for the further development of the reaction. From fig. 3 it is readily shown that the former must be true, for when diffusion is effectively prevented by the addition of 51·7 cm pressure of carbon dioxide the reaction starts at nearly its maximum rate of acceleration. A high rate of acceleration is not therefore contingent upon the occurrence of a certain amount of reaction. Long induction periods, in the oxidation of propane at least, thus result from the removal of an important intermediate at the walls of the reaction vessel and are terminated when the walls become suitably conditioned so that this reaction can no longer occur efficiently.

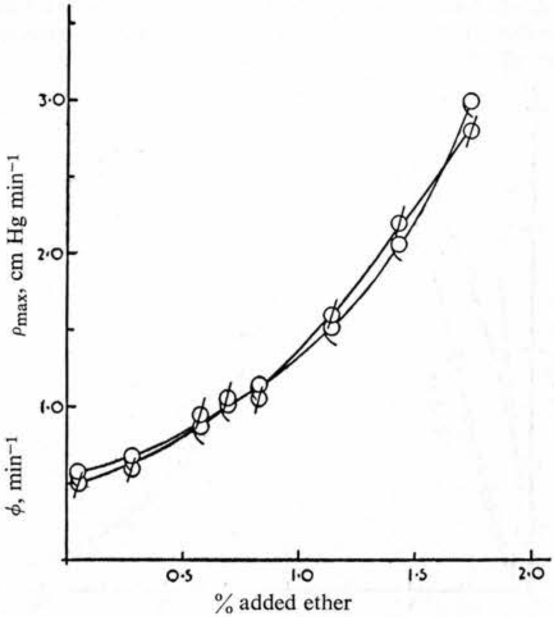

FIG. 4.—Effect of diethyl ether on the maximum rate ρ and acceleration constant ϕ of the oxidation of ethane; mixture: 300 mm ethane + 100 mm oxygen at 318°C.

Although changes of mechanism cannot therefore explain the properties of the reaction during the induction period they will nevertheless occur gradually as the reaction proceeds owing to the oxidation of primary products of the reaction. If these products on further oxidation produce branching intermediates more effectively than the original hydrocarbon, the reaction will tend to accelerate more rapidly as it proceeds. Such substances, which are not themselves branching intermediates, might reasonably be termed reaction promoters. Fig. 4 shows, for example, that the addition of very small percentages of diethyl ether to ethane cause large increases in both ϕ and ρ_{max}. The effect of the ether is maintained throughout the reaction and it therefore behaves differently from a branching intermediate whose addition would introduce a flood of free radicals. The reaction would then commence at a much enhanced rate but with only slight changes in ϕ and ρ_{max}. The ether cannot be consumed immediately but must survive in the oxidizing mixture almost as well as ethane. This conclusion may be unexpected in view of the vast differences in their overall rates of oxidation, but it is borne out by the observations of Knox, Smith and Trotman-Dickenson [13] that substances which undergo oxidation at as different rates as ethane and propane disappear in competitive oxidations at comparable rates. Differences in overall reactivity are therefore no guide to the relative rates of removal of different substances in the oxidation of mixtures. Such differences may often be due to differences in the rates of other rate-determining processes.

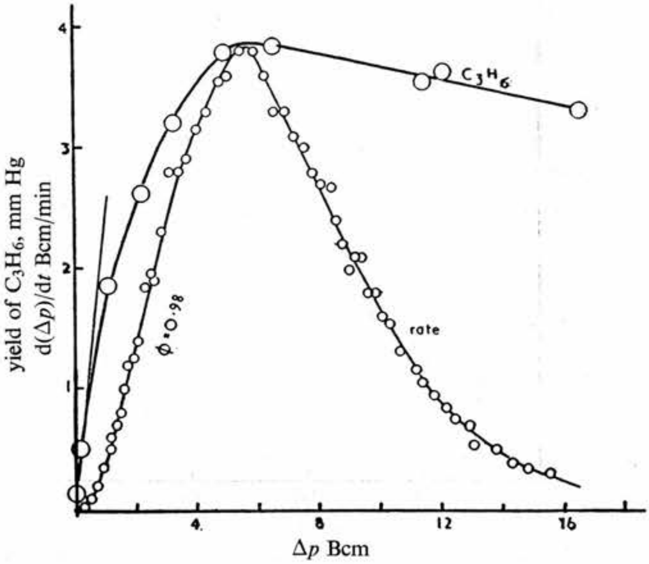

FIG. 5.—Yield of propylene from the oxidation of propane and rate of reaction as a function of pressure rise; mixture: 44 mm propane + 88 mm oxygen at 318°C.

In the oxidation of propane, it appears that propylene acts as a promoter. At 318°C it accounts for approximately 75 % of the propane initially disappearing and the major reactions occurring at this stage must be similar to those now established for the high-temperature oxidation,[5, 14] namely,

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2, \tag{1}$$

$$C_3H_7 + O_2 = C_3H_6 + HO_2. \tag{2}$$

In fig. 5 the fine line gives the initial rate of formation of propylene and it is clear that the rate of formation relative to pressure rise falls off until, at the point of maximum rate, it becomes zero. The concentration is then about 10 % of the propane initially present. Experiments in which some of the propane was initially replaced by propylene (fig. 6) showed that with less than 10 % substitution little change was noted in ϕ, ρ_{max} or the maximum propylene yield (being only 12 % when 10 % propylene was initially present) but τ was greatly reduced. As with inert gas addition the effect on the induction period was to increase both the initial rate and the initial acceleration of the reaction. With more than 10 % substitution both ϕ and ρ_{max} were markedly increased. A promoting effect of propylene is therefore observed whenever its concentration is greater than that normally present at the appropriate stage in the reaction. However, even the normal reaction will be promoted by the propylene actually produced in the reaction and both ϕ and $\rho_{\max}$ would be somewhat less were the propylene removed from the system as soon as it was formed and replaced by propane.

While the main reason for the slow increase in acceleration during the induction period is therefore the gradual poisoning of the walls of the reaction vessel, this process is to some extent aided (at least in the oxidation of propane) by the accumulation of promoters. The processes occurring are therefore most complex and there are a number of quite distinct factors which influence the duration of the induction period. The assumption often made that $1/\tau$ gives a measure of the rate of reaction during the induction period is obviously unsound. In order to obtain useful data from the induction period, one requires to measure not only its duration but also the initial rate, the initial acceleration, the way in which the acceleration changes and the initial distribution of products. These measurements will all require extremely refined techniques.

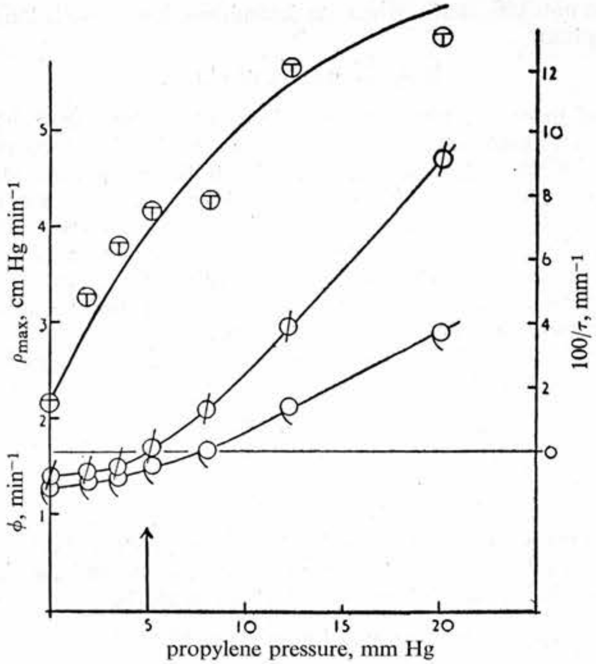

FIG. 6.—Effect of replacement of propane by propylene on the maximum rate ρ, the acceleration constant ϕ and the induction period $\ominus$; mixture: 65 mm hydrocarbon + 65 mm oxygen at 318°C. Arrow indicates the maximum pressure of propylene in the oxidation of 65 mm propane + 65 mm oxygen.

THE ACCELERATION CONSTANT

The rate of acceleration of the intermediate part of the reaction can be much more readily treated than the duration of the induction period. The basic chain reaction which removes the hydrocarbon RH may formally be represented as

$$RH + X^- \xrightarrow{k_p} R^- + XH,$$

with rate constant k_p, followed by

$$R^- + O_2 \xrightarrow{k_{p'}} RO_2^- \xrightarrow{k_{p''}} P + X^-,$$

or

$$R^- + O_2 \xrightarrow{k_{p'}} RO_2^-(\equiv X^-),$$

where X has been variously identified as OH, HO_2, RO_2, etc. When X is not RO_2, it is probable, as suggested in the second reaction above, that the reaction may pass through an unstable radical RO_2 which decomposes before it can abstract a hydrogen atom to form a peroxide. Three distinct termination reactions are then possible:

$$X^- \overset{k_t}{=} \text{inactive products,}$$

$$R^- \overset{k_{t'}}{=} \text{inactive products,}$$

and when X is not RO_2, that is when the second reaction above is the second stage in the propagation,

$$RO_2^- \overset{k_{t''}}{=} \text{inactive products.}$$

The second of these possibilities is considered to be most unlikely, since alkyl radicals probably react with oxygen (cf. Hoare and Walsh [15]) extremely rapidly by a reaction of zero activation energy. Quadratic termination reactions have been suggested by Burgess and Robb [16] for oxidations carried out at temperatures up to about 300°C. These again are unlikely under the present conditions (reaction in the chain-branching region above about 300°C) in view of the well-established exponential acceleration of the oxidations. Such an acceleration cannot be explained if the termination reactions are quadratic, unless quadratic branching reactions are invoked at the same time.

Depending upon the termination reaction selected, the chain length of the basic reaction chains is then given by

$$\nu = k_p[\text{Hy}]/k_t,$$

$$\nu' = k_{p'}[O_2]/k_{t'},$$

or

$$\nu'' = k_{p''}/k_{t''}.$$

If a certain proportion α of the main chain steps produce the branching intermediate I, and if *all* such molecules eventually react to initiate new chains, the net number of new chains initiated by any one chain would be

$$N = (n\alpha\nu - 1),$$

where n is the number of chains initiated by the reaction of one molecule of the intermediate. The value of n would be expected to be 2 as, for example, in the branching reactions

$$R\,.\,CHO + O_2 = R^- + CO + HO_2, \tag{3}$$

or

$$= R^- + CO_2 + OH, \tag{4}$$

$$ROOH = RO^- + OH, \tag{5}$$

but might be unity if one of the radicals formed in the branching reaction were very unreactive. In general, only a fraction β of the molecules of intermediate will actually survive long enough to initiate new chains, the fractions $(1 - \beta)$ being destroyed by other reactions such as

$$ROOH = R'\,.\,CHO + H_2O, \tag{6}$$

$$R\,.\,CHO + 0{\cdot}5\,O_2 = R\,.\,COOH, \tag{7}$$

$$R\,.\,CHO + X^- = R^- + CO + XH. \tag{8}$$

Reactions (6) and (7) could well occur on the walls of the reaction vessel during the induction period, while reaction (8) probably occurs homogeneously during the later stages of the reaction when the free-radical concentration has built up. The net number of new chains initiated by any one chain is then reduced to

$$N = (n\alpha\beta\nu - 1).$$

The rate of acceleration of the reaction is simply the net number of new chains produced per old chain per unit time, and ϕ is accordingly given by

$$\phi = (n\alpha\beta\nu - 1)/\theta,$$

where θ is the average lifetime of a molecule of I with respect to *all* reactions destroying it. An equation similar to this is derived by Semenov.[1] The quantities θ, β and ν may readily be derived in terms of the generalized rate constants given below. On the basis of experimental results reported later it appears that the termination reaction usually involves the radical X, which attacks the hydrocarbon, and for the sake of conciseness the equations derived below will assume that this is the case. However, the appropriate expressions may readily be obtained for systems in which the other termination reactions operate. The generalized rate constants may be defined by the equations:

$$\text{rate of propagation} = R_p = k_p[\text{Hy}][\text{X}],$$

$$\text{rate of termination} = R_t = k_t[\text{X}],$$

$$\text{rate of degenerate branching} = R_b = k_b[\text{I}],$$

rate of destruction of I by non-branching reactions

$$= R_d = k_d[\text{I}],$$

and it is important to note that the rate constants k_t, k_b and k_d may contain further concentration terms. For example, where branching is by reaction (3), then

$$k_b = k_3[\text{O}_2],$$

and where destruction of branching intermediate is by reaction (8),

$$k_d = k_8[\text{X}].$$

If the termination reaction were diffusion controlled, then

$$k_t = k_{td}/[\text{P}],$$

where [P] is a total pressure term of the form $\Sigma m_i[\text{M}_i]$, the $[\text{M}_i]$s being the concentrations of the various species present, and the m_is constants.

We can now write

$$\nu = k_p[\text{Hy}]/k_t, \qquad \beta = k_b/(k_b + k_d),$$

$$\theta = 1/(k_b + k_d),$$

and hence

$$\phi = (k_b + k_d)\left\{n\alpha\frac{k_b}{k_b + k_d}\,\frac{k_p[\text{Hy}]}{k_t} - 1\right\}$$

$$= k_b(n\alpha k_p[\text{Hy}]/k_t - 1) - k_d.$$

In the special case where $k_d = 0$, the acceleration constant of the reaction takes the simplified form

$$\phi = k_b(n\alpha k_p[\text{Hy}]/k_t - 1).$$

The total number of branches per chain is then simply given by the ratio of the two terms in the bracket. When the rate constants do not depend upon concentrations of any of the reactants, plots of ϕ against [Hy] will be straight lines whose intercepts on the ϕ axis give the rate constants for the branching reactions k_b, and whose gradients are $k_b k_p n\alpha/k_t$. By dividing the acceleration constant for any hydrocarbon concentration by the intercept, one obtains the net number of branches per chain at this concentration. Such relations hold for ethane and propane as seen from fig. 7.

The branching rate constants are respectively 0·55 min^{-1} and 0·92 min^{-1} and the lifetimes of the branching intermediates are 1·8 and 1·1 min respectively. It may also be noted that the ϕ against [Hy] lines cut the concentration axis at definite positive concentrations, and in a mixture containing, for example, 225 mm pressure of ethane there is only one net branch per chain. If it is assumed that the branching intermediate in the reaction produces two chain-initiating radicals, i.e., $n = 2$, then it appears that in the mixture each chain forms on the average only one molecule of intermediate. The efficiency factor α must therefore be quite small under the present conditions. This conflicts with most of the mechanisms proposed in the past where it has been assumed to be unity.[2, 17-19] The conclusion is, however, supported by the analytical evidence already mentioned which indicates that the major chain reaction removing propane is one which does not lead to the formation of any branching intermediate except indirectly through the oxidation of the propylene thereby formed. The production of branching intermediate in this case appears to be a side reaction.

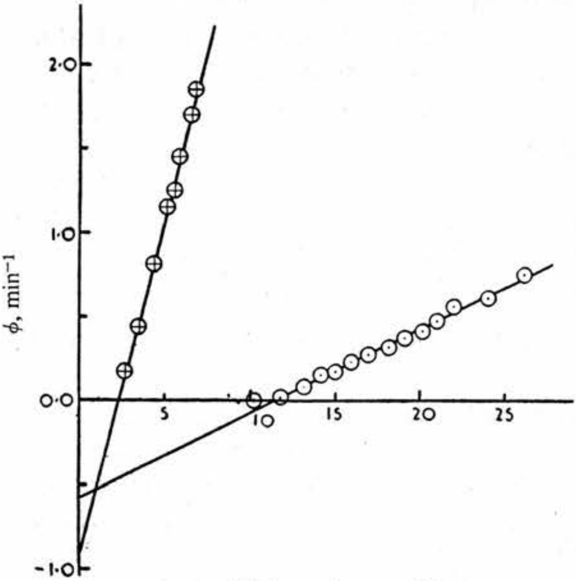

FIG. 7.—Variation of the acceleration constant with hydrocarbon pressure for propane (⊕) and ethane (⊙). Propane mixtures contained 54 mm oxygen; ethane + oxygen mixtures were equimolar; at 318°C.

THE MAXIMUM RATE OF REACTION

The maximum rate of reaction is a variable like the induction period whose interpretation may often be open to question. The maximum rate probably arises from the combined operation of two distinct factors:

(i) the removal of branching intermediate by radical attack by a reaction such as (8) which may be written generally as

$$I + X^- \xrightarrow{k_{d'}} P' + X'^-;$$

(ii) the depletion of the reactants.

The first of these factors may readily be treated within the framework built for the treatment of ϕ. In the expression for the acceleration constant we write $k_d = k_{d'}[X]$,

$$\phi = k_b(n\alpha k_p[\mathrm{Hy}]/k_t - 1) - k_{d'}[X].$$

At maximum rate of reaction $\phi = 0$; hence

$$[X]_{\max} = (k_b/k_{d'})(n\alpha k_p[\mathrm{Hy}]/k_t - 1).$$

The maximum rate of removal of hydrocarbon is then given by

$$\begin{aligned} R_{\max} &= k_p[\mathrm{Hy}][\mathrm{X}]_{\max}, \\ &= (k_p k_b/k_{d'})[\mathrm{Hy}](n\alpha k_p[\mathrm{Hy}]/k_t - 1), \\ &= k_p[\mathrm{Hy}]\phi_0/k_{d'}, \end{aligned}$$

where ϕ_0 is the initial acceleration constant before the effect of radical destruction of I has made itself felt. Experimentally ϕ_0 cannot be taken as the acceleration constant at the very beginning of the reaction owing to the importance of surface effects during the induction period but must be taken as the acceleration constant during the exponential part of the development curve. The rate of removal of hydrocarbon will be simply related to the rate of pressure rise according to an equation $\rho_{\max} = BR_{\max}$, where B has to be determined experimentally by analysis. A simple relationship between the maximum rate of pressure rise and the acceleration constant should therefoer hold

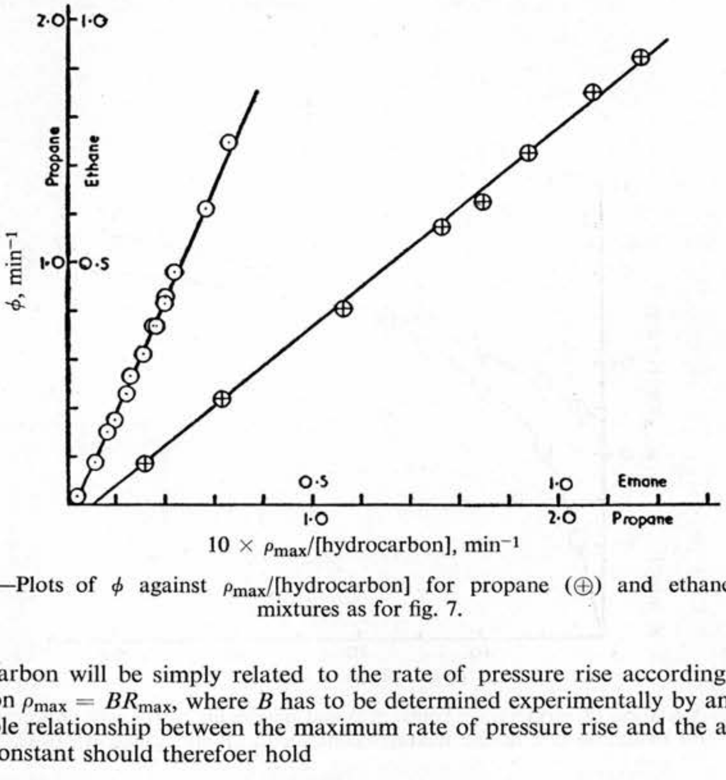

FIG. 8.—Plots of ϕ against $\rho_{\max}$/[hydrocarbon] for propane (⊕) and ethane (⊙); mixtures as for fig. 7.

$$(\rho_{\max}/[\mathrm{Hy}]\phi_0) = (Bk_p/k_{d'}), \tag{A}$$

and plots of $\rho_{\max}$/[Hy] against ϕ_0 should be straight lines. Such relationships hold in the oxidation of ethane and propane at 318°C as illustrated in fig. 8.

The case where consumption of reactants limits the rate of reaction has been treated by Semenov.[1] His analysis applies to branching-chain reactions where termination of chains takes place on the walls of the reaction vessel and is diffusion controlled. Here the chain length is taken as proportional to the square of the reactant pressure. He shows that the rate curves for several branching reactions may be made to coincide by suitable adjustment of the horizontal and vertical scales. In the oxidation of hydrocarbons the development curves are not of the symmetrical form predicted by the Semenov treatment, but nevertheless it is likely that for mixtures of the same overall composition they may be made to fit by suitable scale adjustment. If the degree of advancement of the reaction is defined as

$$\xi = \Delta p_t/\Delta p_\infty,$$

where Δp_t is the pressure rise in the reaction at time t and Δp_∞ the pressure rise at the end of the reaction, and if the relative rate of reaction is defined as

$$P = \rho_t/\rho_{\max},$$

where ρ_t and $\rho_{\max}$ are the rate of pressure rise at time t and the maximum rate of reaction, plots of ξ against P should coincide for different mixtures and will be of a form similar to the curve given in fig. 1 where $P = 1$ when $\xi = 0{\cdot}55$. The complete curve may be expressed as

$$P = f(\xi),$$

then

$$\frac{\mathrm{d}P}{\mathrm{d}\xi} = f'(\xi) = \frac{\Delta p_\infty \mathrm{d}\rho}{\rho_{\max}\mathrm{d}\Delta p}\ ;$$

but

$$\mathrm{d}\rho/\mathrm{d}\Delta p = \phi,$$

thus

$$\rho_{\max}/\phi\Delta p_\infty = f'(\xi).$$

Since

$$p_\infty = k[\mathrm{O_2}],$$

$$\rho_{\max}/\phi[\mathrm{O_2}] = kf'(\xi). \qquad \textbf{(B)}$$

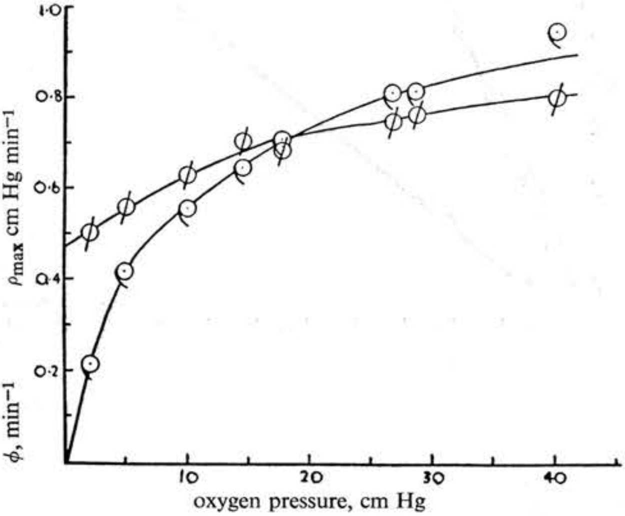

FIG. 9.—Variation of acceleration constant ϕ and maximum rate ρ with oxygen pressure for oxidation of ethane; mixtures contained 250 mm ethane at 318°C.

For a mixture of given composition this is equivalent to the equation derived for maximum rate of reaction determined by factor (i). There does not, however, appear to be any simple method of determining theoretically how $f'(\xi)$ will vary with [hydrocarbon]/[oxygen] ratio. However, in the oxidation of ethane at low $[\mathrm{O_2}]/[\mathrm{C_2H_6}]$ ratios, the reaction is observed to stop suddenly as the oxygen is exhausted. Here the development curves can be fitted for different mixture compositions. As shown in fig. 9, which gives the $\rho_{\max}$ and ϕ values for ethane + oxygen mixtures, $\rho_{\max}/\phi$ depends strongly upon the oxygen pressure for mixtures weaker in oxygen than equimolar but is almost independent of oxygen pressure in richer mixtures. For the oxygen-weak mixtures, there is rough agreement with relation B but in oxygen-rich mixtures, relation A is accurately obeyed as already shown in fig. 7. In the oxidation of oxygen-rich mixtures, it therefore appears that the maximum rate is governed by factor (i) rather than by factor (ii).

It might, however, be argued that while at low $[\mathrm{O_2}]/[\mathrm{C_2H_6}]$ ratios the maximum rate is limited by the consumption of oxygen, at high ratios it should be limited by consumption of the hydrocarbon. This is, however, unlikely since the products of the oxidation are on the whole more reactive than the original hydrocarbon and since analysis shows that the proportion of hydrocarbon consumed at maximum rate of reaction is not normally very high. Thus the reactivity of the remaining hydrocarbon + reaction products at maximum rate is probably not much less than that of the original mixture.

It is therefore felt that verification of relation A over a range of oxygen pressures, particularly in the oxygen-rich region, should be regarded as reasonably good verification that factor (i) limits the reaction rate. This is particularly important since nearly all mechanisms proposed in explanation of maximum rate kinetics have made this assumption.[2, 3, 17] When maximum-rate measurements have been made with oxygen-weak mixtures their interpretation on this assumption may be suspect.

THE DEVELOPMENT OF THE REACTION IN TIME

When factor (i) limits the reaction rate, the development of the reaction in time may readily be worked out. Throughout the reaction the acceleration constant will follow

$$\phi = k_b(n\alpha\beta\nu - 1) - k_{d'}[\mathrm{X}].$$

The rate of the reaction is given by

$$R = k_p[\mathrm{Hy}][\mathrm{X}],$$

thus

$$\phi = k_b(n\alpha\beta\nu - 1) - (k_{d'}R/k_p[\mathrm{Hy}]).$$

If the rate constants and efficiency factors remain constant the acceleration should decrease linearly with increase in the fractional reaction rate (i.e. with $R/[\mathrm{Hy}]$).

A similar result is predicted when factor (ii) limits the reaction rate. Experimentally the variation of ϕ with reactant pressures indicates that the chain length decreases at least linearly with reactant pressure. Accordingly ϕ should decrease at least linearly with the extent of reaction, a conclusion similar to that of Semenov.

These predictions are not in agreement with experiment. It is found in practice (see fig. 1 and 5) that ϕ remains constant until the rate of reaction reaches about 80 % of its maximum value. It then decreases very rapidly to zero and finally becomes negative. This indicates that some additional catalytic agents must be formed during the reaction which prevent the expected decrease in ϕ. The effect is clearly observed in the high-temperature oxidation of propane [5] where in some cases the acceleration actually increases as the reaction proceeds. The explanation advanced there was that the accumulated propylene acted as a promoter. In the oxidation of propane at 318°C, the same explanation appears to hold, and has already been advanced in connection with the effect of propylene on the induction period processes. From fig. 5, it is seen that the pressure of propylene during the linear part of the acceleration rises from about 1·4 mm to 4mm, an increase of 2·6 mm. In the presence of excess propylene (fig. 6), the addition of a further 2·6 mm gives rise to an increase in ϕ of about 0·5 min^{-1}. Since the initial ϕ for the reaction illustrated in fig. 5 is about 1·0 min^{-1} the propylene formed in the reaction could effectively obscure an incipient fall to about 0·5 min^{-1}. The regular decrease which might be expected in ϕ due either to the consumption of reactants or to the radical removal of branching intermediate may thus be prevented by a rapid increase in the concentration of a suitable promoter. At 318° with ethane and propane, the two factors almost exactly cancel out for a considerable part of the development of the reaction and thereby yield a deceptively simple acceleration curve. Only when the rapid rise in the concentration of promoter ceases does the acceleration of the reaction start to fall. It then occurs much more rapidly than might otherwise have been expected.

It is probably a reasonable assumption to take the acceleration constant obtained from the linear part of the development curve as the initial acceleration of the reaction without surface inhibition and ϕ is accordingly probably the parameter with the simplest interpretation. The maximum rate of reaction does not, however, refer to the same reaction mixture as ϕ and the relations between $R_{\max}$ and ϕ derived above are probably only approximations since no account has been taken in deriving them of the presence of quite considerable amounts of important promoters.

In conclusion, one notes that great care has to be used in the interpretation of kinetic data obtained from oxidation experiments and that it is most important always to support kinetic evidence with analytical evidence.

Full details of experimental procedure, purification of reactants, etc., have not been given in the present paper as it is intended to publish them later along with more comprehensive experimental data.

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RATE CONSTANTS OF ELEMENTARY REACTIONS IN HYDROCARBON OXIDATION—LOW TEMPERATURE OXIDATION OF LOWER HYDROCARBONS

J. H. KNOX

The slow oxidation reactions of aliphatic hydrocarbons are among the best examples of degenerately branching chain reactions[1]. Such reactions proceed through the agency of free radical chains of finite length which produce a product, I, of intermediate stability which can react after a delay of the order of minutes to initiate new chains. Provided that any one chain eventually initiates at least one new chain the reaction will accelerate exponentially[2]. Normally the pressure rise gives a reasonably good measure of the extent of reaction[3] (see *Figure 1*) and one accordingly expects that the pressure will increase during the reaction according to the equation

$$\Delta p = A \,.\, e^{\phi t} \quad \text{or} \quad \rho = d(\Delta p)/dt = \phi \,.\, \Delta p$$

where ϕ is the net branching factor or acceleration constant of the reaction. ϕ is thus obtained from a plot of rate of pressure rise, ρ, against pressure rise, Δp. Experimentally such plots are straight over the greater part of the acceleration of the reaction as shown in *Figure 2*.

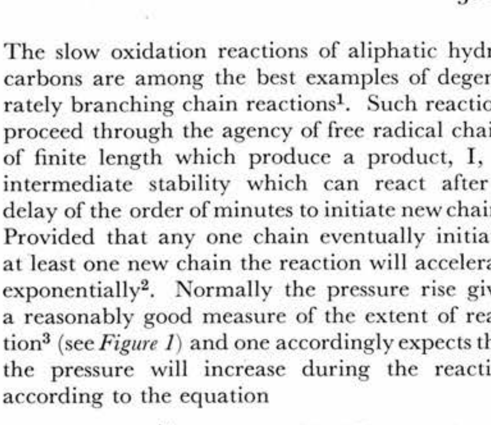

Figure 1. Total pressure rise as a function of initial oxygen pressure in the oxidation of propane at 318°C

The acceleration constant ϕ may be evaluated in terms of the rates of the individual steps in any degenerate branching mechanism as follows. Let the length of the basic chains be ν and let a proportion α of the chain steps produce the active intermediate I. Let a fraction β of these molecules of intermediate I actually react to form free radicals which initiate new chains, and let θ be the lifetime of I with respect to *all* the reactions destroying it, whether or not they finally initiate new chains. The net number of additional chains produced by any one chain is then

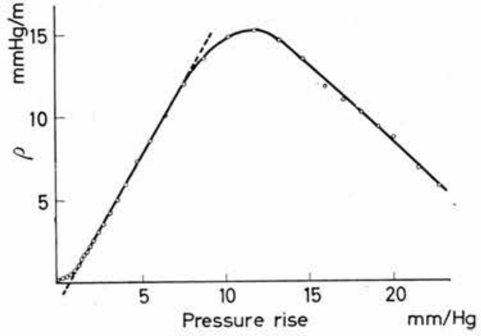

Figure 2. Rate versus *pressure rise curve for oxidation of propane at* 318°C $[C_3H_8] = 54{\cdot}6$ mm Hg $[O_2] = 77{\cdot}2$ mm Hg. $\phi = 1{\cdot}80\ \text{min}^{-1}$

$$n = (2\alpha\beta\nu - 1)$$

and the acceleration constant is

$$\phi = n/\theta = (1/\theta)(2\alpha\beta\nu - 1)$$

The number 2 enters into the equations since each molecule of I will generally yield two free radicals in the branching reaction. If it is assumed that the termination of the reaction chains involves the same radical, X, as normally attacks the hydrocarbon, Hy, the actual rates of the various reactions may be expressed generally as:

Propagation	$R_p = k_p[\text{Hy}][\text{X}]$
Termination	$R_t = k_t[\text{X}]$
Branching	$R_b = k_b[\text{I}]$
Non-branching destruction of intermediate	$R_d = k_d[\text{I}]$

then

$$1/\theta = (k_b + k_d)$$
$$\beta = k_b/(k_b + k_d)$$
$$\nu = k_p[\mathrm{Hy}]/k_t$$

and

$$\phi = (k_b + k_d)\left\{2\alpha \frac{k_b}{k_b + k_d} \times \frac{k_p[\mathrm{Hy}]}{k_t} - 1\right\}$$
$$= k_b\left\{2\alpha \frac{k_p[\mathrm{Hy}]}{k_t} - 1\right\} - k_d$$

In this expression the generalized rate constants may themselves contain concentration factors. If, for example, the branching reaction were second order and of the form

$$\mathrm{I} + \mathrm{O}_2 = 2 \text{ free radicals}$$

then the branching rate constant would be $k_b = k_b'[\mathrm{O}_2]$ where k_b' is independent of reactant concentration. In the simplest case where $k_d = 0$, α is constant and ν is proportional to [Hy], a plot of ϕ against [Hy] should be a straight line whose negative intercept on the ϕ axis gives k_b and whose gradient gives $2\alpha k_b k_p/k_t$. Such straight lines are obtained for ethane and propane but not for *iso*butane where the dependence is more complex (see *Figures 3* and *4*).

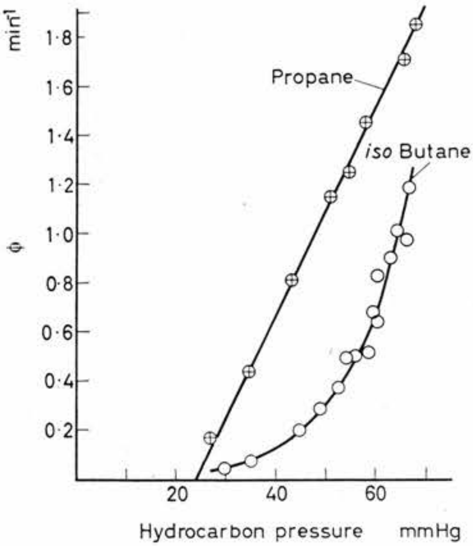

Figure 3. Plots of ϕ against [Hy] *for oxidations at* 318°C. C_4H_{10}/O_2 *mixtures equimolecular;* C_3H_8/O_2 *mixtures contained* $[O_2] = 54$ mm Hg

The maximum rate of reaction, which is a more widely measured reaction parameter than the acceleration constant, is more difficult to interpret. The maximum rate may result either from the consumption of the reactants or from the destruction of the intermediate I by radical attack$^{3-5}$. It appears that both factors are important in most oxidation systems but that to a first approximation the former may be ignored in oxygen rich mixtures. Two pieces of evidence support this conclusion (*a*) that ϕ does not decline until a considerable degree of reaction has occurred (see *Figure 2*) and that the products of reaction are therefore as effective in propagating the reaction as the original reactants, and (*b*) that a 'negative induction period' may often be induced by the addition of sufficient chain initiating substances such as aldehydes^4. With propane the addition of excess propionaldehyde, as shown in *Figure 5*, causes the reaction to start at a greatly enhanced rate, but the rate of reaction finally achieved is found to be only slightly increased by the addition of the aldehyde. There is therefore a maximum rate of reaction which can be

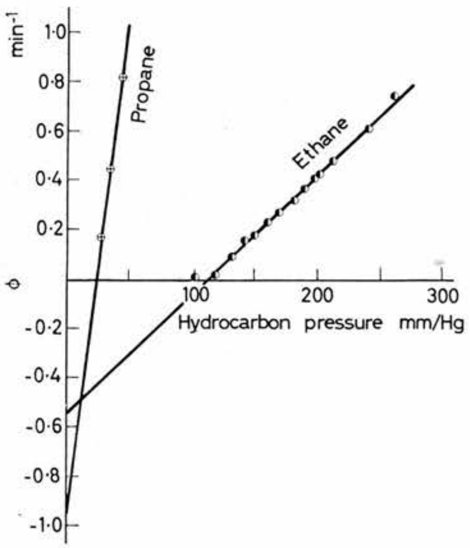

Figure 4. Plots of ϕ against [Hy] *for oxidations at* 318°C. C_3H_8/O_2 *mixtures as in Figure 3;* C_2H_6/O_2 *mixtures equimolecular*

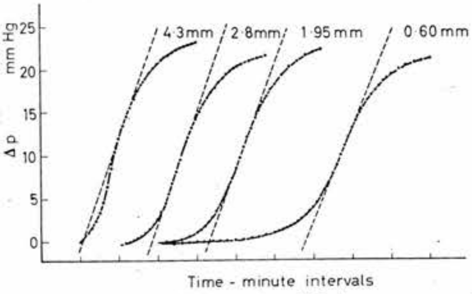

Figure 5. Effect of added propionaldehyde on pressure-time curves for oxidation at 318°C *of mixtures containing* $[C_3H_8] = 50$ mm Hg; $[C_3H_6] = 5$ mm Hg; $[O_2] = 54$ mm Hg. *Propionaldehyde pressures are given on individual lines*

tolerated by the system in the later stages of reaction. This rate is not dependent upon the rate at which the reaction commences.

When free radical removal of the intermediate limits the maximum rate of reaction we may write

$$R_d = k_d[\mathrm{I}] = k'_d[\mathrm{X}][\mathrm{I}]$$

where it is assumed that the radical attacking and destroying I is the same as normally attacks the hydrocarbon. Thus for any stage in the reaction

$$\phi = k_b\left\{2\alpha\frac{k_p[\mathrm{Hy}]}{k_t} - 1\right\} - k'_d[\mathrm{X}]$$

At maximum rate of reaction $\phi = 0$ and therefore rearranging

$$[\mathrm{X}] = \frac{k_b}{k'_d}\left\{2\alpha\frac{k_p[\mathrm{Hy}]}{k_t} - 1\right\} = \phi_0/k'_d$$

where ϕ_0 is the value of ϕ at the beginning of the reaction when [X] is small. The maximum rate of removal of the hydrocarbon is then

$$R_{\max} = k_p[\mathrm{X}][\mathrm{Hy}] = \frac{k_p \times \phi_0[\mathrm{Hy}]}{k'_d}$$

$$\frac{R_{\max}}{\phi_0[\mathrm{Hy}]} = k_p/k'_d$$

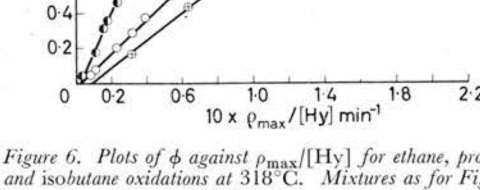

Figure 6. Plots of ϕ against $\rho_{\max}$/[Hy] for ethane, propane and iso*butane oxidations at* 318°C. *Mixtures as for Figures 3 and 4. For ethane, ordinates and abscissae should be halved*

$R_{\max}$ is however the rate of removal of the hydrocarbon while the quantity measured experimentally is the rate of pressure rise. The two are simply connected. The total pressure rise in the reaction is proportional to the initial oxygen pressure (*Figure 1*), that is $\Delta p_{\max} = B \times [\mathrm{O_2}]$ where B is found experimentally to be independent of hydrocarbon concentration. It is therefore almost certain that the rate of pressure rise during the reaction is proportional to the rate of disappearance of oxygen. In the mechanisms so far proposed for low temperature oxidations$^{6-9}$ one molecule of oxygen is initially consumed for each molecule of hydrocarbon used and it is therefore reasonable to identify the rate of disappearance of oxygen with the rate of disappearance of hydrocarbon. Thus $\rho_{\max} = B \,.\, R_{\max}$ and

$$\frac{\phi_0[\mathrm{Hy}]}{\rho_{\max}} = \frac{k'_d}{B \,.\, k_p}$$

This relation holds well for ethane, propane and *iso*butane (see *Figure 6*) provided that the $[\mathrm{O_2}]/[\mathrm{Hy}]$ ratio is not less than unity. For lower ratios the maximum rate is largely limited by the consumption of oxygen and the reaction ceases suddenly when all the oxgyen is consumed. The experimental values of $\phi_0[\mathrm{Hy}]/\rho_{\max}$ then increase with decreasing oxygen concentration. However, for oxygen rich mixtures, where the ratio is constant and independent of oxygen pressure, the rate constant ratio k'_d/k_p may be obtained. The values obtained for k_b, $2\alpha k_p/k_t$, B and k'_d/k_p for ethane, propane and *iso*butane at 318°C are given in Table 1.

TABLE 1

	k_b min^{-1}	$2\alpha k_p/k_t$ (cm Hg)$^{-1}$	B	k'_d/k_p
Ethane*	0·55	0·089	0·245	5·4
Propane	0·98†	0·425‡	0·415	2·9†
*Iso*butane §	—	—	0·40	4·1

* Equimolecular ethane/oxygen mixtures.
† Oxygen pressure larger than 50 mm Hg.
‡ Oxygen pressure 54 mm. Hg.
§ Equimolecular *iso*butane/oxygen mixtures.

The values for the rate constants of branching do not vary as much as might have been expected from ethane to propane, the half-lives of the intermediates being of the order of 2 and 1 minutes respectively. The values appear to be almost independent of oxygen pressure although preliminary results with propane indicate that k_b falls off when the oxygen pressure falls below 50 mm Hg. From *Figures 3* and *4* it can be seen that the number of branches per chain under the experimental conditions used was always small and never exceeded about three. This implies that either the reaction chains are very short or that the quantity α is very much less than unity. It appears unlikely that the chains can be as short as say ten units and therefore likely that α is small and that only a fraction of the chain steps actually produce branching intermediate. This is contrary to most of the theories so far put forward where the branching intermediate is formed in every complete chain cycle.

It is also of note that k'_d/k_p does not vary widely from one hydrocarbon to another. This is in agreement with the results presented in another paper[10] where the rates of radical attack on ethane, propane and *iso*butane are shown to differ by much less than the overall reactivity of the hydrocarbons. These results can be combined with those of the present paper to give the relative rates of attack of the radicals on the branching intermediates in the oxidations of the three hydrocarbons, and also the relative values of α/k_t. The results are presented in Table 2.

TABLE 2

	Ethane	*Propane*	Iso*butane*
Propagation rate constant relative to k_p for ethane	1·0	2·3	3·4
k'_d/k_p	5·4	2·9	4·1
Rate constant for destruction of I by radicals relative to k_p for ethane	5·4	6·7	14·0
α/k_t relative to value for ethane	1·0	2·1	—

They show that there are only moderate differences in the reactivity of the intermediates with respect to the radicals present and probably only moderate differences in the efficiency of production of branching intermediate, α.

The differences in reactivity of various hydrocarbons are therefore probably due not to major differences in the rates of any one critical reaction such as branching or chain propagation. There appear, in fact, to be at least five factors which are important in determining the overall reactivity of a hydrocarbon towards oxygen: (1) the rate of the branching reaction, (2) the chain length of the basic chain, (3) the fraction of chain steps which produce branching intermediate, (4) the fraction of molecules of I which, once formed, react to initiate new chains, and (5) the rate at which radicals attack the branching intermediate compared to the rate at which they attack the hydrocarbon. The contribution of each factor to the overall reactivity as measured by ϕ or $R_{\max}$ may vary only slightly from one hydrocarbon to another but their cumulative effect can very well result in the very large differences in reactivity observed in practice from one hydrocarbon to another.

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[22]

THE PYROLYSIS OF ALKYL HYDROPEROXIDES IN THE GAS PHASE

By Alexander D. Kirk * and John H. Knox
Dept. of Chemistry, University of Edinburgh

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Ethyl, isopropyl and t-butyl hydroperoxides have been pyrolyzed in benzene as carrier between 280° and 380°C and the rate constants for the homogeneous decomposition obtained from measurement of the diphenyl produced. The rate constants for the heterogeneous reactions have also been determined. The data are summarized in table 1. The three peroxides have activation energies for homogeneous decomposition of about 39 kcal $mole^{-1}$ and A factors close to 10^{14} sec^{-1}. They decompose some 100-300 times more slowly than the dialkyl peroxides. The heterogeneous decomposition reactions have activation energies of about 20 kcal $mole^{-1}$. It is concluded that hydroperoxides are unlikely to play an important role in hydrocarbon oxidation above 300°C.

Hydroperoxides have often been postulated as the branching intermediates in hydrocarbon oxidations in the gas phase [1-3] but this proposal has never been critically tested by measurement of their rates of homogeneous decomposition into free radicals. The rates of decomposition of the simpler dialkyl peroxides in the gas phase are known with some precision and the position has recently been summarized by Hanst and Calvert.[4] Their values for the Arrhenius parameters of four dialkyl peroxides are recorded in table 1. Although the parameters vary over quite a range the actual rate constants at, say, 450°K, vary only from $2{\cdot}5 \times 10^{-3}$ to 8×10^{-3} sec^{-1}. Their lifetimes at temperatures normally employed in hydrocarbon oxidations (300-500°C) are so small that they cannot seriously be considered as possible branching agents.

Table 1

R	dialkyl peroxides [4] ROOR		alkyl hydroperoxides ROOH			
	E (kcal/mole)	log A (sec^{-1})	E_{hom} (kcal/mole)	log A_{hom} (sec^{-1})	E_{het} (kcal/mole)	log A_{het} (sec^{-1})
hydrogen [1]			48·0	12·0	20	
methyl	36·1	15·4	—	—	—	—
ethyl [3]	34·1	14·2	37·7±0·7	13·4±0·3	18	6
isopropyl	—	—	40·0±0·7	15·2±0·3	17	6
n-propyl	36·5	15·4	—	—	—	—
t-butyl	37·5	15·6	37·8±0·7	13·7±0·3	25	8
mean[2]	36·2	15·2	38·5	14·1		

[1] A factor for H_2O_2 is calculated for a pressure of 15 mm Hg of H_2O_2 from data in ref. (16)

[2] Mean values are the average for the organic peroxides.

[3] Error limits are standard errors.

[4] Values from ref. (4).

Accurate data for the rates of homogeneous decomposition of the alkyl hydroperoxides (ROOH) are lacking mainly because they readily undergo heterogeneous decomposition, as was shown by Harris [5] and by Medvedev and Podyapolskaya.[6]

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* present address: Department of Chemistry, University of British Columbia, Canada.

The only peroxide of the present series for which data on the homogeneous decomposition are available is t-butyl hydroperoxide. Bell, Raley, Rust, Seubold and Vaughan [7] examined the decomposition both in the gas and liquid phases. In the liquid phase the rate of decomposition followed

$$k = 10^{15\cdot 1} \exp(-39{,}000 \text{ cal mole}^{-1}/\boldsymbol{R}T) \text{ sec}^{-1}.$$

The decomposition in the gas phase did not yield quantitative results but showed that at least some homogeneous decomposition took place. When the peroxide was pyrolyzed in a stream of cyclohexene at 190°C the products included cyclohexyl alcohol which could have been formed only as a result of initial addition of OH radicals to the cyclohexene. The pyrolysis of a number of other hydroperoxides has been studied in the liquid phase.[8-10] Their activation energies range from 27 to 39 kcal/mole and their *A* factors from 10^{10} to 10^{15} sec^{-1}. The rate constants at 450°K are, however, much closer than the Arrhenius parameters would indicate. They range from 2×10^{-4} to 1×10^{-3} sec^{-1}. These values almost certainly apply to the homogeneous decomposition of the peroxides at the O—O bond. While there is clearly a great decrease in stability when one H atom in hydrogen is replaced by an alkyl group, the change is much less when the second H atom is replaced. We therefore expected that the homogeneous decomposition of the alkyl hydroperoxides would be observable in the temperature range of 200-400°C.

In devising a method of determining the rate of the homogeneous reaction the major difficulty is to separate the homogeneous and heterogeneous reactions. The Szwarc [11] toluene-carrier method was developed for this purpose. The compound under investigation is passed at low concentration in a stream of toluene through a heated reaction vessel. Free radicals formed by the homogeneous decomposition react with the toluene to give benzyl radicals which being unreactive, eventually dimerize. Measurement of the yield of dibenzyl gives the rate of the homogeneous reaction. For the present purpose, toluene is not a suitable carrier since the methyl and alkoxy radicals formed by the decomposition of the peroxides would react only partially with the toluene. The dibenzyl formed would then not give a true measure of the extent of the homogeneous reaction. Benzene however, appeared to be a suitable carrier. Under the experimental conditions the approximate lifetime of a radical with respect to recombination assuming this to occur at every collision is 10^{-3} sec or more. Ethoxy, isopropoxy and t-butoxy radicals undergo unimolecular decomposition into a methyl radical and a carbonyl compound in 10^{-7}-10^{-5} sec at 600°K [12] if a normal *A* factor is assumed. We are therefore safe in assuming that all the alkoxy radicals formed in the pyrolyses will decompose into methyl radicals before they can undergo any other reaction. The peroxide pyrolyses may therefore be regarded essentially as reactions producing equal numbers of OH and CH_3 radicals. It can be shown from the available rate constant data for methyl radicals [13] that less than 2 % would abstract hydrogen from benzene under the conditions of our experiments. Hydroxyl radicals on the other hand would be expected to abstract almost 100 %. There are several reasons for this.

(i) The activation energies of OH radical abstraction reactions are likely to be low because of the strength of the H—OH bond formed and because of the high electronegativity of the OH radical which is close to that of a bromine atom [14] and well above that for a CH_3 radical. This is confirmed experimentally by the rather complex experiments of Avramenko and Lorentzo [15] who showed that the activation energies for OH abstraction reactions were at least 4 kcal/mole lower than those for methyl radical reactions.

(ii) The recombination of OH radicals is certainly third order [16] and will be much slower than the recombination of methyl radicals at the working pressure in our experiments (10-20 mm Hg). It must therefore be an unimportant competitor for OH radicals.

(iii) The combination of OH with phenyl radicals might occur to some extent but all attempts to identify phenol in the reaction products failed. The diphenyl formed contained less than 1 % of phenol.

(iv) OH+CH_3 is likely to be a third-order reaction and since no phenol is formed it is unlikely that any removal of OH by reaction with methyl can occur.

(v) OH+ROOH is unlikely as the concentration of hydroperoxide was not more than 2 % that of benzene.

(vi) Diffusion of OH to the walls of the reaction vessel (cylindrical and 25 mm diam.) would on the average take about 10^{-2} sec. This is considerably greater than the probable lifetime of OH with respect to abstraction from benzene at the concentration in our experiments.

It is therefore tolerably certain that the great majority of the OH radicals formed in the pyrolyses will give rise to phenyl radicals, whereas the methyl radicals will not. The mechanism of the homogeneous part of the reaction may therefore be written in a simplified form as ($\phi = C_6H_5$)

$$\mathrm{ROOH = RO+OH} \tag{1}$$

$$= \mathrm{R_1R_2CO+CH_3+OH} \tag{2}$$

$$\mathrm{OH}+\phi\mathrm{H} = \mathrm{H_2O}+\phi \tag{3}$$

$$\phi+\phi = \phi_2 \tag{4}$$

$$\phi+\mathrm{CH_3} = \phi\mathrm{CH_3} \tag{5}$$

$$\mathrm{CH_3+CH_3 = C_2H_6}. \tag{6}$$

If reaction (5) is unimportant the rate of the homogeneous reaction can be determined from the yield of diphenyl formed in (4). There is no direct evidence that (5) is not important. However, Trotman-Dickenson [17] has shown that the reaction of $CH_3+\phi CH_2$ is so slow that it does not compete effectively with the dimerization of benzyl radicals in toluene carrier experiments with methyl radicals. In the present work this is confirmed by the observation in many experiments that the amount of diphenyl formed accounts for a high percentage of the peroxide decomposed (70 % or more) so that the formation of major amounts of toluene may be discounted. It is therefore probably justifiable to use the yield of diphenyl as a measure of the extent of the homogeneous reaction provided only that diphenyl is not formed by the pyrolysis of benzene alone or by the heterogeneous reaction. This was checked by showing that benzene gave no diphenyl when pyrolyzed at 600°C and that packing the reaction vessel increased typically heterogeneous reaction products but decreased the yield of diphenyl.

The experimental method was therefore to pass a mixture of about 2 % peroxide in benzene through a heated reaction vessel at a known rate, and to measure the yield of diphenyl and the amount of peroxide consumed. The fraction of homogeneous decomposition in any experiment is then

ϕ = 2 (moles of diphenyl formed)/(moles of peroxide consumed).

If both the homogeneous and heterogeneous reactions are first order, an assumption justified later, the rate constant of the homogeneous reaction is given by

$$k_{\mathrm{hom}} = \phi k_{\mathrm{total}} = (2{\cdot}303\phi/t)\log_{10}[a/(a-x)]. \tag{A}$$

where a = total peroxide passed through system, $(a-x)$ = amount of peroxide recovered undecomposed, and t = contact time.

The flow system used in the work was unfortunately not suitable for extensive variation of the total pressure and we were therefore not able to establish whether the reactions were in their first-order regions or not. However, with molecules as complex as ethyl hydroperoxide and the higher hydroperoxides it seems unlikely that the " fall-off " region would start at pressures as high as 10 mm Hg. This is confirmed by the general agreement between the value of rate constants for the three peroxides studied and the agreement between our values for t-butyl hydroperoxide and those of Raley *et al.*[7] The unimolecular decomposition of CH_3OOH on the other hand might well be in the fall-off region at 10 mm pressure.

EXPERIMENTAL

A flow system was used for the work, the reaction vessel being a 90-ml, 25-mm diam. Pyrex or quartz tube which was housed in an electric furnace thermostatted to within 0·5°C. The temperature within the reaction vessel was constant to within ±2° under working conditions. All tubing within which undesirable condensation could have occurred was heated to 60°C. Benzene vapour was supplied from a thermostatted reservoir and the hydroperoxide was injected into the benzene stream from a narrow capillary tube leading from a second thermostatted reservoir containing the hydroperoxide. Both reservoirs were fitted with taps and joints and could be detached for weighing. The concentration of peroxide obtained in this way was about 2 % that of the benzene, but could be reduced by a factor of up to ten by changing the temperature of the reservoir or altering the size of the capillary. The pressure in the reaction vessel was between 10 and 20 mm Hg and was measured by means of a glass spoon-gauge to within ±2 %. After leaving the reaction vessel the gases passed through a capillary into cooled traps which were continuously evacuated by means of a mercury pump backed by a Toepler pump. The diphenyl was collected at −20°C in the first of these traps which was of small volume; benzene and unused peroxide were condensed in a second trap at −80°C. Products uncondensable at −80°C were pumped by means of the mercury-vapour pump through a trap cooled to −200°C in liquid oxygen under reduced pressure. The permanent gases still uncondensed were taken off from time to time by the Toepler pump and analysed soon after completion of the run which normally took 7·5 min. The last trap was then warmed to −80°C and the volatile components again taken off with the Toepler pump. Analysis was carried out as follows.

DIPHENYL was determined by weighing the first trap before and after each experiment. The weight was accurate to 0·1 mg but two corrections have to be applied. (i) Diphenyl has an appreciable vapour pressure at −20°C and losses were expected due to incomplete condensation. However, blank experiments in which pure diphenyl was vaporized and condensed under conditions identical to those of the flow experiments showed that the loss was insignificant. The weight of diphenyl vaporized was 1·06 times that collected. (ii) The diphenyl formed was not pure. Its melting point indicated a 25 % molar impurity content, which was not phenol. If the impurity did not arise from phenyl radicals the observed rate constants would require to be decreased by 25 %.

PEROXIDE.—The total peroxide passed through the system in any experiment was determined from the change of weight of the peroxide container assuming that the composition of the peroxide vapour was the same as that of the liquid. The unchanged peroxide at the end of an experiment which was collected in the second trap along with the benzene was determined by a simplified form of the iodimetric method of Wagner, Smith and Peters.[18] The hydroperoxide+benzene mixture was washed into a 250-ml conical flask with about 50 ml isopropanol. 1 g glacial acetic acid was added and the solution de-aerated by bubbling carbon dioxide through the solution for 15 min. 1 g of sodium iodide was added, and dissolved; the flask was fitted with a Bunsen valve, heated almost to boiling and maintained at this temperature for 3 min. 50 ml of water was added and the solution titrated with N/10 sodium thiosulphate.

BENZENE used in the experiment was determined from the change in weight of the benzene container. The contact time was calculated from the duration of the run, benzene used, reaction pressure, reaction vessel volume, and reaction temperature. It could be varied from 0·2 to 3 sec by changing the outlet capillary from the apparatus.

THE GASEOUS PRODUCTS were analysed in two fractions by gas chromatography. Gases uncondensed at −200°C (H_2, O_2, CO and CH_4) were determined on a column containing activated carbon at room temperature. The second fraction was analysed on a column containing 30 % nitrobenzene supported on firebrick at room temperature. This fraction could contain C_2-C_4 hydrocarbons and CO_2. Nitrogen was used as the carrier gas and a katharometer as the detector. Calibrations were carried out for each major component. Reaction products condensable at −80°C apart from these already mentioned were not determined.

The materials were obtained as follows.

BENZENE was May and Baker A.R. reagent dried over sodium wire. As no diphenyl was formed in pyrolysis at 600°C the benzene was not purified further apart from careful degassing by distillation under vacuum into the benzene reservoir before each run.

t-BUTYL HYDROPEROXIDE, 250 ml of commercial material (approx. 70 % peroxide) was fractionated on a 3 ft. distillation column under 16 mm pressure. The fraction boiling at 38°C/16 mm Hg was retained for use. It was 98·5 % pure by titration and 98 % pure by gas chromatography.

ISOPROPYL HYDROPEROXIDE was prepared by the method of Williams and Mosher.[19] The overall yield was 15 %. The hydroperoxide was purified by large-scale gas chromatography. It was not possible by this method to increase the purity beyond 81·2 % (by titration). The purity by gas chromatography was 81 %.

ETHYL HYDROPEROXIDE was prepared by oxygenating ethyl magnesium chloride.[20] The overall yield was about 15 %. The hydroperoxide purified by large-scale gas chromatography was 78·8 % pure (by titration).

RESULTS AND DISCUSSION

The Arrhenius parameters for the homogeneous and the heterogeneous decomposition of the three hydroperoxides are summarized in table 1 and compared with Hanst and Calvert's values for some dialkyl peroxides.

t-Butyl hydroperoxide was the first and most extensively studied of the three peroxides. Initially it was expected that ethane and diphenyl would be formed in the homogeneous reaction and that both of these could be used as a measure of the rate of O—O bond split. However, it soon became clear that the products of the heterogeneous reaction were complex and themselves contained ethane. Other products identified were H_2, O_2, CO, CH_4, C_3 hydrocarbons, isobutene and other C_4 hydrocarbons. All these products, except hydrogen were increased by packing the reaction vessel. Only diphenyl could therefore be used as a measure of the extent of the homogeneous reaction.

We have already advanced reasons for believing that the yield of diphenyl gave a quantitative measure of the amount of OH radical formed in the homogeneous decomposition. However, the evaluation of the homogeneous rate constant by use of the formula (A) requires, in addition, that both the homogeneous and heterogeneous reactions be first order. Several independent observations confirm this.

(i) Packing the reaction vessel so as to increase the surface/volume ratio about 10 times increased the rate of the heterogeneous reaction by roughly this amount. However, the homogeneous rate constants evaluated from the diphenyl yield on the basis of formula (A) were not significantly affected (fig. 1). Had the heterogeneous reaction been other than first order k_{hom}, derived in this way, would have been considerably affected by packing. It is, moreover, notable that the homogeneous reaction was considerably more reproducible than the heterogeneous reaction, confirming that the heterogeneous reaction was being properly allowed for by formula (A).

(ii) When the peroxide concentration was decreased ten times from 0·3 mm Hg to 0·03 mm Hg without changing the contact time or benzene pressure there was no systematic variation in k_{hom}.

(iii) Methane, a major heterogeneous reaction product, increased linearly with peroxide concentration at 574, 612 and 648°K, when the contact time and benzene concentration were kept constant. This could only occur if the part of the heterogeneous reaction forming methane was first order. Unfortunately, the yields of the other heterogeneous products did not increase in such a simple way with peroxide concentration.

(iv) Attempts to measure the overall order of the reaction yielded only a rough value of 1·25. The irreproducibility of the heterogeneous reaction made accurate determination impossible but there was no doubt that the order of the reaction was much less than two. The error involved in taking formula (A) as correct is therefore not likely to be large.

isoPropyl hydroperoxide gave rather more reproducible results for the overall reaction than t-butyl hydroperoxide. This is shown in fig. 2. The proportion of heterogeneous reaction is higher than for t-butyl hydroperoxide. This is due partly to a slower homogeneous reaction and partly to a faster heterogeneous reaction. The products of the latter were again complex and contained hydrocarbons up to C_3.

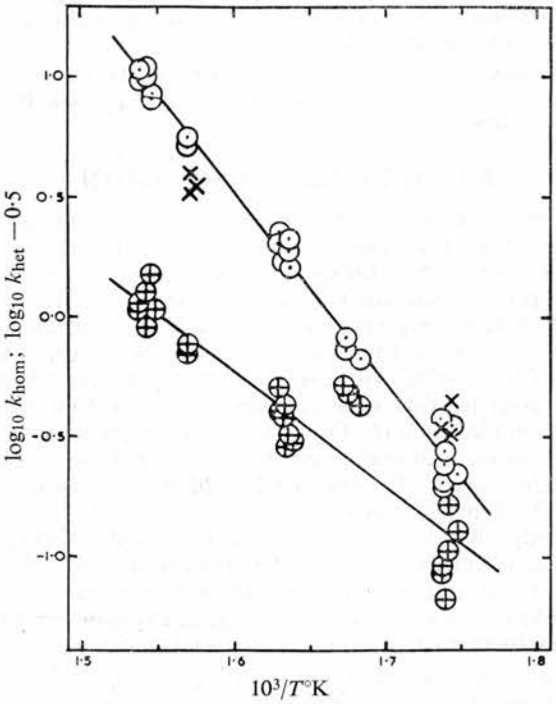

FIG. 1.—Arrhenius plots for the decomposition of t-butyl hydroperoxide. Homogeneous reaction in unpacked vessel ⊙, in packed vessel ×. Heterogeneous reaction in unpacked vessel ⊕.

Ethyl hydroperoxide behaved similarly to isopropyl hydroperoxide (fig. 3). The rate of the homogeneous reactions were almost identical for the two peroxides. Heterogeneous reaction was slightly slower with ethyl hydroperoxide. The products were again complex, and similar to those reported by Harris.[5]

The rates of homogeneous decomposition of the three peroxides fall in the order $k_{\text{TBHP}} > k_{\text{IPHP}} \geqslant k_{\text{EHP}}$. This order is the opposite of that found for the dialkyl peroxides where di-t-butyl peroxide is the most stable of the simpler members. The differences in either series are not, however, large. Although the Arrhenius parameters for the homogeneous decomposition of the two types of peroxide (table 1) show considerable variations, the values of the rate constants over the experimental ranges fall within a factor of 3. In order to compare the two groups of peroxides it is therefore better to take average activation energies and average values of log A for each type than to compare individual values. The " mean

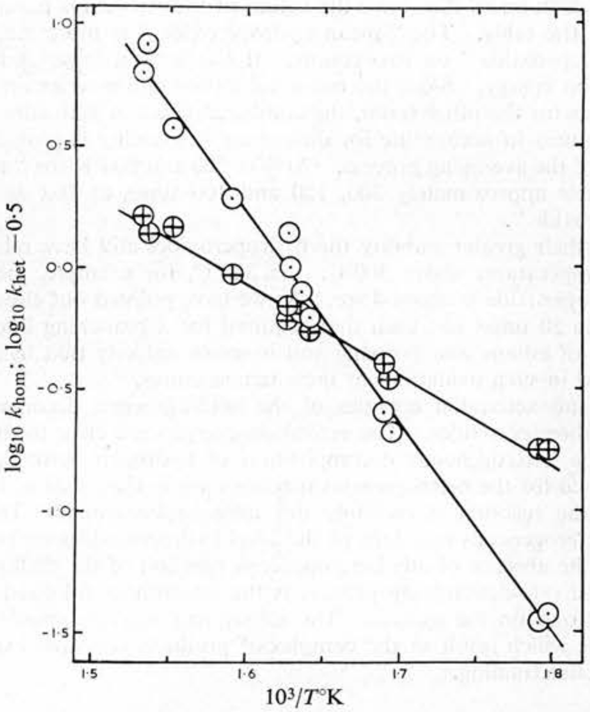

FIG. 2.—Arrhenius plots for the homogeneous ⊙ and heterogeneous ⊕ decomposition of isopropyl hydroperoxide in unpacked reaction vessel.

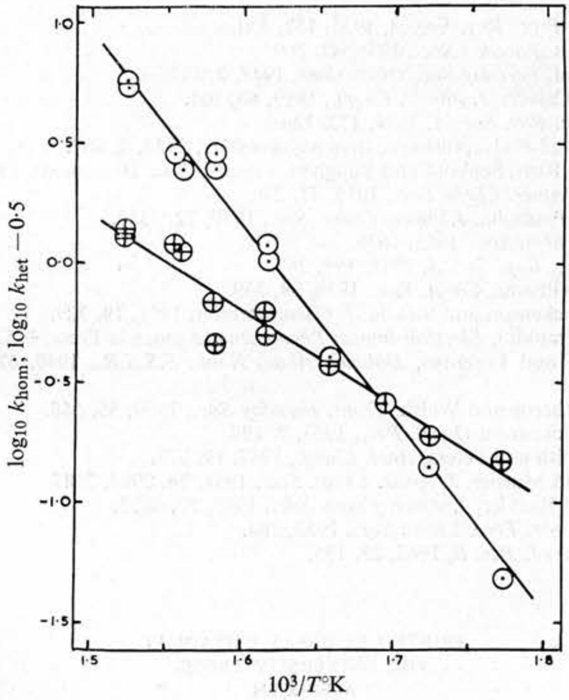

FIG. 3.—Arrhenius plots for the homogeneous ⊙ and heterogeneous ⊕ decomposition of ethyl hydroperoxide in unpacked reaction vessel.

peroxides " of each series then have the values of the Arrhenius parameters given at the foot of the table. The " mean hydroperoxide " is more stable than the " mean dialkyl peroxide " on two counts. It has both a lower *A* factor and a higher activation energy. Since the mean values for either series are outside the spread of values for the other series, the combined effect of activation energy and *A* factor differences in accounting for differences in stability is probably real and not the result of the averaging process. At 400, 500 and 600°K the " mean dialkyl peroxide " reacts approximately 300, 150 and 100 times as fast as the " mean alkyl hydroperoxide ".

In spite of their greater stability the hydroperoxides still have relatively short lifetimes at temperatures above 300°C. At 320°C, for example, the lifetime of the mean hydroperoxide is about 4 sec. As we have pointed out elsewhere,[21] this lifetime is some 20 times less than that required for a branching intermediate in the oxidations of ethane and propane and it seems unlikely that hydroperoxides are ever formed in such oxidations at these temperatures.

The rates and activation energies of the heterogeneous decompositions are similar for all three peroxides. The activation energies are close to that found by Giguere for the heterogeneous decomposition of hydrogen peroxide.[22] The *A* factors calculated for the heterogeneous reactions are in the range of 10^6-10^8 sec^{-1} showing that the reaction is certainly not diffusion-controlled. The similarity between the heterogeneous reactions of the alkyl hydroperoxides and of hydrogen peroxide, and the absence of any heterogeneous reaction of the dialkyl peroxides, suggest that the rate-determining process is the attachment followed by reaction of the OOH group on the surface. The subsequent rearrangements of the rest of the molecule which result in the complex of products observed experimentally cannot be rate determining.

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The Role of Hydroperoxides in the Oxidation of Ethane and Propane at 320°C

By A. D. Kirk and J. H. Knox
(University of Edinburgh)

Hydroperoxides have often been postulated[1] as the degenerate branching intermediates in hydrocarbon oxidation up to 400°C but in spite of extensive efforts to identify them in oxidation products it is only recently that this has been convincingly achieved by Cartlidge and Tipper[2] who isolated heptyl hydroperoxide, amongst others, from the products of oxidation of heptane at 270°. There is therefore still some doubt as to whether hydroperoxides are of importance above 300°C.

The importance of any particular substance as a branching intermediate in an oxidation may be critically assessed by comparing its lifetime in the proposed branching reaction with the lifetime of the real branching agent as deduced from the oxidation kinetics. It has long been thought that the slow autocatalytic acceleration of the oxidation of the lower paraffins requires an intermediate with a lifetime of the order of a minute.[3] This has recently been confirmed by a more detailed analysis of the kinetics of the oxidations of ethane and propane[4] which led to values of 110 and 65 sec. respectively for the lifetimes of the intermediates therein. With these values in mind we have now measured the rates of homogeneous gas-phase decomposition of the hydroperoxides EtO·OH, Pr^{i}O·OH, and Bu^{t}O·OH between 270° and 380°: $\mathrm{RO{\cdot}OH} \rightarrow \mathrm{RO{\cdot}} + \mathrm{{\cdot}OH}$.

The rates of the reactions were obtained by using a benzene carrier technique very similar to the Szwarc toluene method.[5] A mixture of $\sim 2\%$ of the hydroperoxide in benzene at a total pressure of about 15 mm. Hg was passed through a heated tube. Only the hydroxyl radicals reacted with the benzene and they gave a quantitative yield of biphenyl. Thus the extent of the homogeneous reaction could be measured independently of the considerable heterogeneous reaction which also occurred (between 30 and 90% of the total reaction).

The Arrhenius parameters derived for the decompositions of the three peroxides are given in the Table. Their lifetimes at 318° and 270°, and the lifetimes of the branching intermediates in the oxidations of ethane and propane are also given. It is clear that the lifetimes of the peroxides are an order of magnitude smaller than the lifetimes of the branching intermediates in the oxidations.

Rate constants for $\mathrm{RO{\cdot}OH} = \mathrm{RO{\cdot}} + \mathrm{{\cdot}OH}$ at 280—380°: *lifetimes of peroxides and oxidation intermediates.*

Hydro-peroxide	$\log_{10} A$ (sec.$^{-1}$)	E (kcal. mole^{-1})	Lifetime (sec.) of RO·OH 318°	270°	Lifetime (sec.) of oxidn. intermeds. at 318°
Et	13·4	37·7	3·6	58	Ethane 110
Pr^i	14·5	40·7	3·8	71	Propane 65
Bu^t	13·7	37·8	2·0	32	Isobutane ?

The major conclusion from the results is that ethyl and isopropyl hydroperoxides are unimportant as branching agents in the oxidations of ethane and propane at 318°. In fact the evidence must be interpreted as showing that these peroxides are never formed at this temperature. If they were formed, the rate of branching would be much higher and the dependence of the net branching factor on hydrocarbon concentration much steeper than is observed. One would expect that with peroxide branching the transition from negligible reaction to rapid cool-flame reaction would be very sharp, with only a narrow intermediate zone of slow isothermal reaction. With ethane and propane this region of slow reaction at 320° is quite extensive and covers pressures differing by a factor of at least two.[4]

(*Received, October* 13*th*, 1959.)

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COMPETITIVE OXIDATIONS

PART 1.—ETHANE + PROPANE MIXTURES

COMPETITIVE OXIDATIONS

PART 1.—ETHANE + PROPANE MIXTURES

BY JOHN H. KNOX, ROBERT F. SMITH AND A. F. TROTMAN-DICKENSON
Chemistry Dept., The University, Edinburgh

Received 23rd December, 1957

When mixtures of ethane and propane react with oxygen the relative rate of disappearance of the two gases is 0·44 ± 0·03 : 1. This value is almost independent of temperature, composition and total pressure between 274° and 495°C. The chain propagation reactions in the oxidations of ethane and propane therefore have equal activation energies and the radicals formed in the two propagation reactions attack a given hydrocarbon (ethane or propane) at equal rates. It is probable that the same radical is involved in both oxidations throughout the whole range of temperature and that this radical reacts with low activation energy with both hydrocarbons.

The slow oxidation of hydrocarbons in the gas phase is believed to proceed by a degenerately branching free-radical chain mechanism. The products of the reaction chains, which are straight and of finite length, are normally molecules with no special reactivity but occasionally some reactive intermediates are also formed. These react after an interval, long in comparison with the lifetime of a straight chain, and initiate new chains. If each chain produces, on the average, sufficient branching intermediate to initiate more than one fresh chain, the reaction will accelerate exponentially.

A number of reaction schemes have been proposed to account for the main features of hydrocarbon oxidation,[1-4] but there is still little agreement as to either the basic chain propagating steps or the intermediate product responsible for branching. It was with a view to shedding light on the basic chain-propagating steps that the present work was carried out. Since the basic chain must be mainly responsible for the disappearance of hydrocarbon in the oxidation, the relative rates of the main propagating reactions in a mixed oxidation may be found either by measurement of the relative rates of disappearance of the two hydrocarbons or by measurement of the rates of appearance of characteristic products formed from them. The latter method has the disadvantage that it is not easy to select products that are truly characteristic of each hydrocarbon and which can provide an accurate measure of their disappearance. We have accordingly employed the former method. The relative rates of disappearance of the two hydrocarbons have been measured by analyzing the reaction products for ethane and propane using gas chromatography.

In the oxidation of the pure hydrocarbons R_aH and R_bH, the chain propagating reactions may be writen:

$$X_1 + R_aH = X_1H + R_a, \qquad k_{1a}$$
$$R_a \rightarrow X_1,$$
$$X_2 + R_bH = X_2H + R_b, \qquad k_{2b}$$
$$R_b \rightarrow X_2,$$

where X_1 and X_2 are oxygenated radicals such as OH, HO_2, RO or ROO. When a mixture of two hydrocarbons is oxidized two further propagating reactions will occur:

$$X_2 + R_aH = X_2H + R_a, \qquad k_{2a}$$
$$X_1 + R_bH = X_1H + R_b. \qquad k_{1b}$$

If we define the overall rate constants for the removal of the two hydrocarbons as k_a and k_b, then the overall ratio k_a/k_b can be obtained from the analytical data using the expression,

$$\frac{k_a}{k_b}=\frac{\log\{[\mathrm{R_aH}]_{\mathrm{initial}}/[\mathrm{R_aH}]_{\mathrm{final}}\}}{\log\{[\mathrm{R_bH}]_{\mathrm{initial}}/[\mathrm{R_bH}]_{\mathrm{final}}\}}.$$

In addition

$$\frac{k_a}{k_b}=\frac{k_{1a}[\mathrm{X_1}]+k_{2a}[\mathrm{X_2}]}{k_{1b}[\mathrm{X_1}]+k_{2b}[\mathrm{X_2}]},$$

and if the chains are long it can readily be shown by the stationary-state method that

$$\frac{k_a}{k_b}=\frac{k_{2a}}{k_{1b}}\left\{\frac{k_{1a}[\mathrm{R_aH}]+k_{1b}[\mathrm{R_bH}]}{k_{2a}[\mathrm{R_aH}]+k_{2b}[\mathrm{R_bH}]}\right\}.$$

The experimental ratio k_a/k_b will in general depend upon the ratio $[\mathrm{R_aH}]/\mathrm{R_bH}]$ but should not depend upon the total pressure of reactants or upon the total hydrocarbon to oxygen ratio. If, however, $k_{1a}/k_{2a}=k_{1b}/k_{2b}$, and in particular if $\mathrm{X_1}$ and $\mathrm{X_2}$ are identical so that $k_{1a}\equiv k_{2a}$ and $k_{1b}\equiv k_{2\mathrm{b}}$, the ratio k_a/k_b will be independent of the ratio of the concentrations of the two hydrocarbons.

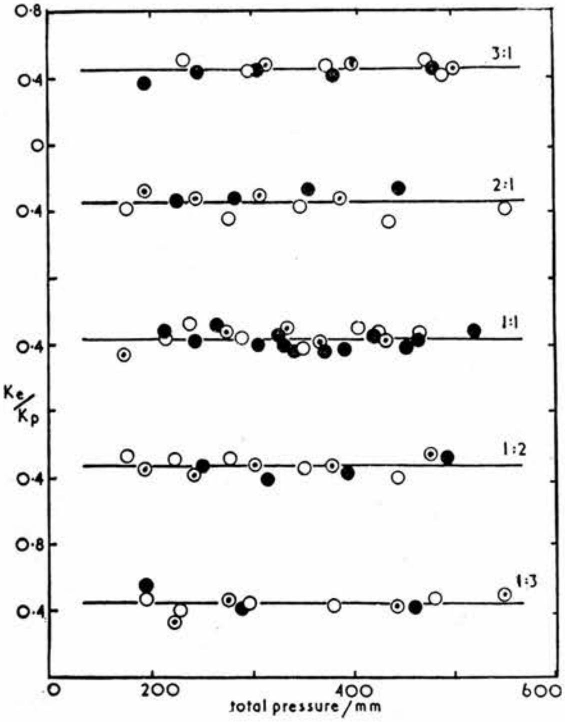

FIG. 1.—Variation of k_e/k_p with total pressure at 310°C. Initial ethane : propane ratios as given for each line. Hydrocarbon : oxygen ratios: ● 4 : 1, ○ 2 : 1, ⊙ 4 : 3.

Fig. 1 shows that variation of total pressure and of hydrocarbon/oxygen ratio has indeed no effect upon the ratio k_e/k_p for ethane/propane ratios from 3/1 to 1/3. In fig. 2 the average values obtained from each line in fig. 1 are plotted against the ethane propane ratio along with similar results for the six other temperatures investigated. In this figure and in fig. 3 the sizes of the points give the standard deviation of the averaged results. The absence of any dependence of k_e/k_p upon the composition of the mixture is clearly demonstrated. It therefore appears that $k_{1e}\mid k_{2e}=k_{1p}\mid k_{2p}$ for ethane and propane between 274 and 495°C.

The dependence of k_e/k_p upon temperature is shown in fig. 3 where the mean values of k_e/k_p taken from fig. 2 are plotted against temperature (the numbers beside each point give the number of values averaged for the particular point). The variation with temperature is very slight and the overall activation energy difference is $E_e - E_p = -300 \pm 46$ cal/mole. At the lower temperatures there appears to be a slight increase in the ratio k_e/k_p with a weak maximum at about 340°C. Although this increase and subsequent decrease occur at a temperature where one normally expects to observe similar effects in the overall rates of slow oxidation of ethane and propane [5, 6] the effect in the present case is so slight that it is probably due to experimental error. The highest activation energy which can reasonably be attached to the results between 274 and 340°C is $E_e - E_p = 1000$ cal/mole. The mean value of k_e/k_p between 274 and 495°C is

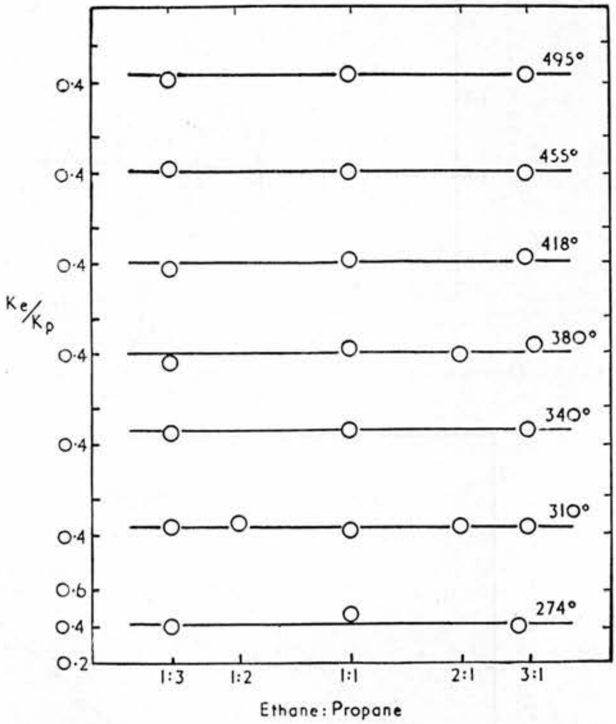

FIG. 2.—Mean values of k_e/k_p for various initial ratios of the hydrocarbons at the temperatures indicated. Each point is the mean of values obtained for different total pressures and ratios of hydrocarbon : oxygen.

$$k_e/k_p = 0{\cdot}44 \pm 0{\cdot}03.$$

If the primary C — H bonds in propane and ethane are attacked at exactly the same rate, as seems to be roughly the case for attack by chlorine atoms [7] and methyl radicals,[8] the relative rates of attack on the secondary and primary bonds in propane are given by

$$k_{\text{sec}}/k_{\text{pri}} = 3{\cdot}8.$$

In view of the approximation involved this result is in reasonable agreement with that of Burt, Ebeid and Minkoff [9] who found that the relative rates of attack of radicals at the primary and secondary bonds in the oxidation of propane at 360-420°C were given by

$$k_{\text{sec}}/k_{\text{pri}} \geqslant 1{\cdot}9.$$

Their results were obtained by infra-red analysis of the products from oxidation of $CH_3CHD \, . \, CH_3$ for OH and OD. They may be questioned on the grounds that all OH and OD may not necessarily have come from the *initial* removal by radicals of H and D respectively.

The rather small difference in the reactivity of propane and ethane in competitive oxidation contrasts with the much greater difference in overall reactivity when they are oxidized separately. Fig. 4 shows the overall rates of oxidation of ethane and propane over a range of pressure at 455°C. Propane reacts approximately 16 times faster than ethane. At lower temperatures a similar difference in reactivity is noted. It is clear that the differences in overall rates of oxidation of ethane and propane are due not to differences in the rates of chain propagation but to differences in the rates of other important reactions such as branching and the formation of the branching intermediate.

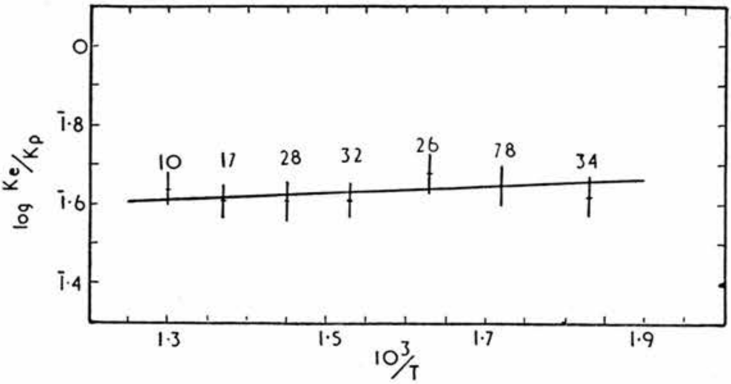

FIG. 3.—Dependence of k_e/k_p on temperature; the superscripts indicate the number of runs averaged to obtain each point.

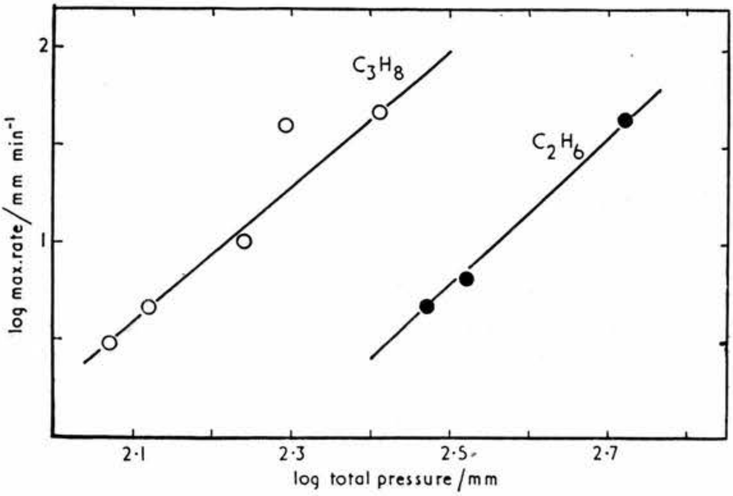

FIG. 4.—Rates of oxidation of ethane (●) and propane (○) at 455°C; hydrocarbon : oxygen, 2 : 1.

The smallness of the activation energy difference in the competitive oxidation suggests that the radicals attacking the hydrocarbon are extremely reactive and that the absolute values of their activation energies are probably low. This conclusion is supported by the figures in table 1 where the activation energy differences ΔE for reactions of a number of radicals with ethane (E_e) and propane (E_p) are tabulated. For the radicals so far investigated E_e appears to be some five times ΔE. If this holds for the propagation in hydrocarbon oxidation the activation energy of the propagation steps for ethane and propane are probably not more than 1000 cal/mole. It may also be noted that for chlorine atom attack on ethane and propane the relative rate constants at 380°C are $k_e/k_p = 0{\cdot}47$,[7] a value close to that found in the competitive oxidation. The radical involved in the oxidation therefore appears to be similar in its reactivity to a chlorine atom; both the energy and entropy of activation of the two reactions must be similar.

TABLE 1

radical	E_e cal/mole	$\Delta E = E_e - E_p$ cal/mole	$\Delta E/E_e$	ref.
oxidation		-300 ± 46		
Cl atoms	1,050	190	0·18	7
CF_3	7,500	1,300	0·2	10
CH_3	10,500	1,900	0·2	8

Only ΔE for chlorine atoms is of high precision. Errors of up to 500 cal/mole are probable in the other values given.

The oxidation of both ethane and propane are probably propagated either by the same radical over the whole temperature range or, if different radicals operate at different temperatures, by radicals having very similar properties. In the temperature range below 400°C both OH and peroxy radicals have been suggested as chain carriers. The evidence presented above supports OH rather than the peroxy radical. The OH radical is small and probably has properties similar to the chlorine atom. Its reactions with hydrocarbons are considerably exothermic, while those of ROO are likely to be endothermic. In addition, liquid-phase oxidations involving ROO are known to have activation energies of the order of 6-13 kcal/mole.[11] The radicals C_2H_5OO and C_3H_7OO might furthermore be expected to react at different rates with a given hydrocarbon. This would result in a composition dependence of k_e/k_p which is not observed.

In oxidations at temperatures above 400°C there is now considerable independent evidence that the chain carrier is an HO_2 radical,[3, 4] and indeed an HO_2 chain has been proposed for the oxidation of ethyl alcohol at a temperature as low as 270°C.[12] The chief evidence for HO_2 chains in these oxidations is the formation of propylene without hydrogen, as the major initial product of the oxidation of propane above 400°C, and the formation of acetaldehyde and hydrogen peroxide in equal amounts as the *only* products in the early stages of the oxidation of ethyl alcohol. The only acceptable explanation of these findings is that the following reactions occur:

$$C_3H_7 + O_2 = C_3H_6 + HO_2,$$
$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2,$$

and

$$C_2H_5O + O_2 = CH_3CHO + HO_2,$$
$$C_2H_5OH + HO_2 = C_2H_5O + H_2O_2.$$

Recently Foner and Hudson [13] have reported that $D[\text{H—OOH}]$ in hydrogen peroxide is $89{\cdot}5 \pm 3$ kcal/mole. On this basis the reactions of HO_2 with ethane and propane would be several kcal/mole endothermic and the difference between the activation energies of attack on ethane and propane should be at least 3 kcal/mole. The earlier value of $D[\text{H—OOH}] = 102$ kcal/mole given by Evans, Hush and Uri [14] would, however, make the reactions of HO_2 with hydrocarbons exothermic, and a low activation energy difference would be possible. The earlier value is thus in better agreement with the present work and would also more readily account for the formation of acetaldehyde and hydrogen peroxide in the low-temperature oxidation of ethyl alcohol.

The unequivocal determination of the heat of formation of HO_2 is thus clearly of the greatest importance for theories of hydrocarbon combustion. If the high heat of formation is in fact correct, the present results point strongly to the conclusion that the HO_2 radical is the main chain propagator in hydrocarbon oxidation at all temperatures between 274° and 495°C.

EXPERIMENTAL

MATERIALS

Ethane and propane were obtained from cylinders and after thorough degassing were stored in 2-l. bulbs. Analysis of these hydrocarbons showed them to contain the following impurities:

ethane: 2 % ethylene;
propane: 0·5 % ethane; 1 % *iso*butane.

As these impurities can have no effect on the results reported it was not considered necessary to purify the gases further. Oxygen was obtained from B.O.G. cylinders. Acetaldehyde used as an initiator in some runs was A.R.

APPARATUS AND ANALYSIS

The apparatus was a conventional static high-vacuum system. Reaction mixtures were made up in a mixing vessel, the required quantities of each gas being measured out from a constant volume gas burette. The reactions were carried out in either a 100 ml or a 35 ml reaction vessel. The former was used at the higher temperatures where only low pressures of reactants could be used. The reaction vessel was housed in an electric furnace thermostatted to ± 1°C; the temperature along the length of the reaction vessel was constant to 1°C.

The reactions were followed by measurement of the pressure rise on a mercury manometer and samples for analysis were normally withdrawn when some 90 % of reaction had occurred. It was, however, found that k_e/k_p did not depend upon the extent of reaction when the sample was taken for analysis. In some of the runs, particularly at the lower temperatures, 1-2 % of acetaldehyde was added to the reaction mixture as an initiator. This addition was shown to have no effect on the observed rate constant ratio.

Analysis was carried out entirely by gas chromatography using the Janak technique.[15] The total contents of the reaction vessel were pumped through a W-tube cooled in liquid nitrogen and the condensate was then analyzed for ethane and propane. A column packed with 32-52 mesh activated alumina, 250 cm in length and 6 mm in diameter was used for the separation; the column temperature was 20°C. In the Janak method carbon dioxide is used as carrier gas and after emerging from the column it is completely absorbed in 50 % w/w potassium hydroxide solution. Insoluble gases such as the lower hydrocarbons can then be collected in a gas burette; oxygenated organic products are absorbed by the alkali and do not interfere. A plot of gas volume against time then gives a step-like chromatogram. Using this method volumes of individual gases may be measured to ± 0·02 ml. In the present work standardization runs were carried out at each temperature using the normal procedure for an oxidation but omitting the oxygen from the original mixture. In this way systematic errors of calibration of the apparatus were eliminated and it is estimated that the accuracy of the analytical results was about 1 %.

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22

RATE CONSTANTS OF ELEMENTARY REACTIONS IN HYDROCARBON OXIDATION—COMPETITIVE OXIDATION OF LOWER HYDROCARBONS

J. H. KNOX, R. F. SMITH and A. F. TROTMAN-DICKENSON

Although there are considerable differences between the various current theories of the low temperature oxidation of hydrocarbons, they are in agreement in assigning the main consumption of hydrocarbons to the chain-propagating steps. The present work was carried out to throw light on the nature of these steps. As there did not appear to be any way of measuring the rates of these reactions directly, a competitive method of measuring their relative rates was employed. This could be done either by measuring the relative rates of disappearance of the two hydrocarbons from a mixture with oxygen or by the measurement of the rates of appearance of characteristic products formed from them. The latter method has the disadvantage that it is not easy to select products that are truly characteristic of each hydrocarbon and which may be presumed to provide an accurate measure of the rates of reaction. This presumption can only be accepted if it is backed up by a full analytical study of the products. We have accordingly employed the former and more direct method.

In the oxidation of the pure hydrocarbons R_1H and R_2H, the chain-propagating reactions may be written:

$$X_1 + R_1H = X_1H + R_1 \; k_{11}$$

$$X_2 + R_2H = X_2H + R_2 \; k_{22}$$

where X_1 and X_2 are oxygenated radicals such as OH, HO_2, RO or RO_2. When a mixture of the two hydrocarbons is oxidized, two further propagating reactions will occur:

$$X_2 + R_1H = X_2H + R_1 \; k_{12}$$

$$X_1 + R_2H = X_1H + R_2 \; k_{21}$$

If we define the overall rate constants for the removal of the two hydrocarbons as k_1 and k_2, then the ratio k_1/k_2 can be obtained from analysis of the amounts of each hydrocarbon present at the beginning and end of the reaction from the relation

$$\frac{k_1}{k_2} = \frac{\log\left([R_1H]_{\text{initial}}/[R_1H]\right)_{\text{final}}}{\log\left([R_2H]_{\text{initial}}/[R_2H]\right)_{\text{final}}}$$

If $k_{11} \neq k_{12}$ and $k_{22} \neq k_{21}$, the experimental value of k_1/k_2 will depend upon the composition of the mixture.

In the present experiments known amounts of two hydrocarbons were mixed with oxygen in the reaction vessel. After a convenient time, which was usually close to the time required for the increase in pressure to cease, the mixture was analysed by gas chromatography. An alumina column was used with carbon dioxide as the carrier gas. The gases were estimated by the Janak technique. Ethane, propane, *iso*butane, ethylene and propylene were all cleanly separated.

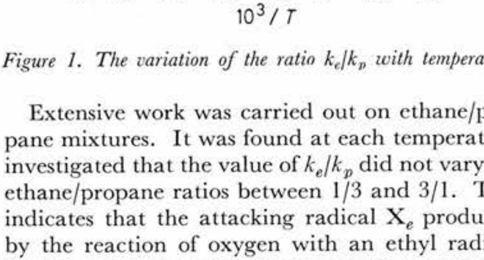

Figure 1. The variation of the ratio k_e/k_p with temperature

Extensive work was carried out on ethane/propane mixtures. It was found at each temperature investigated that the value of k_e/k_p did not vary for ethane/propane ratios between 1/3 and 3/1. This indicates that the attacking radical X_e produced by the reaction of oxygen with an ethyl radical has the same reactivity and is therefore probably the same substance as the radical X_p produced from propyl. k_e/k_p was also found to be independent of the hydrocarbon/oxygen ratio between 5 and 1·3 and of the total pressure in the system between 100 and 600 mm. The dependence of k_e/k_p upon temperature is shown in *Figure 1* (the numbers beside each point give the number of values averaged to obtain the plotted point).

Similar though less extensive experiments were carried out with propane/*iso*butane mixtures at 310° and 420°. Again no change in k_b/k_p was found for variations in the *iso*butane/propane ratio from 3/1 to 1/3 or for hydrocarbon/oxygen ratios between 2 and 4 to 1.

The remarkable constancy of the ratios

$$k_p/k_e = 2{\cdot}27 \pm 0{\cdot}05 \quad \text{and} \quad k_b/k_p = 1{\cdot}5$$

strongly indicates that the same radical X carries the chains in all three oxidations. The results show that the differences in the activation energies for attack on the three hydrocarbons are very small indeed; the slope of the line in the Arrhenius plot shown in *Figure 1* corresponds to $E_e - E_p = -300 \pm 46$ cal mole^{-1}. It is reasonable to conclude from this small difference that the absolute activation energies must also be very small, probably not more than two or three kcal mole^{-1} at the most.

If the assumption is made that all primary hydrogen atoms react with X at the same rate, it can readily be shown that the values of $k_{\text{primary}} : k_{\text{secondary}} : k_{\text{tertiary}}$ are in the ratio 1 : 3·8 : 11. Since the primary hydrogens in propane and *iso*-butane are probably more reactive than those in ethane, these figures probably overestimate the differences in the reactivities.

Recently, two papers have been published[1,2] in which the relative rates of attack of X on the different positions in propane and 2-methylpentane have been estimated. The estimates are only reliable if the assumed reaction schemes are correct in every detail. The authors recognize that both types of scheme appear doubtful on a number of counts and that the results cannot be accepted without reserve until full detailed analyses of the products have been made.

The comparatively small differences in the reactivities of the hydrocarbons and the apparent absence of activation energy differences make it extremely unlikely that X is a radical of the type ROO. Work on autoxidations in solution indicates that these radicals are markedly selective and react with activation energies of 6 or more kcal mole^{-1} even with olefins. Their reactions with alkanes would probably be considerably endothermic. Furthermore it might be expected that C_2H_5OO would have a detectably different reactivity from C_3H_7OO. Much the same type of argument serves to rule out alkoxy radicals.

The highly reactive radical OH might be expected to have the attributes of X, but it is difficult to explain the results on several oxidations, particularly those at high temperatures, on the assumption that OH is the main chain carrier, whereas an HO_2 chain fits the facts most satisfactorily. For instance, it explains the formation of propylene without hydrogen as the major product of the oxidation of propane above 400°C, and the formation of acetaldehyde and hydrogen peroxide in equal quantities as the only products in the oxidation of ethyl alcohol[3,4] as low as 300°C. However, the presently accepted value of 89·5 ± 3 kcal mole^{-1} for D(HOO–H) makes it very difficult to accept it as the universal chain carrier. It seems that the problem of the nature of X will only be settled by the study of further hydrocarbons and the acquisition of further knowledge of the properties of the different kinds of oxygenated radicals.

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169. *Competitive Oxidations. Part II.* The Lower Alkanes and Cyclopropane.*

By W. E. Falconer, J. H. Knox, and A. F. Trotman-Dickenson.

The oxidation of binary mixtures containing methane, ethane, propane, cyclopropane, isobutane, and neopentane has been studied. The relative rates of removal of the hydrocarbons have been measured by gas-chromatographic. The relative reactivites of different C–H bonds have been derived. Previous work is discussed, and the nature of the chain-carrying radicals considered.

Studies in oxidation of hydrocarbons ranging from the measurement of knock ratings to that of the rates of slow oxidation emphasise the important effect of structure. Cullis, Hinshelwood, and Mulcahy [1] measured such differences roughly by determining the rates of pressure rise in the oxidation of pairs of hydrocarbons under the same conditions. They recognised that differences in overall reactivity probably resulted from the combined effects of several processes, such as chain initiation, chain propagation, and chain branching. The detailed investigation of these component reactions is clearly important in elucidating the general mechanism of oxidation of hydrocarbons. In this work we have attempted to measure the relative rates of the chain-propagating reactions for a number of hydrocarbons.

The first products of oxidation of a hydrocarbon are likely to be alkyl radicals containing the same number of carbon atoms as the parent hydrocarbon. For most hydrocarbons there will be more than one such radical. These radicals can either decompose or react with oxygen, and their rates of formation can be found by determining the yields of products which are characteristic of the radicals initially formed. This approach has been used by Burt, Cullis, Larsen, and Minkoff,[2] and by Cullis, Hardy, and Turner.[3]

The former measured the relative yields of OH and OD in the products from the oxidation of a number of deuteropropanes at 423°, using infrared spectroscopy. They found that the chance of a given secondary hydrogen atom's appearing in the products as OH was about twice that of a given primary hydrogen atom so appearing. They argued that initial attack at a given secondary C–H bond was twice as fast as initial attack at a primary C–H bond. Since water and hydrogen peroxide are the main hydroxyl-containing products their conclusion requires that both the hydrogen atoms in these products arise from the initial removal of hydrogen from propane. It is impossible to devise a plausible mechanism for which this is true. If one accepts the HO_2 chain mechanism for the high-temperature oxidation of propane,[4,5] the water and hydrogen peroxide should contain equal quantities of primary and secondary hydrogen atoms: the chance that a given secondary atom appears in the water is thus three times the chance that a given primary hydrogen atom so appears. The value obtained by Burt *et al.* is not far from this, but it indicates that considerable secondary oxidation must have taken place and that, in the later stages, oxidation to water of the hydrogen initially on primary carbon atoms predominates. The results give no information about the relative rates of initial attack at different positions in the propane molecule.

Cullis, Hardy, and Turner [3] determined the points of origin of the carbon in carbon monoxide and carbonyl groups formed in the oxidation of ^{14}C-labelled 2-methylpentanes (isohexane) at 242° and assumed that the relative yields gave the relative rates of initial

* Part I, Knox, Smith, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509.

attack at different points in isohexane. They assumed that all alkyl radicals initially formed gave rise to the appropriate hydroperoxide, and that in the subsequent reactions of the hydroperoxide the C–O bond remained unbroken. They also assumed that primary and secondary hydroperoxides gave carbon monoxide in the same proportion and that the tertiary hydroperoxide gave equal molar yield of (carbon monoxide + carbonyl compounds). Kirk and Knox [6] have shown that carbon monoxide arises in roughly equal yields (about 10%) on heterogeneous decomposition of ethyl, isopropyl, and t-butyl hydroperoxides. Carbonyl compounds are formed as a result of the homogeneous decomposition from pyrolysis of alkoxy-radicals. There is no reason to believe that the carbon in the carbon monoxide was that originally attached to the oxygen in the hydroperoxide, and one cannot add the yield of carbon monoxide to the yield of carbonyl to obtain the original amount of hydroperoxide. While it is conceivable that the yields of carbon monoxide may give a measure of the initial attack on the isohexane molecule, we do not as yet known enough about the mechanism of the oxidation at 242° to justify this conclusion.

There is therefore no reliable information about the relative rates of initial attack at different points in a given hydrocarbon undergoing oxidation in the gas phase.

Knox, Smith, and Trotman-Dickenson [7] estimated the rates of attack at different points in hydrocarbons from measurements of the rates of consumption of hydrocarbons in binary mixtures.

If two hydrocarbons R^1H and R^2H form alkyl radicals R^1 and R^2, and if these radicals eventually produce oxygenated radicals X^1 and X^2 which then attack the hydrocarbons, we can write four propagating reactions which remove the hydrocarbons:

$$\begin{aligned} X^1 + R^1H &= X^1H + R^1 \qquad k_{11} \\ X^2 + R^2H &= X^2H + R^2 \qquad k_{22} \\ X^2 + R^1H &= X^2H + R^1 \qquad k_{12} \\ X^1 + R^2H &= X^1H + R^2 \qquad k_{21} \end{aligned}$$

Experimentally we measure the relative rates of removal of the two hydrocarbons and obtain an experimental rate constant ratio given by

$$\frac{k_1}{k_2} = \frac{\log \{[R^1H]_{\text{initial}}/[R^1H]_{\text{final}}\}}{\log \{[R^2H]_{\text{initial}}/[R^2H]_{\text{final}}\}}$$

If $k_{11} \neq k_{12}$ and $k_{22} \neq k_{21}$ the experimental ratio k_1/k_2 will depend upon the composition of the mixture. The original work on propane–ethane and propane–isobutane mixtures showed that k_1/k_2 was independent of $[R^1H]/[R^2H]$, independent of $[O_2]/[\text{total RH}]$ with less than 33% of oxygen, and independent of temperature from 274° to 495°. The present work, which uses the same experimental technique, has substantiated the findings of the earlier work but has revealed a dependence of k_1/k_2 upon oxygen concentration in mixtures containing more than 33% of oxygen.

RESULTS

Methane–Ethane.—The oxidation of methane–ethane mixtures was studied only at 495° since the rate of oxidation at lower temperatures was very low at accessible pressures. The study was complicated because methane is an important product of the oxidation of ethane, and in certain instances so much methane was thus formed that the methane content of the mixture actually increased. In order to minimise the effect of the methane formed from ethane, all mixtures studied contained at least as much methane as ethane. Studies of the oxidation of ethane alone showed that with oxygen pressures below about 100 mm. the methane yield was 16 ± 2% of the ethane initially present (see Table 1). At higher oxygen pressures, the yield of methane was dependent on pressure in mixtures of given $[O_2]/[C_2H_6]$ ratio falling to a minimum value of about 2% at high pressures. Addition of nitrogen had no significant effect. In view of this, experiments were carried out only under conditions where a 16% yield of methane was to be expected. An appropriate correction to the methane concentration was made in calculating k(methane)/k(ethane). The reproducibility of this ratio at constant oxygen concentration when $[CH_4]/[C_2H_6]$ varies between 4 : 1 and 1 : 1 is evidence for the validity of the practice.

The relative rate of consumption of methane and ethane under these conditions is strongly dependent upon $[O_2]/[RH]$, but independent of the total pressure in a mixture of given composition (see Table 2 and Fig. 1).

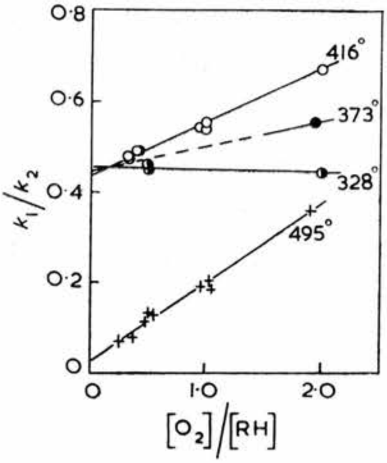
FIG. 1. *Variation of the relative rates of oxidation with* $[O_2]/[RH]$. k(*cyclopropane*)/k(*ethane*) (○, ●, ◑); k(*methane*)/k(*ethane*) (+).

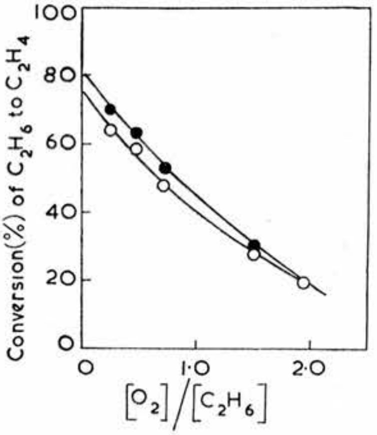
FIG. 2. *Dependence of the conversion of ethane into ethylene at 495° upon* $[O_2]/[C_2H_6]$. ○ *Average values for* $[O_2]$ = 100 *mm.* ● *Values for* $[O_2]$ = 0 (*extrapolated*).

Preliminary study of the oxidation of ethane alone showed that ethylene was a major product. The conversion of ethane into ethylene was almost independent of pressure for a given value of $[O_2]/[C_2H_6]$ with $[O_2]$ below 100 mm., but fell at higher oxygen pressures. The

TABLE 1. *Oxidation of ethane at* 495°.

No. of expts.	$\frac{[O_2]}{[C_2H_6]}$	$\frac{[N_2]}{\text{total press.}}$	Total press. (mm.)	$\frac{C_2H_4}{C_2H_6 \text{ (cons.)}}$ *	$\frac{100CH_4}{C_2H_6 \text{ (cons.)}}$ *
5	0·25	Nil	100—360	0·64	15 ± 2
5	0·48	0·32	110—400	0·59	17 ± 2
5	0·72	Nil	105—300	0·48	18 ± 2
1	1·50	,,	108	0·28	15·6
1	,,	,,	149	—	15·4
1	,,	,,	165	0·26	15·2
1	,,	,,	179	0·13	7·5 †
1	,,	,,	201	0·03	6·6 †
1	,,	,,	250	0·01	1·7 †
1	,,	,,	288	0·01	1·5 †
1	1·93	0·33	96	0·20	15·0
1	,,	,,	153	0·20	13·2
1	,,	,,	204	0·20	11·3
1	,,	,,	272	0·00	1·9 †
1	,,	,,	355	0·01	0·4 †

* C_2H_6 (cons.) is the amount of ethane consumed in a run.

† These values are not included in the average value used as a correction factor in calculating k(methane)/k(ethane).

TABLE 2. *Oxidation of methane–ethane mixtures at* 495°.

No. of expts.	Press. range (mm.)	$\frac{[CH_4]}{[C_2H_6]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(CH_4)}{k(C_2H_6)}$	No. of expts.	Press. range (mm.)	$\frac{[CH_4]}{[C_2H_6]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(CH_4)}{k(C_2H_6)}$
4	188—363	2·0	0·26	0·07	2	187—327	2·0	0·96	0·19
5	211—353	2·0	0·38	0·08	3	237—318	4·0	1·03	0·20
6	111—352	2·0	0·49	0·12	4	153—290	2·0	1·05	0·19
3	255—339	4·0	0·50	0·13	3	203—303	2·0	1·90	0·36
6	133—422	1·0	0·55	0·13					

variation of the low-pressure conversion into ethylene with $[O_2]/[C_2H_6]$ is shown in Fig. 2. Extrapolation to zero $[O_2]/[C_2H_6]$ shows that in oxygen-weak mixtures about 80% of the ethane removed is converted into ethylene. This value is in general agreement with the known yields of olefins obtained in other high-temperature oxidations (*e.g.*, of propane; Satterfield and Wilson,[5] Falconer and Knox [4]). It also agrees with a figure obtained by Knox and Wells [8] for the initial conversion of ethane into ethylene at 360°. When $[O_2]$ exceeded 100 mm., the conversion into ethylene fell sharply with pressure. The ethylene yield was low when the amount of residual methane was also low.

Cyclopropane–Ethane.—The oxidation of this mixture is complicated by the possible isomerisation of cyclopropane to propene at higher temperatures. Below 416° less than 1% of the cyclopropane isomerised during a run. The relative rates of consumption were independent of $[O_2]/[RH]$ at 328° but increased markedly at 416° (Table 3, Fig. 1). The value (0·45) of k(cyclopropane)/k(ethane) at zero $[O_2]/[RH]$ is independent of temperature from 328° to 416°.

TABLE 3. *Oxidation of cyclopropane–ethane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_3H_6]}{[C_2H_6]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_3H_6)}{k(C_2H_6)}$
3	328°	200—390	2·0	0·49	0·46
8	328	104—360	0·5	0·50	0·45
9	328	110—442	1·0	2·00	0·44
3	373	176—245	2·0	1·96	0·55
4	416	98—355	0·33	0·33	0·48
5	416	85—293	3·0	0·35	0·47
8	416°	79—403	3·0	0·50	0·49
4	416	114—405	0·33	0·51	0·49
2	416	188—325	1·0	0·95	0·54
5	416	89—430	3·0	1·00	0·54
7	416	85—437	0·33	1·00	0·55
6	416	260—456	1·0	2·00	0·67

TABLE 4. *Oxidation of ethane–neopentane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_2H_6]}{[C_5H_{12}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_2H_6)}{k(C_5H_{12})}$
3	328°	230—320	1·0	0·33	0·53
4	328	180—330	2·0	0·64	0·51
5	328	245—390	2·0	1·50	0·54
3	328	270—405	2·0	2·96	0·54
5	421	180—330	2·0	0·25	0·47
4	421	205—320	0·5	0·25	0·48
6	421	160—300	1·0	0·50	0·48
7	421	170—405	3·0	0·50	0·49
5	421	130—380	0·5	0·50	0·48
5	421	200—400	2·0	0·82	0·51
5	421°	185—425	2·0	1·22	0·54
4	421	210—310	0·5	1·26	0·53
4	421	180—340	2·0	2·00	0·59
5	421	250—390	2·0	2·92	0·73
3	495	210—370	2·0	0·25	0·40
3	495	160—315	0·5	0·50	0·46
3	495	225—365	2·0	0·50	0·43
3	495	175—290	2·0	1·00	0·51
3	495	225—290	2·0	2·06	0·66

Ethylene was again a major product. The ethylene conversions for $[O_2]/[RH] = 0$ rose from about 60% at 328° to nearly 100% at 416°.

Ethane–Neopentane.—Neopentane is a particularly interesting hydrocarbon from the point of view of oxidation since no pentene can be formed from it by an HO_2 radical chain. Oxidation of neopentane might therefore involve radicals different from those taking part in the oxidations of other hydrocarbons, and there might be a strong dependence of the relative rates of removal on [Neopentane]/[Ethane]. Variation of this ratio over a six-fold range at 421° (Table 4) showed that this is not the case. The rate of removal of ethane relative to neopentane is independent of $[O_2]/[RH]$ at the lowest temperature (328°) but increases with $[O_2]/[RH]$ at higher temperatures (Fig. 3). Whereas in the oxidations of methane–ethane and cyclopropane–ethane mixtures the ethane becomes relatively less reactive as $[O_2]/[RH]$ is increased, it becomes relatively more reactive in ethane–neopentane mixtures. For $[O_2]/[RH] = 0$, the relative rates of removal are given by:

$$k(\text{ethane})/k(\text{neopentane}) = 0{\cdot}14 \exp\,(1600/\boldsymbol{R}T)$$

A brief study of the oxidation of neopentane alone at 495° showed that although no pentene was formed, isobutene was a major product. It is presumably formed by the pyrolysis of the neopentyl radical: $\cdot CH_2\cdot CMe_3 \longrightarrow CH_2{:}CMe_2 + Me\cdot$. In the competitive oxidations, the proportion of neopentane converted into isobutene increases with temperature, probably because the decomposition of the neopentyl radical has a higher activation energy than its oxidation.

Neopentane–Isobutane.—Only 1 : 1 mixtures were investigated (Table 5). At 326° there was no dependence upon $[O_2]/[RH]$, but at higher temperatures the neopentane became relatively more reactive as $[O_2]/[RH]$ was increased (Fig. 3). For $[O_2]/[RH] = 0$, the relative rates of oxidation are given by:

$$k(\text{neopentane})/k(\text{isobutane}) = 0{\cdot}26 \exp(1000/\boldsymbol{R}T)$$

for the range 328—495°. Isobutene is a major product of the oxidation of both isobutane and neopentane.

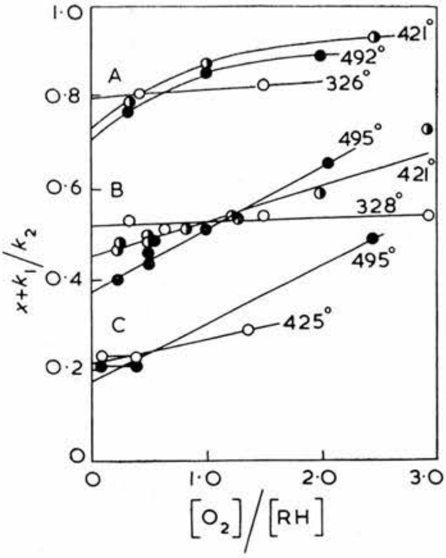

FIG. 3. *Variation of the relative rates of oxidation with* $[O_2]/[RH]$.
(A), k(*neopentane*)/k(*isobutane*), $x = 0{\cdot}20$;
(B), k(*ethane*)/k(*neopentane*), $x = 0$;
(C), k(*ethane*)/k(*propane*), $x = -0{\cdot}20$.

The oxygen-dependence for this and the previous mixture indicates that there should be a strong oxygen-dependence in the ethane–isobutane oxidation.

Propane–Isobutane.—The results of a number of experiments carried out by Smith on this mixture are recorded in Table 6. The range of oxygen concentration is too small to disclose any dependence upon $[O_2]/[RH]$. The mean value of k(propane)/k(isobutane) between 310° and 420° is 0·67.

Ethane–Propane.—This system was extensively studied by Knox, Smith, and Trotman-Dickenson [7] with mixtures in which $[O_2]/[RH]$ was less than 0·50. In this region no dependence upon $[O_2]/[RH]$ was noted. A few experiments with much higher $[O_2]/[RH]$ ratios summarised

TABLE 5. *Oxidation of neopentane–isobutane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$[C_5H_{12}]/[C_4H_{10}]$	[Oxygen]/[Hydrocarbon]	$k(C_5H_{12})/k(C_4H_{10})$	No. of expts.	Temp. (°c)	Press. range (mm.)	$[C_5H_{12}]/[C_4H_{10}]$	[Oxygen]/[Hydrocarbon]	$k(C_5H_{12})/k(C_4H_{10})$
2	326°	255—365	1·0	0·52	0·61	2	492°	265—295	1·0	0·33	0·57
2	326	235—295	1·0	1·50	0·63	2	492	160—180	1·0	1·00	0·66
						2	492	165—180	1·0	2·00	0·69
2	421	195—330	1·0	0·35	0·59						
2	421	275—345	1·0	1·00	0·68						
2	421	270—285	1·0	2·45	0·73						

TABLE 6. *Oxidation of propane–isobutane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$[C_3H_8]/[C_4H_{10}]$	[Oxygen]/[Hydrocarbon]	$k(C_3H_8)/k(C_4H_{10})$	No. of expts.	Temp. (°c)	Press. range (mm.)	$[C_3H_8]/[C_4H_{10}]$	[Oxygen]/[Hydrocarbon]	$k(C_3H_8)/k(C_4H_{10})$
5	310°	140—420	1·0	0·50	0·66	3	420°	170—400	1·0	0·50	0·60
4	310	180—315	3·0	0·50	0·70	2	420	155—245	0·33	0·50	0·73
3	420	145—335	0·33	0·40	0·68	3	420	155—345	3·0	0·75	0·68

in Table 7, show that the dependence upon $[O_2]/[RH]$ is comparable with that in the neopentane–ethane system. The ethane appears more reactive as $[O_2]/[RH]$ is raised. Thus the relative oxidation rates of propane and neopentane should be nearly independent of $[O_2]/[RH]$.

Additives.—One of the most striking effects noted in the present work is the relative independence of the relative rates of oxidation on $[O_2]/[RH]$ at low temperatures and the very marked effect of changes in this ratio at 400° and above. These results can indicate only that the products play an important part in governing the composition of the free-radical mixture which removes the parent hydrocarbons in the later stages of oxidation at higher temperatures. With this in mind, experiments were carried out with ethane–propane mixtures to ascertain whether any of the more probable initial products could account for the change.

The results presented in Table 7 show that addition of ethylene, propene, methanol, or formic acid has no measurable effect at 425°. Hydrogen and formic acid were likewise ineffective at 495°.

TABLE 7. *Effect of additives on ethane–propane oxidations at* 425° *and* 495°.

No. of expts.	Additive	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	Temp. (°c)	$\frac{k(C_2H_6)}{k(C_3H_8)}$	No. of expts.	Additive	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	Temp. (°c)	$\frac{k(C_2H_6)}{k(C_3H_8)}$
—	None	<0·50	425°	0·43 [7]	2	2% $CH_3{\cdot}CHO$	0·34	495°	0·45
2	None	1·35	425	0·49	2	11% $CH_3{\cdot}CHO$	0·50	495	0·54
3	40% C_2H_4	0·25	425	0·45	2	25% $CH_3{\cdot}CHO$	0·33	495	0·53
2	50% C_2H_4	0·25	425	0·43	2	10% $CH_3{\cdot}CHO$ 10% C_2H_4	0·42	495	0·52
2	23% C_2H_4	1·35	425	0·51					
3	23% C_3H_6	0·50	425	0·43	2	10% $CH_3{\cdot}CHO$ 10% C_3H_6	0·41	495	0·51
3	26% $CH_3{\cdot}OH$	0·47	425	0·41					
3	6% $H{\cdot}CO_2H$	0·57	425	0·45	1	6% $H{\cdot}CO_2H$	0·42	495	0·39
					2	19% H_2	0·34	495	0·41
—	None	<0·50	495	0·41 [7]					
1	None	0·34	495	0·41					
2	None	2·45	495	0·79					

TABLE 8. *Oxidation of olefins at* 425° *and* 495°.

Olefin	$\frac{[\text{Oxygen}]}{[\text{Olefin}]}$	Extent of reaction	Temp. (°c)	$\frac{100\ C_2H_6}{\text{Olefin (cons.)}}$ *	$\frac{100\ C_3H_8}{C_3H_6\ \text{(cons.)}}$
C_2H_4	0·50	Complete	425°	8	—
	0·50	2/3 complete	425	0	—
	0·50	Complete	495	11	—
	0·50	2/3 complete	495	2	—
C_3H_6	0·50	Complete	425	2·5	3·5
	0·50	2/3 complete	425	0	0

* Olefin (cons.) is the amount of olefin consumed in a run.

Acetaldehyde, normally regarded as a potent accelerator of oxidations, had only a slight effect at 495° and no effect at 425°. At 495°, 10% was required to give a moderate increase in $k(\text{ethane})/k(\text{propane})$. This amount is far in excess of that likely to be present in the oxidations, and its effect is considerably less than that obtained by adding more oxygen. We therefore have no direct experimental evidence as to the cause of the marked dependence of the relative oxidation rates on the oxygen to hydrocarbon ratio. It is not caused by the oxidation of any of the products mentioned above.

During the study of the effect of addition of ethylene it was noted that the ethane consumption was sometimes unexpectedly small. This was shown to be due to the formation of saturated hydrocarbons from the last stages of the oxidation of the olefin. As is shown in Table 8, up to 11% of the ethylene can be converted into ethane during the later stages of its oxidation at high temperatures. If, however, the reaction mixture is removed from the reaction vessel before the oxygen is exhausted, the conversion into saturated hydrocarbon is greatly reduced. With propene, both ethane and propane are formed. It is clear, therefore, that transfer of hydrogen to the olefin occurs, and that this is followed by abstraction of a hydrogen atom by the alkyl radical thereby formed. A suggested reaction is:

$$C_2H_4 + HO_2 = C_2H_5 + O_2$$

Hydrogen abstraction will only occur when the oxygen concentration is very low. Alternatively, two alkyl radicals can disproportionate to form molecules of alkane and olefin.

DISCUSSION

The main experimental findings may be summarised as follows: (1) All the oxidations studied show the same basic features. (2) The overall relative rate constants k_1/k_2 do not depend upon $[R^1H]/[R^2H]$. (3) The ratios k_1/k_2 are independent of $[O_2]/[RH]$ at 328°, but are dependent on it at temperatures above 400°. As $[O_2]/[RH]$ increases the values tend to unity. (4) The temperature variations of k_1/k_2 at zero $[O_2]/[RH]$ are slight. The largest temperature effect was for the ethane–neopentane mixture, for which the activation energy difference was about 1·6 kcal. mole^{-1}. (5) While the overall rates of oxidation of hydrocarbons differ greatly, the relative rates of oxidation in mixtures studied differ by factors of not more than 2 in all cases except methane–ethane.

The independence of the relative rate constants on $[R^1H]/[R^2H]$ indicates that the reactivities of the propagating radicals derived from different hydrocarbons are identical. In terms of the mechanism given in the introduction, $k_{11} = k_{12}$, and $k_{22} = k_{21}$. This applies over the whole temperature range and at all ratios of oxygen to hydrocarbon, even when the value of k_1/k_2 depends upon $[O_2]/[RH]$.

TABLE 9. *Relative reactivites of saturated hydrocarbons.*

Attacking radical:	F	Cl	Oxid.*	CF_3	MeO	CH_3	Br
Methane	0·6	0·02	0·03	0·05	—	0·03	0·002
Ethane	1	1	1	1	1	1	1
Propane	1·4	2·0	2·3	3·0	3·3	3·3	43
Cyclopropane	0·9	0·03	0·45	—	0·3	0·55	—
Isobutane	1·7	2·0	3·6	7·5	5·3	10	1050
Neopentane	1·8	2·1	2·0	1·5	1·5	1·7	0·75
Temp.	25°	250°	350°	182°	250°	182°	98°
Ref.	12	10	7	15	11	14	13

* " Oxid." refers to the chain-carrying radical in oxidations when $[O_2]/[RH] = 0$.

It has been shown [4,9] that variation of the oxygen concentration in the oxidation of propane between 320° and 480° has little effect upon the yields of the major products formed in the initial stages of reaction. The effect of oxygen is basically to increase the extent of reaction and thereby to alter the nature of the final products. The effect of $[O_2]/[RH]$ on k_1/k_2 at the higher temperatures does not therefore necessarily reflect any change in the initial rates of removal of the two hydrocarbons. It is more likely that the rates of removal in the later stages of reaction differ. This implies that the nature of the radical or radicals that remove the hydrocarbons changes as the reaction proceeds.

Analytical evidence presented here and elsewhere shows that in the early stages of oxidations the olefins corresponding to the original hydrocarbon are the major initial products. The only chain scheme that satisfactorily explains this is an HO_2 radical chain:

$$\text{Alkyl radical} + O_2 = \text{Olefin} + HO_2$$

$$\text{Alkane} + HO_2 = \text{Alkyl radical} + H_2O_2$$

It therefore seems likely that the values of k_1/k_2 that we have obtained by extrapolation to zero oxygen concentration apply to the HO_2 radical. This could be checked in detail by measurement of the initial olefin yields in competitive oxidations. The relative reactivites obtained (Table 9) may be compared with the relative reactivities of other radicals which have been studied in competitive systems.[10-15] The radical operative in oxidations is of relatively high reactivity, comparable with that of a chlorine atom [10] or a methoxyl radical.[11] The radical is less reactive than a fluorine atom [13] and more reactive than a methyl radical.[14] The identification of the radical in oxidations as HO_2 suffers from the difficulty that the commonly accepted strength [16] of the first O–H bond in hydrogen peroxide is 89·5 kcal., whereas the observed reactivities must be attributed to a radical that forms a bond of about 100 kcal. mole^{-1} with a hydrogen atom.

With chlorine [10] and bromine [12] atoms and with methyl radicals,[14] the reactivity does not vary much from one hydrocarbon to another for bonds of a given order. It is therefore reasonable to assume that this holds approximately for the radical involved in oxidations, and hence to derive the relative reactivities in Table 10. Apart from the expected trend in the direction of primary, secondary, and tertiary, it is notable that the CH bond of cyclopropane is about 8 times less reactive than a normal secondary bond, and the CH in methane about 20 times less reactive than a normal primary bond.

The identity of the radical or radicals responsible for the removal of hydrocarbon in the later stages of oxidation is not at all clear. Studies of propane oxidation [4,9] show that a major feature of the oxidation in the later stages is the removal of olefin. It appears that olefins react much faster than saturated hydrocarbons of the same carbon number. It was therefore possible that addition of olefin could induce behaviour characteristic of a mature reaction from the start of an oxidation. The experiments in which ethylene and propene were added to ethane–propane mixtures showed that this was not the case. Even the addition of acetaldehyde had little effect,. The product from which the later-stage radicals are derived is therefore still uncertain but might be formaldehyde. From the fact that there is no dependence of the *k* ratio upon the relative concentrations of the two hydrocarbons, we deduce that the important radicals at this stage are not characteristic of the hydrocarbons forming them. Since this applies even to methane–ethane mixtures, it is likely that the radical contains at most one carbon atom. We are therefore limited to OH, CHO, CH_3, $CH_3{\cdot}O$, and $CH_3{\cdot}O{\cdot}O$. The absence of methane as a product, except at the very end of the reactions, suggests that methyl radicals are oxidised before they have time to abstract hydrogen. The formation of methanol [17] suggests that methoxyl radicals are present, but the relative reactivities of the hydrocarbons with them,[11] as with methyl radicals,[14] do not correspond to those observed. The low strength of the H–CHO bond eliminates formyl radicals. Alkylperoxy-radicals seem unlikely for several reasons. They would be expected to behave very like hydroperoxy-radicals. They would be expected to be present at low temperatures and should, if they are highly reactive, be the chain carriers. Further, preliminary results indicate that their reactivities do not meet the requirements. Hence we conclude that hydroxyl radicals are the most probable chain carriers responsible for removal of the saturated hydrocarbons in the later stages of the reactions at high temperatures.

TABLE 10. *Relative reactivities of hydrogen atoms.*

	Relative reactivity towards:						
Type of H atom	F	Cl	Oxid.*	CF_3	MeO	CH_3	Br
Methyl	0·8	0·03	0·05	0·08	—	0·04	0·002
Cyclopropyl	0·9	0·03	0·45	—	0·29	0·55	—
Primary	1	1	1	1	1	1	1
Secondary	1·2	3	4	6	8	7	250
Tertiary	1·4	3	11	36	26	50	6300
Temp.	25°	250°	350°	182°	250°	182°	98°
Ref.	12	10	7	15	11	14	13

" Oxid." refers to the chain-carrying radical in oxidations when $[O_2]/[RH] = 0$.

EXPERIMENTAL

Materials.—Methane, ethane, cyclopropane, isobutane, and neopentane were obtained from cylinders, thoroughly degassed, and stored in 2-l. bulbs. The ethane used in ethane–cyclopropane and ethane–methane oxidations was passed through a column packed with a mercuric acetate–mercuric nitrate–ethylene glycol solution supported on 20—30-mesh firebrick [18] to remove the ethylene present in the cylinder gas; that used in neopentane–ethane oxidations was freed from ethylene by passing it through sulphuric acid and charcoal saturated with bromine. Bromine vapour and bromides were removed by 30% *NN*-dimethyl-*p*-toluidine supported on 40—60-mesh firebrick. Ethylene and propene were free from ethane and propane. Analysis of the hydrocarbons showed them to be better than 99·5% pure. Oxygen was obtained from B.O.G. cylinders. The acetaldehyde used as an initiator was of " AnalaR " quality.

Apparatus and Procedure.—Oxidations were carried out in a conventional static high-vacuum apparatus. The reaction vessel (107 ml.; Pyrex) was enclosed in an electric furnace controlled by a thermostat to ±1°; the temperature along the length of the reaction vessel was constant within 1°.

The hydrocarbons and oxygen, measured in a constant-volume gas burette, were mixed before each series of runs. Some mixture was allowed to enter the pre-heated reaction vessel, and the initial pressure of the gases was noted on a mercury manometer. The reactions were followed by the pressure rise on the manometer and when this rise had ceased the condensable gases were frozen into a sampling tube at −183° for analysis; the non-condensable gases were pumped off. In order to analyse mixtures containing methane, the sampling tube was packed with activated alumina to condense the methane. Samples were normally withdrawn after the reaction had run to completion. However, k_1/k_2 was independent of the extent of reaction beyond 80%. Small quantities of acetaldehyde introduced as an initiator in some of the low-temperature oxidations of ethane–cyclopropane mixtures had no effect on the observed rate constant ratio.

Analysis.—Analysis was by gas chromatography, carbon dioxide being used as the carrier gas; the gases were determined with a Janak nitrometer.[19]

Ethane, ethylene, and cyclopropane were separated on an 80-cm. column of silver nitrate–ethylene glycol–30—40 mesh firebrick [20] followed by 280 cm. of 40—60-mesh activated alumina poisoned with $\frac{3}{4}$% of squalane.

Methane, ethane, and ethylene were separated with split columns. The first column consisted of 80 cm. of the silver nitrate mixture followed by 160 cm. of poisoned alumina. The second was 240 cm. of Sutcliffe and Speakman's 32—40-mesh activated charcoal. During analysis the two columns were at first connected in series, and the methane and other permanent gases eluted on to the charcoal column and isolated. The ethane and ethylene were then eluted from the first column directly into the detector. Finally, the permanent gases were eluted from the charcoal column.

For ethane, ethylene, isobutene, and neopentane a three-section column was employed. The first section was 240 cm. of 20% nitrobenzene on 52—72-mesh firebrick; the second, 80 cm. of silver nitrate mixture followed by 160 cm. of poisoned alumina; the third 120 cm. of the silver nitrate mixture. In analysis, sections one and two were first connected in series, and carbon dioxide passed until the ethane and ethylene were isolated on the second section of the column. Sections one and three were then connected in series, and the isobutene and neopentane eluted directly into the detector. Finally, the ethane and ethylene were eluted from section two.

Isobutene, isobutane, neopentane, and the C_2 and C_3 hydrocarbons were separated as follows: The contents of the sample tube were eluted on to a column of 10 cm. of poisoned alumina followed by 230 cm. of 20% nitrobenzene on firebrick, and the C_2 and C_3 hydrocarbons were eluted into the atmosphere. The column was then connected in series with 120 cm. of silver nitrate mixture, and the C_4 and C_5 hydrocarbons were eluted.

All columns were operated at room temperature. Standardisation runs were carried out for each furnace temperature, the normal procedure being used for an oxidation, but with omission of the oxygen from the original mixture. In this way systematic errors of calibration were eliminated. The accuracy of the analytical results was about ±1%.

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CHEMISTRY DEPARTMENT, EDINBURGH UNIVERSITY. [*Received, July 25th,* 1960.]

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844. *Competitive Oxidations. Part III.*[1] *Oxidations at Low Temperatures Induced by Light.*

By W. E. Falconer, J. H. Knox, and A. F. Trotman-Dickenson.

The relative rates of consumption of alkanes by the attack of radicals generated by photolysis of ketones in the presence of an excess of oxygen have been determined. The relative reactivities of different C–H bonds towards these radicals, which are presumed to be alkylperoxy, have been estimated. The reactivities are the same as those found for the chain-carrying radicals in hydrocarbon oxidations at low temperatures and are intermediate between those found for chlorine atoms and methoxyl radicals.

Although the oxidation of hydrocarbons has been extensively studied above 290°, little work has been done on photo-initiated oxidations at lower temperatures. This is understandable, because much of the high-temperature work has consisted of the measurement of induction periods and maximum rates of pressure change. Neither sort of observation is appropriate to photolytic systems. This series of papers [1,2] describes studies of competitive oxidations in which the relative rates of consumption of two hydrocarbons mixed with oxygen are measured. These measurements were first made with and without initiators present above 290° and are here extended to lower temperatures with the oxidation initiated by the photolysis of ketones.

The photolysis of a symmetrical ketone effectively yields two alkyl radicals at 145° or above. These radicals react rapidly with oxygen to form alkylperoxy-radicals. Our experiments show that a radical, which may be alkylperoxy, its isomer, or its decomposition product, exists which will attack alkanes. If this radical is called Y·, then we can write

$$\mathrm{Y\cdot} + \mathrm{R_aH} \xrightarrow{k_a} \mathrm{R_a\cdot} + \mathrm{YH}$$
$$\mathrm{Y\cdot} + \mathrm{R_bH} \xrightarrow{k_b} \mathrm{R_b\cdot} + \mathrm{YH}$$

The relative rate constants, k_a and k_b, are given by

$$\frac{k_a}{k_b} = \frac{\log\,[\mathrm{R_aH}]_{\text{initial}} - \log\,[\mathrm{R_aH}]_{\text{final}}}{\log\,[\mathrm{R_bH}]_{\text{initial}} - \log\,[\mathrm{R_bH}]_{\text{final}}}. \qquad (1)$$

This relation is accurate only if Y· truly represents a single species (or, if a mixture, then species of identical reactivity), if alkanes are consumed by no other reactions, and if the alkyl radicals $\mathrm{R_a\cdot}$ and $\mathrm{R_b\cdot}$ are efficiently prevented (by reaction with oxygen or by other means) from re-forming alkanes. Consideration of the validity of these assumptions is best deferred until after the results have been presented.

Table 1 shows that k(neopentane)/k(propane) obtained from the above equation is independent of total pressure (100—500 mm.), oxygen : hydrocarbon ratio (2 : 1 to 10 : 1), hydrocarbon : ketone ratio (1·5 : 1 to 15 : 1), and relative hydrocarbon concentration (3 : 1 to 1 : 3), and of whether the initial source of radicals is acetone or diethyl ketone. Table 2 shows k(ethane)/k(neopentane) to be independent of the period of illumination (30—170 min.) at 230°. The conditions were varied at random for all hydrocarbon pairs studied over as wide a range as would permit adequate consumption of reactants in a reasonable time; k_a/k_b was never found to depend on them. It was necessary to use an oxygen : ketone ratio of at least 3 : 1 to suppress completely the formation of alkanes and the dimer corresponding to the alkyl radical formed in the ketone photolysis; usually the excess of oxygen was much greater. Table 3 lists the results for all hydrocarbon pairs when the ketones photolysed were acetone, diethyl, di-isopropyl, and di-t-butyl ketone. From these figures the relative reactivities at 230° listed in Table 4 were calculated.

The assumptions made in the deduction of equation (1) can now be considered. The photolyses of the ketones are known to yield alkyl radicals and carbon monoxide. There are three reasons for thinking that the alkyl radicals do not attack the hydrocarbons directly. Methyl radicals yield no methane when acetone is photolysed in the presence of even a few mm. of oxygen under comparable conditions;[3] alkanes that might come from such alkyl attack are not formed; and the relative reactivities are different from those found for methyl radicals.

TABLE 1.

Reaction of neopentane–propane mixtures is oxygen sensitized by alkyl radicals.

[Ketone]	[O_2]	[Neopentane]		[Propane]			
init. (mm.)	init. (mm.)	init. (mm.)	final (mm.)	init. (mm.)	final (mm.)	$\frac{k(\text{neopentane})}{k(\text{propane})}$	
Methyl radicals, (i) *at* 145.							
14a	320	3·85	2·90	11·65	7·90	0·72	Mean 0·67
12b	160	6·08	4·94	18·32	13·57	0·69	
14a	240	11·34	9·64	3·76	2·96	0·67	
17a	70	15·47	12·86	5·13	3·81	0·63	
15c	245	10·74	8·60	3·56	2·52	0·65	
	(ii) *At* 230°.						
17	65	9·28	7·76	26·70	21·05	0·76	Mean 0·74
15	330	9·44	7·95	27·15	21·55	0·74	
5	70	13·27	12·30	38·13	34·08	0·68	
20	440	29·52	24·10	9·78	7·62	0·80	
18	75	40·57	36·40	13·43	11·50	0·72	
19	460	28·47	22·05	9·43	6·75	0·76	
4	205	30·20	27·45	10·00	10·00	0·73	
16	90	16·53	13·44	5·48	5·48	0·70	
Ethyl radicals, (i) *at* 145°.							
14c	180	4·04	3·14	12·16	8·36	0·67	Mean 0·67
15d	265	11·64	10·06	3·86	3·08	0·66	
17c	365	14·34	11·23	4·76	3·32	0·67	
	(ii) *At* 230°.						
19	280	10·11	7·88	29·09	20·90	0·76	Mean 0·76
19	95	10·16	7·71	29·24	20·15	0·75	
18	435	32·70	23·45	10·83	7·10	0·78	
11	70	27·35	21·90	9·04	6·86	0·78	
8	85	27·41	22·70	9·09	7·02	0·73	
12	155	17·05	12·59	5·65	3·80	0·76	

All runs were of 30 min., except *a* 160, *b* 260, *c* 180, and *d* 145 min.

TABLE 2.

Reactions of ethane–neopentane mixtures at 230°.

	[Ketone]	[O_2]	[Ethane]		[Neopentane]			
Exp. (min.)	init. (mm.)	init. (mm.)	init. (mm.)	final (mm.)	init. (mm.)	final (mm.)	$\frac{k(\text{ethane})}{k(\text{neopentane})}$	
Methyl radicals.								
30	12	115	13·77	12·62	7·03	6·08	0·59	Mean 0·57
60	16	130	20·05	16·48	10·25	7·28	0·57	
90	16	115	23·90	18·42	12·20	7·54	0·54	
170	15	80	24·23	17·28	12·37	6·78	0·57	
Ethyl radicals.								
30	14	320	17·34	14·22	8·86	6·14	0·54	Mean 0·56
60	16	415	34·96	25·06	17·84	10·10	0·58	

The reaction of methyl radicals with oxygen is of the third order:[3] first order with respect to methyl radicals, oxygen molecules, and third bodies. The reaction, $Me\cdot + O_2 + M \longrightarrow MeO_2\cdot + M$, is the only one that is likely to show this behaviour. It is possible that the high pressure of oxygen may have been needed partly to serve as a third body in the suppression of the formation of ethane from acetone. There is good evidence, therefore, that methyl radicals yield methylperoxy-radicals and that the other radicals react similarly. The alkyl radicals formed by hydrogen abstraction must also react with oxygen and cannot re-form their parent alkane. Hence an alkylperoxy-chain could be established. The relative rates of attack observed might therefore be attributable to the radicals released by the alkane mixture, not to those that come from the ketone. The similar behaviour of systems with initial radicals as different as methyl and t-butyl suggests that a chain might not affect the results. This conclusion is supported by the observation that alteration in the proportions of the hydrocarbons does not alter the ratio of the rate constants.

TABLE 3.

Reaction of hydrocarbon mixtures.

Hydrocarbon pair	Temp.	Alkyl radical	No. of runs	k_a/k_b
Methane–cyclopropane	230°	Me	4	0·13 ± 0·03
	230	Et	5	0·12 ± 0·02
Cyclopropane–ethane ……	145	Me	4	0·45 ± 0·02
	145	Et	3	0·45 ± 0·02
	145	Pr^i	1	0·48
	145	Bu^t	2	0·54 ± 0·02
	230	Me	5	0·49 ± 0·02
	230	Et	6	0·52 ± 0·01
	230	Pr^i	3	0·52 ± 0·00
	230	Bu^t	3	0·55 ± 0·03
Ethane–propane	145	Me	7	0·39 ± 0·04
	145	Et	4	0·39 ± 0·02
	230	Me	13	0·04 ± 0·02
	230	Et	5	0·42 ± 0·01
	230	Pr^i	2	0·43 ± 0·01
	230	Bu^t	2	0·45 ± 0·01
Ethane–neopentane	230	Me	4	0·57 ± 0·01
	230	Et	2	0·56 ± 0·02
Neopentane–propane	145	Me	5	0·67 ± 0·03
	145	Et	3	0·67 ± 0·00
	230	Me	8	0·74 ± 0·03
	230	Et	6	0·76 ± 0·01
Propane–isobutane	145°	Me	3	0·70 ± 0·02
	145	Et	3	0·70 ± 0·01
	145	Pr^i	1	0·67
	145	Bu^t	1	0·68
	230	Me	4	0·69 ± 0·02
	230	Et	4	0·70 ± 0·00
	230	Pr^i	3	0·73 ± 0·02
	230	Bu^t	3	0·70 ± 0·01
Propane–butane	145	Me	1	0·59
	145	Et	2	0·61 ± 0·04
	230	Me	5	0·61 ± 0·02
	230	Et	4	0·60 ± 0·01
Butane–propene	145	Me	3	0·20 ± 0·02
	145	Et	4	0·22 ± 0·02
	230	Me	3	0·38 ± 0·01
	230	Et	3	0·38 ± 0·01

TABLE 4.

Initial radical	Methane	Ethane	Propane	Cyclopropane	n-Butane	Isobutane	Neopentane
Me …………………	0·06	1	2·5	0·49	4·1	3·6	1·8
Et …………………	0·06	1	2·4	0·52	4·1	3·5	1·8
Pr^i …………………	—	1	2·3	0·52	—	3·2	—
Bu^t …………………	—	1	2·2	0·54	—	3·2	—

An attempt was made to measure the chain length in one system. Acetone was photolysed in the presence and absence of an isobutane–oxygen mixture. 0·6 molecule of isobutane was removed for each methyl radical released (as determined from the yield of carbon monoxide in the absence of the mixture). This indicates that two-thirds of the attack can be attributed to radicals from (methyl + oxygen) and one-third from (isobutane + oxygen). This argument is over simplified, since the oxygen may quench excited acetone molecules and lower the primary quantum yield. Hence the chains could be longer.

Even if alkylperoxy-radicals are initially formed by the alkyl radicals it is not certain that they attack the hydrocarbons. They might decompose to yield other radicals. Methylperoxy- might form methoxyl radicals,[4] but it is unlikely that methoxyl radicals play a great part in the system as the observed consumption of hydrocarbons is very different from that predicted by the methoxyl results shown in Table 5. Other alkoxyl radicals probably react like methoxyl. Alternatively, methylperoxy-radicals could decompose to formaldehyde and hydroxyl, and the hydroxyl radicals could attack the alkanes. The other alkyl radicals might decompose to hydroxyl radicals and acetaldehyde or ethylene oxide, acetone or propylene oxide, and isobutene oxide respectively. Table 5 shows that hydroxyl radicals in aqueous solution at 17·5° are clearly less selective than the radicals studied here, and at higher temperatures the hydroxyl radicals are probably still less selective. Thus chlorine atoms react like hydroxyl radicals near room temperature and are much less selective at 250°. Further, hydroxyl is probably more solvated by water than the activated complex that it forms. As with chlorine atoms,[5] this circumstance will increase its observed selectivity above the level for the gas phase. Accordingly it is unlikely that much alkane is removed by hydroxyl attack.

It is most straightforward to suppose that the alkylperoxy-radicals attack the alkanes directly to form hydroperoxides. The nature of the alkyl groups would not be expected to have much effect on the reactivities of the radicals, when the free electron is so far removed from the point at which the structures vary. The hydroperoxy-radical, which we have previously suggested is the chain carrier in the higher-temperature oxidations, might by the same reasoning be expected to have the same reactivity as methylperoxy. It is unlikely that the hydroperoxy-radical is important at low temperatures because it can only readily be released by a reaction such as $Me_3C{\cdot}O{\cdot}O \longrightarrow Me_2C{:}CH_2 + HO_2{\cdot}$ which results in the formation of an equivalent amount of olefin. Olefins are indeed the major initial products of alkane oxidations at about 300° but were not detected in the present work at low temperatures. The decomposition of alkylperoxy- to hydroperoxy-radicals and olefin must therefore have a high temperature coefficient.

TABLE 5.

Relative reactivities of hydrogen atoms in hydrocarbons, $X{\cdot} + RH = XH + R{\cdot}$.

		Environment of hydrogen atom						
Radical	Temp.	Methyl	Cyclopropyl	Prim.	Sec.	Tert.	*E* † (ethane)	Ref.
F	25°	0·8	0·9	1	1·2	1·4	0·3	*a*
OH	17·5	0·6	0·18	1	4·7	9·8	—	*b*
Cl	25	0·004	0·003	1	4·6	8·9	1·0	*c*
	250	0·03	0·03	1	3	3	1·0	*c*
Oxid.*	230	0·09	0·52	1	4·5	13·2	—	1
$MeO{\cdot}O$	230	0·10	0·52	1	4·8	13·4	—	*h*
$EtO{\cdot}O$	230	0·10	0·55	1	4·6	12·4	—	*h*
$Pr^iO{\cdot}O$	230	—	0·52	1	4·0	13·2	—	*h*
$Bu^tO{\cdot}O$	230	—	0·54	1	3·0	13·1	—	*h*
MeO	230	—	0·35	1	8	27	7·1	*d*
CF_3	182	0·08	—	1	6	36	7·5	*e*
Me	182	0·04	0·55	1	7	50	11	*f*
Br	98	0·002	—	1	250	6300	13·4	*g*

* This refers to the chain-carrying radical in oxidations; the figures quoted were obtained by a small extrapolation of the results to the condition where $O_2/RH = 0$.

† *E*(ethane) is the activation energy in kcal. mole^{-1} for the abstraction of H from ethane by a radical.

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The only considerable difficulty in accepting the hypothesis that attack is by hydroperoxy-radicals is that the selectivities correspond to those for radicals which would attack ethane with activation energies of 5—6 kcal. mole^{-1}. This is low by comparison with the activation energies of the chain-carrying steps in the autoxidation of olefins in solution;[6] It is also low compared with the value reported by Burgess and Robb[7] for the attack of t-butylhydroperoxy-radicals on isobutane in the mercury-photosensitised oxidation above

300°, but this value is reliable only if their mechanism is strictly correct, the mechanism does not allow for the formation of isobutene which is obtained in large quantities in oxidations at these temperatures. The present work on butane–propene gives

$$k(\text{butane})/k(\text{propene}) = 8{\cdot}2 \exp(-3070/\boldsymbol{R}T) \text{ with acetone}$$
$$= 5{\cdot}7 \exp(-2710/\boldsymbol{R}T) \text{ with diethyl ketone}$$

This difference in activation energy suggests a value of 8—10 kcal. mole^{-1} for butane. On the other hand, the mode of attack on olefins is not known. The removal may occur in two steps, one of which may involve an equilibrium and could result in a negative overall activation energy. The negligible differences in activation energy for attack on primary and tertiary hydrogen atoms are evidence in favour of low activation energies for the primary removal of hydrogen atoms from alkanes.

EXPERIMENTAL

Materials.—Methane, ethane, propane, cyclopropane, butane, isobutane, and neopentane, obtained from cylinders, were degassed and stored in 2-l. bulbs. Ethylene was removed from the cylinder ethane by passing the gas through sulphuric acid and a column of charcoal saturated with bromine. Bromine vapour and bromides were removed by a 30% *NN*-dimethyl-*p*-toluidine–firebrick mixture. Propene was prepared by dehydration of isopropyl alcohol. Chromatography showed the hydrocarbons to be at least 99·5% pure. B.O.C. cylinder oxygen was used.

Acetone and diethyl ketone were of " AnalaR " grade. The di-isopropyl ketone, given by Shell Chemicals, was 99% pure. Di-t-butyl ketone was prepared by condensing t-butyl chloride and methyl pivalate over sodium sand and oxidizing the resultant mixture of ketone and alcohol with concentrated nitric acid, according to the method of Bartlett and Schneider.[8] it had b. p. 153—156°, n_D^{20} 1·4200 and chromatography indicated 95% purity; its photolysis yielded no products characteristic of alkyl radicals other than t-butyl; it was stored in a trap immersed in carbon dioxide–acetone.

Apparatus, Procedure, and Analysis.—The high-vacuum system was of conventional static design constructed of Pyrex glass except for the 300 c.c. spherical quartz reaction vessel which was enclosed in an insulated electric furnace and illuminated by a 125 w medium-pressure mercury arc focused by a quartz lens. The lamp was backed by a polished aluminium reflector, and an aluminium shutter separated the lamp from the reaction vessel.

An excess of oxygen was added to a mixture of two hydrocarbons and ketone in the reaction vessel before each run. The gases were allowed to equilibrate, and the lamp to become stable, for 15 min. before the shutter was opened to start the reaction. The temperature of the reaction vessel rose by ~5° to the stable reaction temperature when the shutter was opened. After a suitable interval the lamp was turned off and the condensable gases were frozen into a W-tube packed with crushed glass helices and immersed in liquid oxygen; the non-condensable gases were pumped through the sample tube to remove remaining condensable material. For mixtures containing methane, the W-tube was packed with activated alumina to condense the methane.

A chromatographic system of the Janak design [9] was used for analysis. Methane and cyclopropane were separated with split columns. The first column contained 120 cm. of 40—60 mesh activated alumina poisoned with 1½% of squalane; the second was 240 cm. of Sutcliffe and Speakman 32—40 mesh activated charcoal. During the analysis the two columns were first connected in series, and the methane and other permanent gases eluted on to the charcoal column and isolated. The cyclopropane was then eluted from the first column directly into the detector. Finally, the permanent gases were eluted from the charcoal. All other samples were separated on 120 cm. of 40—60 mesh activated alumina poisoned with 1½% of squalane. For ethane–propane and ethane–cyclopropane mixtures the column was operated at room temperature; for propane–isobutane, propane–butane, and propene–butane at 40—45°; and for ethane–neopentane and neopentane–propane at 65—70°.

Standardization runs were carried out at each furnace temperature, by the normal procedure for a reaction but without oxygen and ketone. Systematic errors of calibration were thus eliminated. The analytical accuracy was about ±1%.

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CHEMISTRY DEPARTMENT, EDINBURGH UNIVERSITY. [*Received, April* 21*st*, 1961.]

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[28]

160. *The Competitive Oxidation of Propene and Alkanes.*

By Michael D. Carabine and John H. Knox.

The relative rates of removal of propene and ethane in the oxidation of mixtures has been determined at 383° and 449°, and the limiting rate constant ratio $k_{\text{ethane}}/k_{\text{propene}}$ found for zero extent of reaction. With the value known for this ratio, the ratio $k_{\text{propane}}/k_{\text{propene}}$ is found. The values obtained agree well with those deduced from studies of the oxidation of propane alone.

In the oxidation of an alkane above 320°C the major initial product is the alkene with the same number of carbon atoms.[1-4] In the later stages of the reaction the concentration of the alkene passes through a maximum owing to its own oxidation and it is possible to derive the relative reactivities of the alkane and the alkene in the prevailing free-radical mixture from their concentrations at this maximum. As a check on the mechanism for the formation and removal of the alkene it is important to show that the relative reactivities obtained in this way agree with those obtained from competitive oxidations such as those previously carried out on alkanes.[5,6]

In the present work we have oxidised mixtures of ethane, propene, and oxygen in order to obtain the rate constant ratio $k_{\text{ethane}}/k_{\text{propene}}$, that is, the ratio of the rate constants of reactions (1) and (2):

$$C_2H_6 + \times = C_2H_5 + XH \qquad (1)$$

$$C_3H_6 + \times = C_3H_5 + XH \text{ or } C_3H_6X \qquad (2)$$

where X is the single free radical or a mixture of free radicals which removes the two hydrocarbons.

The apparatus was similar to that previously described.[5,6] Oxidations were carried out in the gas phase at 383° and 449° in a 100-ml. cylindrical Pyrex vessel. The reactions were taken nearly to completion and the products were analysed for unchanged hydrocarbons by gas chromatography by the Janak technique. An experimental ratio R was obtained for each oxidation:

$$R = \log\{[\mathrm{RH}]_i/[\mathrm{RH}]_f\}/\log\{[\mathrm{A}]_i/[\mathrm{A}]_f\}, \qquad (A)$$
$$(\mathrm{RH} = C_2H_6;\ \mathrm{A} = C_3H_6)$$

where the subscripts " i " and " f " refer to initial and final concentrations of hydrocarbons. Initial concentrations were determined from standardisation experiments in which mixtures were removed from the reaction vessel for analysis before the end of the induction period. The reproducibility of the standardisation experiments was about ±1% but, since the evaluation of R depends essentially upon differences in concentrations, values of R are less precise; duplicate oxidations gave values of R which were generally within 5%.

When X is a single species, R is equal to the rate constant ratio $k_{\text{ethane}}/k_{\text{propene}}$,[5] the relation being true even when [X] changes throughout the reaction. If, however, X represents a mixture, as is likely in a hydrocarbon oxidation, the interpretation of R is more difficult and three situations must be considered:

(1) X is a mixture whose composition depends only on temperature but not on the composition of the mixture. R is then still a ratio of rate constants $k_{\mathrm{RH}}/k_{\mathrm{A}}$, but k_{RH} and k_{A} are now linear sums of elementary rate constants. Any activation energies derived from plots of log R against $1/T$ will then be complex and may not have a simple interpretation.

(2) The composition of X may depend upon the ratio of the two hydrocarbons RH and A. Except above 500° or when the oxygen is nearly exhausted, X will be made up of oxygenated radicals. If these radicals reflect the structure of RH and A (*e.g.*, RO, AOH,

RO_2, AO_2H), R might be expected to depend upon [RH]/[A], and for each mixture R would be equal to a ratio of complex rate constants such as the linear sums mentioned under (1). If the oxygenated radicals do not reflect the structure of the hydrocarbons (*e.g.*, OH, CH_3O, HO_2, CH_3O_2, CHO), then R should be independent of [RH]/[A]. With alkane mixtures [5,6] and with the ethane–propene mixtures used here, where the ratio [ethane]/[propene] was varied over a factor of four at 383°, the ratio R was independent of hydrocarbon ratio. In view of the range of hydrocarbons which has now been studied it is probable that X consists of simple radicals which do not reflect the structure of the original hydrocarbons.

(3) X may change in composition throughout the oxidation with the extent of reaction. There is substantial evidence that this does happen. The extent of reaction can be varied simply by controlling the initial oxygen concentration, since studies of the oxidation of single hydrocarbons [1-4] have shown that the concentration has little effect on the yields of products at a given stage in the reaction (measured by, say, the quantity of oxygen used).

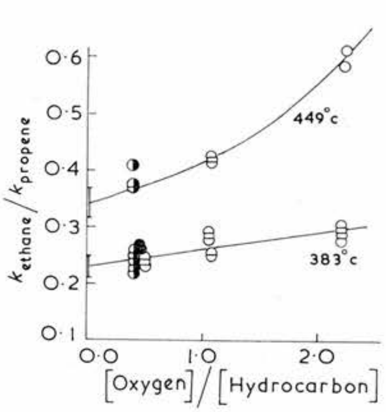

FIG. 1. Effect of oxygen : hydrocarbon ratio on $k_{ethane}/k_{propene}$ for ethane : propene ratios as follows: ○ = 1 : 1; ◑ = 1 : 1·5; ● = 3 : 1.

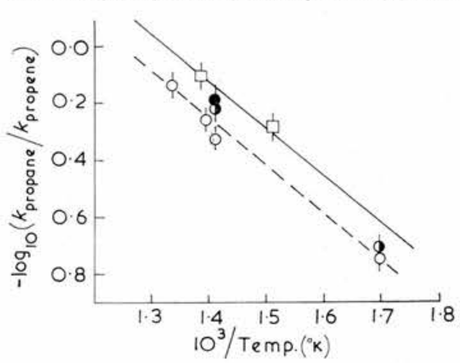

FIG. 2. Effect of temperature on $k_{propane}/k_{propene}$.

□ This work. Oxidation of (○) pure propane, (◑) propane (90%) + propene (10%), and (●) propane (80%) + propene (20%). Broken line through points for oxidation of pure propane. Full line through points extrapolated to start of reaction.

The major effect of increasing the initial oxygen pressure is simply to increase the final extent of reaction. When analysis for residual hydrocarbon is made towards the end of the reaction, the values of R might be expected to vary with [oxygen]/[total hydrocarbon]. When the composition of X changes and so produces a variation of R with extent of reaction, the value of R cannot be simply interpreted but must be in the nature of an average rate constant ratio.

Dependence of R upon [oxygen]/[hydrocarbon] has been found for alkane mixtures, the dependence being more pronounced at higher temperatures.[6] Fig. 1 shows a similar dependence for ethane–propene mixtures. Interpretable values of R can be obtained only when the extent of reaction is so low that the composition of X may be regarded as constant. Such values are obtained by extrapolation of R to zero [oxygen]/[hydrocarbon], that is, to zero extent of reaction. There is evidence that under these conditions the major radical which removes the hydrocarbons is HO_2.[1-4,7]

The extrapolated values of R at 383° and 449° are $0{\cdot}23 \pm 0{\cdot}02$ and $0{\cdot}34 \pm 0{\cdot}03$, respectively. These values are now identified with $k_{ethane}/k_{propene}$. Using the value of $k_{ethane}/k_{propane}$ of 0·44 which is independent of temperature [5] we obtain $0{\cdot}52 \pm 0{\cdot}05$ and $0{\cdot}77 \pm 0{\cdot}08$ for $k_{propane}/k_{propene}$ at 383° and 449°, respectively. These values may be compared with those derived directly from the oxidation of propane (Fig. 2).

The maximum in the yield of alkene in the oxidation of an alkane may be considered to arise from the following reactions:

$$RH + X = R + XH \tag{1}$$

$$R + O_2 = A + HO_2 \tag{3}$$

$$= \text{Other products} + X' \tag{4}$$

$$A + X = \text{Products} + X'' \tag{2}$$

The fraction, f, of alkyl radicals which react with oxygen to give the alkene can be determined by analysis of the products from the early stages of the reaction when oxidation of the alkene is negligible: $f = k_3/(k_3 + k_4)$. Since the rate of formation and of destruction of the alkene must be equal when its concentration is a maximum, we obtain

$$k_1/k_2 = k_{RH}/k_A = f^{-1}[A]_{max.}/[RH]_{max.}, \tag{B}$$

where the subscript " max." implies concentrations of RH and A when the yield of the alkene is a maximum. Since the maxima do not occur at the start of the reaction, the results obtained in this way are not strictly comparable with those obtained in competitive experiments by extrapolation to low oxygen mole fractions. However, the point in the reaction at which the maximum occurs for any hydrocarbon can be considerably advanced by oxidising alkanes which are somewhat contaminated with the appropriate alkene, for example, propane containing 10—20% of propene.[1,2] The more propene that is initially present the earlier the maximum occurs and, as shown in Fig. 2, the higher is the ratio $k_{propane}/k_{propene}$ derived from equation (B). The agreement between the two methods of determining this rate constant ratio is satisfactory if attention is confined to the early stages of the reaction (□ and ● in Fig. 2), and it provides a good confirmation that the oxidation mechanism which we have assumed, and the competitive experiments, are basically reliable.

The strong temperature-dependence of the rate constant ratio may be expressed by the relation

$$k_{propane}/k_{propene} = 120 \exp(-7000 \text{ cal. mole}^{-1}/\boldsymbol{R}T).$$

The extreme Arrhenius parameters suggest that the simple interpretation in terms of two competing free-radical reactions may not be correct. There are two obvious alternatives: (1) While the composition of X may be constant at any one temperature it may vary with temperature and so contribute to E. (2) Reaction 2 may involve an equilibrium and the rate-determining step may be the slow decomposition of the addition product of X to A. One possible such scheme is

$$A + HO_2 = AO_2H \tag*{(5), (−5)}$$

$$AO_2H = \text{Products} + X'' \tag{6}$$

Since the initial products of oxidation of olefins [4,8] appear to demand a four-membered ring transition-state complex, reaction (6) may well have the very low A factor required for such a scheme to explain the unusual Arrhenius parameters.

Department of Chemistry,
The University, Edinburgh, 9.

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[29]

446. *The Micro-flame Detector in Gas–Liquid Partition Chromatography: Correlation of Response with Heats of Combustion.*

By J. I. Henderson and J. H. Knox.

Gas–liquid partition chromatography is carried out with nitrogen or carbon dioxide as carrier gas. Hydrogen is added to the gas stream as it emerges from the column, and the resultant mixture burnt in a draught-free housing in contact with a thermocouple. The temperature rise of the thermocouple during the combustion of any band is found to be directly proportional to the rate of liberation of heat in the combustion of the band.

Recently a novel method of detection for use in gas–liquid partition chromatography has been described by Scott [1] in which hydrogen is used as carrier gas and is burnt at a jet at the outlet of the column. By measuring the changes in the temperature of a thermocouple placed in the flame, the elution of various bands can be observed as peaks on a temperature–time plot. It appeared to us that a direct correlation should exist between the areas of such peaks and the heats of combustion of the substances which gave rise to them. Using a simple apparatus, we have in fact been able to show that a good linear relation exists between the peak area per mole of some 24 organic substances and their molar heats of combustion. As a result of the work we have also concluded that the micro-flame detector has approximately the same sensitivity as the more widely used thermal conductivity type and that it is considerably less temperamental at high sensitivity.

The method originally described suffered from the disadvantage that during the elution of a band the basic thermocouple temperature rose in the direction of higher temperature. This effect, which renders quantitative results unreliable, is apparently due to a slight increase in the hydrogen flow rate as the band emerges from the column, the band acting as a viscous plug when within the column. This disadvantage has been overcome by Wirth,[2] who uses, instead of hydrogen, an inert carrier gas such as nitrogen or carbon dioxide. The hydrogen is passed through a separate column and mixed with the carrier gas immediately before combustion. In this way a constant flow of hydrogen is ensured irrespective of what may pass through the chromatography column proper. This modification of the original design has been found to be completely satisfactory in removing base line steps and has no detrimental effect on the stability or sensitivity of the apparatus.

The greatest difficulty in construction of the micro-flame detector lies in ensuring an absolutely stable flame when no foreign gas is passing through the flame. In order that the apparatus used in the present work should be able to measure a heat output of 0·5 cal./min. with an accuracy of 1% (this corresponds roughly to the maximum rate of heat liberation during the elution of 100 μg. of benzene under our experimental conditions), a flame stable to ±0·01° at an ambient temperature of 600—800° is required. The flow of hydrogen must therefore be stabilised to about 1 part in 10^5 and the flame itself must be mounted in an absolutely draught-free housing. In our apparatus the flow rate was stabilised by passing the hydrogen, kept at a pressure of some 20 cm. Hg above atmospheric by a water bubbler, through a series of six stabilising vessels each consisting of a length of fine capillary leading into a volume of about 20 c.c. The hydrogen was then passed through a " dummy " chromatographic column before being mixed with the carbon dioxide or nitrogen which was used as carrier gas for the chromatography proper. The flow of the carrier gas was similarly stabilised by two stabilising vessels.

The prevention of draughts was ensured by mounting the jet inside an asbestos pipe, 50 cm. long and 10 cm. in diameter, lined with five spaced concentric layers of fine copper gauze. The jet itself was made of quartz and had a diameter of 0·2 mm. The thermocouple was mounted about 1 cm. above the jet and was contained in a very thin-walled quartz capillary which served to minimise corrosion and prevented any catalysis of the combustion. The output of the thermocouple was balanced by means of a potentiometer and the off-balance e.m.f. supplied to a sensitive galvanometer. With this arrangement a flame stability of ±0·03° was achieved. We were therefore in a position to analyse mixtures containing quantities of the order of 300 μg., but in practice, owing to the difficulty of adding such minute amounts of liquids, samples of the order of 2—5 mg. were used. The thermocouple used in the experiments was of platinum–platinum-13% rhodium which gave a deflection of 3 cm./°c with the galvanometer employed. Random fluctuations were of the order of 1 mm. The chromatography column was 100 cm. long, 8 mm. in diameter, and was packed with a 3 : 2 mixture of Celite 545 and Silicone oil D.C. 500. The column temperature was 65°, and the flow rates of hydrogen and carbon dioxide (used throughout the experiments as carrier gas) were 100 and 66 c.c./min., respectively. The basic thermocouple temperature with these flow rates was 650° above room temperature.

Before commencing experiments on the relation between the heats of combustion of various substances and the sensitivity of the micro-flame detector it was necessary to confirm that the response of the detector was a linear function of the amount of any component passed. Since it is extremely difficult to add accurately very small amounts of liquids, a number of mixtures of different compositions were made up with acetone and benzene. A logarithmic plot of the relative peak areas against the relative amounts of the two components is shown in Fig. 1. The line, which has been drawn with unit gradient, passes within experimental error through all the points and confirms that the response is in fact linear. More extended experiments by Wirth have led to the same conclusions.

FIG. 1. *Linearity of response of detector to mixtures of different compositions.*

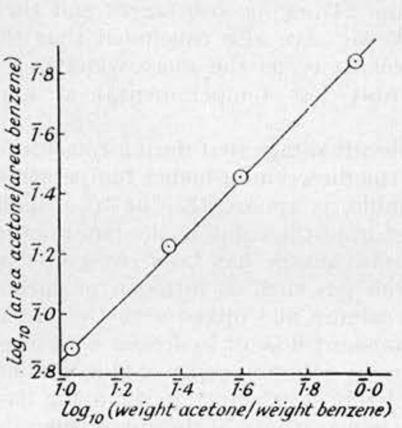

FIG. 2. *Variation of sensitivity of flame detector with heat of combustion of various substances.*

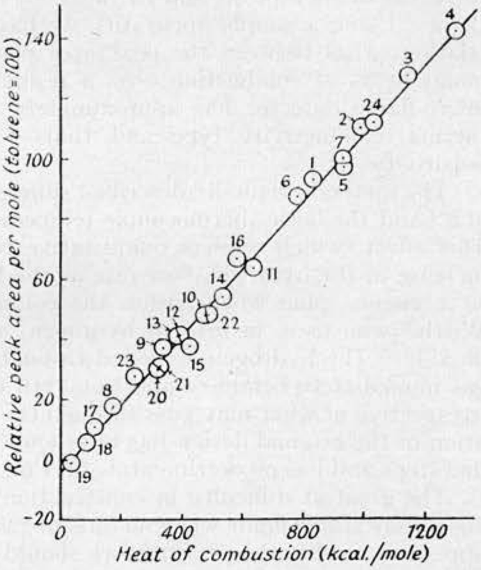

FIG. 2.

(1) *n*-Pentane; (2) *n*-hexane; (3) *n*-heptane; (4) *n*-octane; (5) *cyclo*hexane; (6) benzene; (7) toluene; (8) methyl alcohol; (9) ethyl alcohol; (10) *n*-propyl alcohol; (11) *n*-butyl alcohol; (12) ethyl formate; (13) methyl acetate; (14) ethyl acetate; (15) acetone; (16) ethyl methyl ketone; (17) methylene chloride; (18) chloroform; (19) carbon tetrachloride; (20) ethyl chloride; (21) ethyl bromide; (22) *iso*propyl bromide; (23) carbon disulphide; (24) triethylamine.

In correlating peak areas with the heats of combustion, an analogous method was used. Solutions of a variety of substances were made up in toluene by accurate weighing, and 2—5 mg. of each mixture used for chromatography, the mixtures being injected into the column by means of a hypodermic syringe through a serum cap. The peak areas were then measured, and the peak areas per mole calculated relative to a value of 100 for toluene. These values are plotted in Fig. 2 against the heats of combustion per mole of the various substances. The heat of combustion values are those for 25°; no correction has been made for the temperature of the flame since other sources of error are probably greater and the correction term would in any case be roughly proportional to the heats of combustion for any series of compounds. The results all fall on a good straight line and therefore establish that the heat of combustion is the major factor influencing the sensitivity of the micro-flame detector. Changes in the shape of the flame appear to have only a secondary effect on the response.

In order to obtain an absolute calibration of the instrument some experiments were carried out with a 1 : 5 (v/v) solution of benzene in carbon tetrachloride. Using about 6 μl. of the mixture we were thus able to inject with reasonable accuracy about 1 μl. of benzene. In this way reproducibility of the order of 5% was obtainable for the benzene peak area over several experiments and a rough value for the sensitivity of the detector per calorie was obtained.

With a hydrogen flow of 100 c.c./min. the basic rate of heat production by the flame is 240 cal./min.; 0·88 mg. of benzene, which has a heat of combustion of 8·8 cal., gave a peak of mean area 19·2° min., with a maximum temperature rise during elution of 11·2°. The rise in flame temperature for an excess heat production at the rate of 1 cal./min. is therefore:

$$\Delta T = 19{\cdot}2/8{\cdot}8 = 2{\cdot}18^\circ \text{ min. cal.}^{-1}$$

Extrapolation of this value to a rate of heat production equal to that of the hydrogen flame itself gives a temperature rise of 520°. This value may be compared with the actual basic thermocouple temperature of 650°. A very rough estimate of the sensitivity of the micro-flame detector can thus be made on the assumption that the temperature of the thermocouple above room temperature is directly proportional to the heat liberated in the flame. Alternatively, if T is the thermocouple temperature and Q the heat liberated in the flame, the temperature increase δT due to an excess heat production δQ is given by $\delta T = \delta Q \times aT/Q$, where a is a constant close to unity, in our case 0·80.

The results which have been described emphasise a number of useful points regarding the micro-flame detector in gas–liquid partition chromatography. This detector has a sensitivity of the same order as that of the thermal conductivity detector but it is considerably simpler to construct and less troublesome in action. It responds to various substances according to their heats of combustion rather than to the number of moles in the sample. The method is therefore particularly suitable for the analysis of compounds of high molecular weight. While the thermal conductivity detector has roughly the same sensitivity per mole for any homologous series, the micro-flame detector has roughly the same sensitivity per g. The thermal conductivity detector should therefore be employed in the analysis of permanent gases, non-combustibles, and substances of low heats of combustion (nitrogen, oxygen, rare gases, hydrogen, methane, ethane, carbon tetrachloride, chloroform, etc.), while the micro-flame detector is the more suitable in the analysis of mixtures containing substances of higher molecular weights and higher heats of combustion such as those found in petroleum distillates.

THE UNIVERSITY, WEST MAINS ROAD, EDINBURGH.

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[1] Scott, *Nature*, 1955, **176**, 973.
[2] Wirth, personal communication.

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[30]

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77. *The Speed of Analysis by Gas Chromatography.*

By John H. Knox.

Expressions are derived for the minimum possible analysis times on capillary and packed columns in terms of the separation S and the column-pressure drop Δp. It is shown that there is little to choose between the speed of packed and of capillary columns.

There is still some difference of opinion as to whether analysis by gas chromatography is faster on a packed or on a capillary column. Soon after capillary columns were first described[1] it was clear that their use enabled columns of very high theoretical plate efficiency to be operated successfully, and analyses of a given plate efficiency to be carried out much faster than had been possible with packed columns. It was therefore natural that capillary columns were considered to be faster than packed columns, but Purnell[2,3] has claimed that in certain circumstances the packed column may be faster than the capillary. His analysis is based upon the differences in the operating conditions of the two types of column and rests particularly on the difference between the experimentally important separation factor S and the theoretically important plate number N (see equations 1, 2, and 4 below). As we now show, there is little to choose between the two types of column if one evaluates the minimum analysis time consistent with certain experimental limitations.

An isothermally operated gas-chromatographic column, packed or capillary, can be regarded as a system of five degrees of freedom. The most convenient independent variables are: (1) the column length, l; (2) the column radius for a capillary or the particle radius for a packed column, r; (3) the thickness of the liquid film, d, or alternatively the ratio of film thickness to radius, $\rho = d/r$; (4) the linear gas velocity, u; (5) the solubility, α, of the substance being chromatographed or the closely related column capacity coefficient k (see equation 3).

Two other factors can be varied, but for practical reasons they cannot be regarded as truly independent variables, *viz.*, the properties of the carrier gas and of the liquid phase. They enter into the theoretical equations for the speed of analysis in the form of the diffusion coefficients D_g and D_l of substances in the gas and the liquid phase, and the viscosity η of the gas. Change of carrier gas or liquid phase alters these properties discontinuously, but changes of the column temperature and pressure alter them continuously. In practice, however, both the nature of the phases and their temperature and pressure are fixed by considerations other than the attainment of high analysis speeds. We therefore regard them as variables fixed beforehand and we take D_g, D_l, and η as constants.

The number of theoretical plates, which is the basic measure of the efficiency of any column, is denoted by N and is related to the shape of individual chromatographic peaks by any of several well-known formulæ, one of which is

$$N = 8(V_R/w_e)^2 = 8[(V'_R + v_g)/w_e]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where V_R = total retention volume from the beginning of the chromatogram; V'_R = retention volume from the " air peak," the net retention volume; v_g = gas phase volume of the column = retention volume of the " air peak "; w_e = peak breadth (in same units as V_R) at $1/2{\cdot}718$ of the maximum peak height.*

For the purpose of evaluating the efficiency with which a column can separate substances, a more useful quantity is the separation factor S, defined as

$$S = 8(V'_R/w_e)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

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* All the mathematical symbols used are summarised in an appendix (p.).

The net retention volume, rather than the total retention volume, is related directly to the solubility,

$$\begin{aligned} V'_{\mathrm{R}}/v_{\mathrm{g}} &= k = \alpha v_{\mathrm{l}}/v_{\mathrm{g}} \\ &= \alpha\beta d/r = \alpha\beta\rho \quad \ldots\ldots \quad (3) \end{aligned}$$

where v_{l} and v_{g} are the volumes of the liquid and the gas phase in the column and β is a constant for any type of column. For a capillary $\beta = 2$; for a packed column $\beta = 3(1 - e)/e$ where $e =$ the porosity of the packed column (fraction of total volume occupied by gas). Generally e is about 0·4 and $\beta \approx 4$. S and N are thus related by the equation

$$N = S[(1 + k)/k]^2 \quad \ldots\ldots \quad (4)$$

For a column of length l the height of a theoretical plate (HETP) is

$$H = l/N = (l/S)[k/(1 + k)]^2 \quad \ldots\ldots \quad (4a)$$

Theoretical equations for H in terms of column parameters already defined have been given by van Deempter (see Desty *et al.*[4]) for packed columns

$$H = 4\lambda r + \frac{2\gamma D_{\mathrm{g}}}{u} + \left\{\frac{1}{25}\cdot\left(\frac{k}{(1 + k)}\right)^2 \frac{r^2}{D_{\mathrm{g}}} + \frac{2}{3}\cdot\frac{k}{(1 + k)^2}\cdot\frac{d^2}{D_{\mathrm{l}}}\right\} u \quad \ldots \quad (5a)$$

$$= 4\lambda r + \frac{2\gamma D_{\mathrm{g}}}{u} + \left\{\frac{1}{25}\left(\frac{k}{1 + k}\right)^2 \frac{1}{D_{\mathrm{g}}} + \frac{2}{3}\cdot\frac{k}{(1 + k)^2}\cdot\frac{\rho^2}{D_{\mathrm{l}}}\right\} ur^2 \quad \ldots \quad (5b)$$

$$= A + B/u + (C_1 + C_2)u \quad \ldots\ldots \quad (5c)$$

and by Golay [1] for capillary columns

$$H = \frac{2D_{\mathrm{g}}}{u} + \left\{\frac{1 + 6k + 11k^2}{24(1 + k)^2}\cdot\frac{r^2}{D_{\mathrm{g}}} + \frac{2}{3}\,\frac{k}{(1 + k)^2}\cdot\frac{d^2}{D_{\mathrm{l}}}\right\} u \quad \ldots \quad (6a)$$

$$= \frac{2D_{\mathrm{g}}}{u} + \left\{\frac{1 + 6k + 11k^2}{26(1 + k)^2}\cdot\frac{1}{D_{\mathrm{g}}} + \frac{2}{3}\,\frac{k}{(1 + k)^2}\cdot\frac{\rho^2}{D_{\mathrm{l}}}\right\} ur^2 \quad \ldots \quad (6b)$$

$$= B/u + (C_1 + C_2)u \quad \ldots\ldots \quad (6c)$$

There are four terms in the equation for a packed column, and three in that for a capillary column. They are respectively the contributions of: A) eddy diffusion due to different paths round particles in a packed column, where λ is a constant of the order of unity; this effect is absent in a capillary column; (B) longitudinal diffusion, where γ is a constant of the order of unity; (C_1) and (C_2) the slowness of transverse diffusion in the gas and the liquid phase respectively. It may be noted that the liquid transverse diffusion term is the same for both packed and capillary columns, while the gas-phase transverse diffusion term is generally greater for capillary columns.

Experimentally (A) is apparently relatively unimportant for packed columns with small particles,[5,6] and for convenience we set $A = 0$, noting that we thereby make the packed column rather more efficient than it would actually be in practice. Since we are interested in the separation factor rather than theoretical plate number, we replace H by the value given in equation (4*a*):

$$\text{Packed: } S^{-1} = \left(\frac{1 + k}{k}\right)^2\cdot\frac{2\gamma D_{\mathrm{g}}}{ul} + \left\{\frac{1}{25D_{\mathrm{g}}} + \frac{2}{3}\cdot\frac{1}{k}\cdot\frac{\rho^2}{D_{\mathrm{l}}}\right\} ur^2/l \quad \ldots \quad (7)$$

$$\text{Capillary: } S^{-1} = \left(\frac{1 + k}{k}\right)^2\cdot\frac{2D_{\mathrm{g}}}{ul} + \left\{\frac{1 + 6k + 11k^2}{24k^2D_{\mathrm{g}}} + \frac{2}{3}\cdot\frac{1}{k}\cdot\frac{\rho^2}{D_{\mathrm{l}}}\right\} ur^2/l \;. \quad (8)$$

The two equations may be summarised in the form

$$S^{-1} = P/ul + Qur^2/l \quad \ldots\ldots \quad (9)$$

The retention time of any substance whose column partition coefficient is k is

$$t = (1 + k)l/u \qquad (10)$$

The linear gas velocity is related to column length, the column or particle radius, and the pressure drop Δp across the column by the Poiseuille equation for a capillary tube and by the Kozeny–Carman equation[7] for a packed column. These equations are:

Poiseuille equation: $$u = \Delta p r^2/8\eta l \qquad (11)$$

Kozeny–Carman equation: $$u = (\Delta p r^2/9\eta l)e^2/\mu(1 - e)^2$$
$$= f/ae = f/a_g \qquad (12a)$$

where μ is a constant between 4·5 and 5·0 for spheres; f = volume flow rate through column; a = total cross-sectional area of column. Direct experiment[8] shows that for randomly packed spheres the porosity lies between 0·36 and 0·42. This is confirmed by experiments described later for columns packed by the conventional gas-chromatographic procedure. With $e = 0{\cdot}38$ and $\mu = 4{\cdot}8$, equation (12a) becomes

$$u = \Delta p r^2/115\eta l \qquad (12b)$$

Both equations may be summarised in the form

$$u = r^2/Dl \qquad (13)$$

The variables u and l can thus be replaced by t and D in equation (9), giving

$$S^{-1} = PD/r^2 + Q(1 + k)r^2/t \qquad (14)$$

This equation involves the variables S, k, r, Δp, ρ, and t.

The time for analysis can be varied by changing any of the first five variables and can theoretically be reduced to zero. However, this possibility is not of practical importance since it involves making S zero or Δp infinite. In order to obtain a practicable value for the minimum time these two variables must be restricted. One inevitably works with an apparatus which can develop a maximum pressure drop across any column. Since any increase in Δp (*i.e.*, decrease in D) can be made to increase the speed of analysis we can, for the purpose of evaluating the maximum speed, regard Δp as being a constant.

Further, one is always interested in obtaining a given degree of separation between substances. This implies a minimum S. The separation factor required for any two substances has been evaluated by Glueckauf[9] in terms of the desired purity of the two substances and their relative solubilities in the liquid phase. The closer the solubilities and the higher the purity required the greater is the separation factor required. Purnell has deduced that the separation factor required, when the peaks are separated by six standard deviations, is approximately

$$S = 36[(\alpha_{12}/(1 - \alpha_{12})]^2 \qquad (15)$$

where α_{12} is the ratio of the solubilities of the two substances.

The problem is therefore to derive the minimum time for the elution of a substance from a column with a given separation factor S and working with a pressure drop Δp. We assume, first, that k and ρ are constant and determine the optimum column radius. This is equivalent to considering the elution of a given substance from a series of columns all containing the same percentage of liquid phase. We then examine how the analysis time at the optimum column radius can be further reduced by altering k and ρ.

Differentiating equation (14) and setting $dt/dr = 0$, we have

$$-2PD/r^3 + 2Qr(1 + k)/t = 0 \qquad (16a)$$
$$t = Q(1 + k)r^4/PD \qquad (16b)$$

Substituting into equation (14), we obtain

$$t = 4PDQ(1 + k)S^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$r^2 = 2PDS \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The other parameters can then be evaluated from equations (4*a*), (10), and (13). They are given in Table 1.

The values of H and u evaluated in this way are readily shown to be those for the minimum in the well-known HETP–u curve. Equations (5) and (6) may be written in the form

$$\begin{aligned} H &= 2\gamma D_g/u + [k/(1 + k)]^2 Qr^2 u \quad . \quad . \quad . \quad . \quad . \quad . \quad (19) \\ &= B/u + Cu \end{aligned}$$

The plot of H against u is a curve with a minimum H value given by $H^2 = 4BC$ at a linear velocity given by $u^2 = B/C$; *i.e.*,

$$H^2 = 8\gamma D_g[k/(1 + k)]^2 Qr^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$u^2 = 2D_g[(1 + k)/k]^2/Qr^2 = (2DSQ)^{-1} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

These values are identical with those of Table 1.

TABLE 1. *Columns parameters for minimum analysis times.*

$$\begin{aligned} \text{Time: } t &= 8\gamma DD_g[(1 + k)^3/k^2]S^2Q \\ \text{Radius: } r^2 &= 4\gamma DD_g[(1 + k)/k]^2 S \\ \text{Length: } l^2 &= 2r^4SQ/D \\ \text{Gas velocity: } u^2 &= (2DSQ)^{-1} \\ \text{HETP: } H^2 &= 8\gamma D_g[k/(1 + k)^2]Qr^2 \end{aligned}$$

$$D_{\text{capillary}} = 8\eta/\Delta p \qquad D_{\text{packed}} = (43\eta/\Delta p)(1 - e)^2/e^2 \qquad e = 0{\cdot}38$$

$$\gamma_{\text{capillary}} = 1{\cdot}00 \qquad \gamma_{\text{packed}} = \text{constant of order of unity}$$

$$Q_{\text{capillary}} = \left\{\frac{1 + 6k + 11k^2}{24k^2D_g} + \frac{2}{3k}\cdot\frac{\rho^2}{D_l}\right\} \qquad Q_{\text{packed}} = \left\{\frac{1}{25D_g} + \frac{2}{3k}\cdot\frac{\rho^2}{D_l}\right\}$$

If therefore one has a given Δp and requires a definite S value, and if one can choose the column radius freely, there is no possibility of obtaining a faster analysis by using a longer, wider column with intrinsically a higher S value, even if a high gas velocity is used. Only if one is limited to the available column radii or particle diameters can one hope to increase speed by using too high a gas velocity. In such a situation the column length is decreased and the velocity increased until the separation has declined to the minimum acceptable value. In view of this, the device described by Desty[10] for winding glass capillaries of any desired radius will be a valuable aid in the experimental approach to high-speed gas chromatography.

The explicit equations for the minimum time are

$$\text{Packed:} \qquad t = 8\gamma DS^2 \cdot \frac{(1 + k)^3}{k^2} \cdot \left\{0{\cdot}040 + \frac{2}{3}\frac{\rho^2}{k}\frac{D_g}{D_l}\right\} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$\text{Capillary:} \qquad t = 8DS^2 \cdot \frac{(1 + k)^3}{k^2} \cdot \left\{\frac{1 + 6k + 11k^2}{24k^2} + \frac{2}{3}\frac{\rho^2}{k}\frac{D_g}{D_l}\right\} \quad . \quad . \quad . \quad (23)$$

t can always be reduced by reducing ρ, and a minimum for t is obtained at $\rho = 0$. Variation of k for $\rho = 0$ shows that the ultimate minimum occurs for a value of k close to 2 for both types of column. However, this minimum is unattainable in practice since a value of $\rho = 0$, with $k = 2$, means that the solubility α must be infinite. In order to obtain minimum times for the two types of column which have any physical significance it is necessary to consider a series of values of ρ, which are within a physically acceptable range from the point of view of the solubilities demanded. For organic vapours in hydrogen and nitrogen at atmospheric pressure, D_g takes the values of approximately 0·6 and 0·1 cm.^{2} sec.$^{-1}$. D_l for organic substances in the type of liquid used for gas chromatography is probably between 5×10^{-6} and 5×10^{-7} cm.^{2} sec.$^{-1}$. The ratio D_g/D_l is thus likely to be in the range of 10^4—10^6. In the Figures the values of $t/8\gamma DS^2$ have been plotted against k for the values of $\rho^2 D_g/D_l$ given against the individual curves. The curves have minima depending upon the value of $\rho^2 D_g/D_l$ from $k = 2$ to $k = 30$. The values of k and α for the minimum times are given in Table 2 for both types of column. One notes that the minimum values of $t/8\gamma DS^2$ for the packed column are lower than for the capillary by factors ranging from 2 for rather thick liquid films to 15 for the thinnest films. However, D is about 15 times larger for the packed column than for the capillary. The minimum analysis times are thus comparable on the two columns for very thin films but greater on the packed column for the thicker films. It should, however, be pointed out that this dependence upon relative film thickness results from the different dependence of Q upon k for the two types of column. A unified theoretical treatment of the capillary and packed columns might well eliminate this difference.

Plots of log $(t/8\gamma DS^2)$ *against* log K *for* (A) *packed columns and* (B) *capillary columns.*

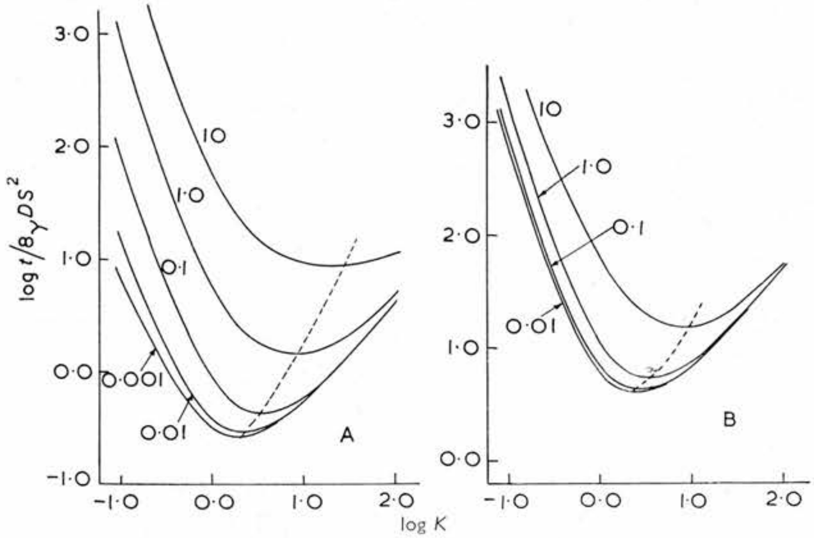

TABLE 2. *Values of k for minimum analysis times at different* ρ *values.*

Log$_{10}$ ρ for D_g/D_l			$\frac{t}{8\gamma DS^2}$	k	Solubility for D_g/D_l		
10^4	10^5	10^6			10^4	10^5	10^6
Capillary columns							
−1·5	−2·0	−2·5	15·3	10	160	500	1600
−2·0	−2·5 *	−3·0	5·5 *	3·3 *	165	520 *	1650
−2·5	−3·0	−3·5	4·2	2·5	400	1250	4000
−3·0	−3·5	−4·0	4·0	2·0	1000	3200	10,000
	zero		4·0	2·0		infinite	
Packed columns							
−1·5	−2·0	−2·5	8·6	30	240	740	2400
−2·0	−2·5	−3·0	1·42	9	220	710	2200
−2·5	−3·0 *	−3·5	0·46 *	4 *	320	1000 *	3200
−3·0	−3·5	−4·0	0·29	2·5	630	2000	6300
−3·5	−4·0	−4·5	0·27	2·0	1700	5300	17,000
	zero		0·27	2·0		infinite	

* Conditions chosen for evaluation of minimum practicable analysis times given in Tables 3 and 4.

The solubility of the chromatographed vapour in the liquid phase at the minimum analysis time for any relative film thickness varies only slightly when the film is thick, but begins to increase rapidly as it decreases below a value for which $\rho^2 D_g/D_l \precsim 10^{-1}$. At this point the time for analysis is only about twice the ultimate minimum. This value thus makes a reasonable compromise between the desirability of a close approach to the ultimate minimum time and the difficulty of meeting the increasingly severe solubility requirements. It may be noted that a slightly higher solubility is required with a packed column for any given approach to the ultimate minimum analysis time than with a capillary column. The difference is however slight and may well result from differences in the methods of derivation of the van Deempter and the Golay equation. The rather high solubilities required for any reasonable approach to the minimum analysis time result from the great difference between the liquid- and the gas-phase diffusion coefficients. If this difference is decreased the solubility required is less. There will therefore be some practical advantage in using nitrogen or argon as carrier gases instead of hydrogen or helium, and in using high pressures (when D_g is lower). Nitrogen, however, has a disadvantage in having a higher viscosity than hydrogen (by a factor of about 2), and since D is proportional to the viscosity one loses some analytical speed if nitrogen is used, but since viscosity does not change with pressure this disadvantage is not encountered when higher operating pressure are used. However, the slight disadvantage of using nitrogen as carrier may be far outweighed by the difficulty of obtaining a high enough solubility to make full use of the advantages of hydrogen or helium. Nevertheless, solubilities of the order of 10^2—10^3 are normal in gas chromatography [11] and there should not be any serious difficulty on this score in approaching the conditions for high speed analysis except when one is dealing with highly volatile substances. For fast analysis of these it will be necessary to work with refrigerated columns. Several liquid phases have already been successfully used by the author for columns operating at −80°.

A rough idea of the minimum practicable analysis times along with the other column mensions may be obtained by taking values of the parameters η, D_g, D_l, ρ, and Δp. The relevant data are given in Tables 3 and 4 for capillary and packed columns. The value of $\rho = 10^{-2{\cdot}5}$ taken for the capillary column is comparable with the current experimental

TABLE 3. *Capillary-column parameters for minimum analysis times: nitrogen as carrier gas.*

$D_g = 0{\cdot}10$. $\eta = 2{\cdot}0 \times 10^{-4}$. $k = 3{\cdot}3$. $\alpha = 520$. $D_l = 10^{-6}$. $D = 1{\cdot}6 \times 10^{-9}$. $Q = 7{\cdot}4$.
$\Delta p = 10^6$ (1 atm.).

(All quantities expressed in c.g.s. units.)

Separation factor	Time for elution (sec.)	Column diam. (mm.)	Column length (cm.)	Gas velocity (cm./sec.)
100	7×10^{-4}	0·0065	0·10	650
1000	7×10^{-2}	0·020	3·2	200
10,000	7	0·065	100	65
100,000	700	0·20	3,200	20
1,000,000	70,000	0·65	100,000	6·5
S	$7 \times 10^{-8} S^2$	$6{\cdot}5 \times 10^{-5} S^{\frac{1}{2}}$	$10^{-4} S^{\frac{3}{2}}$	$6{\cdot}5 \times 10^3 S^{-\frac{1}{2}}$

TABLE 4. *Packed-column parameters for minimum analysis times: nitrogen as carrier gas.*

$D_g = 0{\cdot}10$. $\eta = 2{\cdot}0 \times 10^{-4}$. $k = 4{\cdot}0$. $\alpha = 1000$. $e = 0{\cdot}38$. $D_l = 10^{-6}$. $\Delta p = 10^6$. $Q = 0{\cdot}57$.
$D = 2{\cdot}4 \times 10^{-8}$. $\gamma = 1{\cdot}5$.

(All quantities expressed in c.g.s. units.)

Separation factor	Time for elution (sec.)	Particle diam. (mm.)	B.S.S. mesh	Column length (cm.)	Gas velocity (cm./sec.)
100	0·0013	0·03	420	0·15	600
1000	0·13	0·09	130	5·0	190
10,000	13	0·3	42	155	60
100,000	1300	0·9	13	5,000	19
1,000,000	130,000	3·0	4·2	155,000	6
S	$1{\cdot}3 \times 10^{-7} S^2$	$3{\cdot}0 \times 10^{-4} S^{\frac{1}{2}}$	12·7/(diam.)	$1{\cdot}55 \times 10^{-4} S^{\frac{3}{2}}$	$6 \times 10^3 S^{-\frac{1}{2}}$

values and represents a 0·65% by volume coating with liquid phase. The value of $\rho = 10^{-3}$ taken for the packed column represents a coating of approximately 0·2% of the total volume of the column. When using Celite, which has a packed density of about 0·25 g./ml., this is equivalent to a 0·6% loading by weight. This is rather less than is normal in high-efficiency columns but it is not unreasonably small.

From Tables 3 and 4 it is seen that the particle radius for the packed column is some three times the radius of the equivalent capillary, whereas ρ is about three times less. The liquid film thicknesses are thus similar. For columns giving an S value of 10^3 the film thickness will be only about 400 Å, although for an S value of 10^5 it is 4000 Å. Condon [12] has recently shown that in a working capillary column a film thickness of about 3000—4000 Å appeared quite stable and was evenly deposited. One might question whether thicknesses of less than 1000 Å could be deposited evenly, but this is till a matter for experiment. With such low liquid-phase loading it appears that normal gas-chromatographic supports such as Celite and firebrick should be replaced by more inert materials such as Nylon or glass beads. The rough porous materials which generally are used are only valuable if a high liquid-phase loading is required. They have the disadvantage that the liquid phase may well be trapped in pores which are relatively inaccessible, leading to larger values of C than would be predicted from the theoretical equation. Further, firebricks and Celite have undesirable adsorptive properties which will become increasingly noticeable as the amount of liquid phase is reduced.

It appears then that there is little to choose between the two types of column as far as practicable maximum analysis speeds are concerned. Both appear to be capable of considerably greater speeds than have so far been attained. Theory indicates that the packed column is likely to be somewhat slower than the capillary especially if it is remembered that the eddy diffusion term has been taken as zero throughout the treatment given above.

We are therefore free to consider which type of column is the best for any type of analysis on grounds other than speed. It is clear that the operation of a capillary column with $S = 1000$ where diameter = 0·02 mm. and $l = 3·2$ cm. is going to be exceedingly difficult in practice because of the exceedingly small column volume and the necessity of using an incredibly small sample size and very small injection systems and detectors. With a packed column, the gas-phase volume of the column can be some 100 times greater than that of the corresponding capillary. The sample size, injection system, and detector volume can be correspondingly increased in size. Thus the packed column is certainly the most convenient for analyses requiring values of S up to about 10,000. For higher values of S the size of the packed column makes it unwieldy, and the capillary column has obvious advantages.

EXPERIMENTAL

The Kozeny–Carman equation [7] is known to hold well for spherical particles with the constant $\mu = 5$. The particles used in gas chromatography are not normally spherical and may therefore offer rather different resistances to flow from that predicted by the equation.

In order to test this, columns were prepared by the usual gas-chromatographic procedure containing closely screened fractions of various supports, *viz.*, Celite, firebrick (Moler Products, Colchester), and glass beads. The true porosity of the glass beads was determined by measuring their packed volume and the volume of water displaced by them. Both 60—90 and 2 5—4 mesh beads had a porosity of 0·36—0·38, in agreement with the literature values.[7]

The volume-flow rates through the columns were measured with a soap-bubble flow meter and were linearly proportional to the pressure drop across the columns for all particles studied. The results are presented in Table 5, where the equation is tested by evaluating the viscosity of the gas (oxygen) on the assumption that $\mu = 4·8$ and $e = 0·38$. For glass beads and firebrick the agreement between the calculated and true values of the viscosity is good, but for Celite the calculated viscosities are low, indicating that the porosity is higher than 0·38. Calculations

TABLE 5. *The porosity of gas-chromatographic supports.*

Gas, oxygen. Viscosity of oxygen = $2·0 \times 10^{-4}$ poise. Porosity assumed = 0·38. $\mu = 4·8$.

Material	Mesh B.S.S.	Particle diam. (mm.)	$10^4 \times$ Viscosity by K.–C. eqn.	Calc. porosity
Firebrick	40—43	0·310	1·59	0·40
	60—65	0·203	1·95	0·38
	90—95	0·137	1·98	0·38
	140—150	0·085	1·40	0·41
Glass spheres	60—65	0·203	1·95	0·38
Celite	60—65	0·203	1·09	0·44
	90—95	0·137	0·75	0·47
	140—150	0·085	0·65	0·49

of the porosity assuming $\mu = 4·8$, and taking the correct viscosity for oxygen give the values in the last column of the Table. For Celite the calculated porosity increases as the particle diameter decreases. This suggests that the particles are themselves somewhat porous and that the importance of flow through the particles increases as the space between them becomes more and more constricted. For high-speed chromatography diffusion in and out of the Celite granules may become a limiting process and could reduce efficiencies below the theoretically attainable limit.

Conclusions.—(1) There should in theory be no significant difference in the ultimate speeds attainable with capillary and packed columns if they are operated under the same external experimental conditions and if the same separation number is required. (2) For the highest speed, the column of the correct dimensions has to be operated at the gas velocity which gives the minimum HETP. (3) Hydrogen and helium can give faster analysis than nitrogen and argon if the more severe solubility requirements can be met. (4) The solubility required for maximum speed on a packed column is slightly greater than that required for a capillary column. (5) Maximum speed is obtainable with a coating of roughly 0·5% (by vol.) in a capillary and of 0·2% (by vol.) for a packed column. These represent roughly the same film thickness for equivalent columns. (6) Since such low % coatings are required, it is likely that inert packings such as glass beads, nylon, or Teflon spheres may eventually prove the best supports. Firebrick should certainly not be used for high-performance columns except for the analysis of particular mixtures which are not adsorbed by it. (7) The speed of analysis can be increased by increasing the pressure drop across the column but the average column pressure has little effect upon the speed.

APPENDIX: DEFINITIONS OF SYMBOLS

a, a_g, a_l	Cross-sectional areas of column, gas phase in column, and liquid phase in column.
α	Solubility: concentration of chromatographed substance in liquid phase divided by concentration in gas phase.
A, B, C_1, C_2	Generalised coefficients in plate-height equations defined in equations (5*c*) and (6*c*).
β	Constant characteristic of any type of column defined in equation (3).
γ	Constant in the van Deempter equation.
d	Average film thickness.
D	Generalised coefficient in viscosity (equation 13).
D_g, D_l	Diffusion coefficients of chromatographed substance in gas and liquid phases.
e	Porosity of a packed column.
f	Volume flow rate through column.
η	Viscosity of carrier gas.
H	Height equivalent to a theoretical plate, the HETP.
k	Column capacity coefficient: amount of chromatographed substance per unit length of column in liquid phase divided by amount per unit length in gas phase.
l	Length of column.
λ	Constant in the van Deempter equation.

μ	Constant in the Kozeny–Carman equation.
N	Number of theoretical plates.
P, Q	Generalised coefficients defined in equations 7, 8, and 9.
Δp	Pressure drop across column.
r	Radius of a capillary column, or radius of particles in a packed column.
ρ	Ratio of film thickness to radius: $\rho = d/r$.
S	Separation factor defined in equation (4).
t	Elution time for any substance.
u	Linear gas velocity in column.
v_g, v_l	Volumes of gas and liquid phases in column.
V_R	Total retention volume.
V_R'	Net retention volume: $V_R' = V_R - v_g$.
w_e	Peak breadth at a height 1/2·718 of the maximum.

THE UNIVERSITY, WEST MAINS ROAD,
EDINBURGH, 9.

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The Spreading of Air Peaks in Capillary and Packed Gas Chromatographic Columns

J. H. KNOX and LILIAN McLAREN
Department of Chemistry, University of Edinburgh, Scotland

▶ Current theories for the spreading of packets of unsorbed substances in gas chromatographic columns are considered. It is shown that the usual *HETP* equations can be cast into reduced forms and that various column parameters, in particular the geometrical parameters *A* and *A′*, can be found by curve fitting. The method is applied to the data from a capillary and a packed column. It is shown that within experimental error the Golay equation is obeyed quantitatively. The diffusion coefficient for ethylene in nitrogen is found to be 0.16 cm.^{2} sec.$^{-1}$ Comparison of the *HETP*'s for the capillary and packed column show that the tortuosity factor for glass beads is about 0.8. There is little evidence for eddy diffusion or coupled eddy diffusion as envisaged by Giddings. The eddy diffusion parameter λ is less than 0.15. The gas phase mass transfer coefficient is $C_v = 0.3 \times d_p^2/D_v = 0.0045$ second.

THE SPREADING of bands in gas chromatographic columns is usually considered in relation to an *HETP* equation. The commonest form of such equation can be written

$$H = L(\sigma/l_R)^2 = A + B/u + Cu \tag{1}$$

where u is the linear gas velocity in the column. A is the contribution to the *HETP* from the structural inhomogeneity of the column and is purely geometrical in nature. For open tubes A is zero. B/u results from longitudinal diffusion in the gas phase and Cu from the failure to attain complete equilibrium in and between the gas and liquid phases. The factor C is usually made up of several terms, one for each slow process contributing to the nonequilibrium. In the original van Deemter equation (*5*) only resistance to mass transfer in the liquid phase was considered to be important in making up C. However, Golay (*15*) in his treatment of open tubes showed that resistance to mass transfer in the gas phase should also be considered. Its practical importance for open tubes or capillaries has been established by Desty (*8*) and Scott (*22*). Golay pointed out that contrary to general belief resistance to mass transfer in the gas phase should be much more important in packed columns than in open tubes because of the irregularity of the packing. Recent work has supported this. C_g is often comparable with C_l and in certain cases considerably greater. Dal Nogare and Chiu (*4*) for example have established that C is definitely nonzero for both weakly and strongly sorbed substances. For both types C_l should theoretically be zero and C is therefore due entirely to slow processes in the gas phase. Norem (*20*) has shown that there is a distinct upward trend in the *HETP vs. u* curves for unsorbed peaks and hence C_g must have a significantly positive value. This is supported by the results of Kieselbach (*17*) although his curves for air peaks show only a flattening at high gas velocities.

Several attempts have been made to treat gas phase mass transfer in packed columns quantitatively, but the problem is difficult because of the complex geometry of a randomly packed bed. Nevertheless substantial progress has been made by Jones (*16*), van Deemter (*6*), and Giddings (*9, 10*) although all treatments leave undetermined a number of geometrical constants.

Giddings (*11*) has criticized Equation 1 on the grounds that it misinterprets the role of the structural factors. He points out that the tortuosity of the stream lines in a packed column will tend to assist mass transfer. Thus a molecule in any stream will wander (even in the absence of lateral diffusion) from low to high velocity regions and will from time to time approach the surfaces of particles quite closely. There are thus two alternative ways in which a molecule may move across the gas stream and so encourage mixing of the gas, or approach closely to a particle surface so encouraging mass transfer. These are diffusion across the gas stream and movement along a tortuous stream line. Since the two effects are complementary they should be compounded like resistances in parallel rather than resistances in series, and their combined contribution to H should be written

$$H_g = (1/A' + 1/C_g u)^{-1} \qquad (2)$$

This value is of course less than $C_g u$. Whereas the classical eddy diffusion term A was expected to be of the order of the particle diameter, Giddings' parameter A' should be much larger, possibly some 10 particle diameters. The effect responsible for A' has been called coupled eddy diffusion (*11*). The process envisaged by Giddings which aids mass transfer in the gas phase appears to us to differ from the classical eddy diffusion as envisaged by van Deemter although it still derives from the geometry of the packing. Giddings (*12*) describes classical eddy diffusion as follows: "It arises from the nonequivalence in velocity of various flow paths which a fluid and solute follow in migrating through a porous support. The less tortuous higher velocity paths lead some solute to a position in advance of the bulk solute and vice versa. Because a random distribution of flow paths exists the resulting band spreading is random and the subsequent concentration profile Gaussian." The process so described does not assist mass transfer in the gas phase. Nevertheless, as the molecules of solute follow these tortuous paths they also move from regions of high to regions of low gas velocity which will aid mixing, and from time to time approach so closely to the surface of particles that the diffusional path thereto is substantially reduced which assists mass transfer. It therefore appears to us that both types of structural effect should be considered in a complete equation for the *HETP*, at least for purposes of discussion. Such an equation would read:

$$H = A + B/u + (1/A' + 1/C_g u)^{-1} + C_l u \qquad (3)$$

This equation is unfortunately too complex for a simple experimental test because of the different effects of column pressure drop on C_g and C_l (*13*), and the necessity for covering a wide range of u to isolate the different parameters. However, the equation is much simplified if consideration is restricted to unsorbed substances. C_l is now zero and both the second and third terms are pressure invariant since the pressure dependent quantities u and D_g appear only as the pressure independent ratio u/D_g. D_g and u can thus be taken to have constant values equal to those at the outlet of the column. The *HETP* equation now takes the simplified form

$$H = A + 2\gamma D_g^{\circ}/u^{\circ} + (1/A' + D_g^{\circ}/(\omega d_p^2 u^{\circ}))^{-1} \qquad (4)$$

The parameter ω introduced by Giddings (*9*) represents the square of the average distance in particle diameters that a solute molecule diffuses during the period of the gas phase equilibration process. According to Giddings ω is expected to be about unity for a packed column. This has been confirmed by the experiments of Norem (*20*) and Dal Nogare and Chiu (*4*). It is of interest to consider what value ω would take if a packed column could indeed be regarded as equivalent to a bundle of capillaries with the same linear flow resistance. The Kozeny-Carman equation (*1*) shows that a column of randomly packed spheres has the same linear flow resistance as a capillary whose radius is 0.135 times the particle diameter. If r in the Golay equation is replaced by 0.135 d_p, the factor C_g for $k = 0$ becomes $C_g = r^2/24D_g = d_p^2/1300D_g$ hence $\omega = 1/1300$. This comparison illustrates the enormous difference in performance between a packed and capillary column as far as gas phase mass transfer is concerned, and it encourages the hope that there is room for substantial improvement in the design of the former.

In the present work we have attempted to obtain information on the magnitudes of A, A' and ω for a packed column with unsorbed gas samples, and to verify the Golay equation quantitatively. The capillary column was 1664 cm. of 0.88-mm. i.d. nylon tubing and the packed column was four 150-cm. lengths of 3.8-mm. tubing packed with 0.50-mm. diameter glass beads.

When $A' = \infty$ Equation 4 reduces to the van Deemter form, Equation 1. This equation is symmetrical in u and $1/u$ and can be cast into a reduced form

$$h = v^{-1} + \alpha + v \qquad (5)$$

where $h = H/(BC)^{1/2}$; $v = u(C/B)^{1/2}$; and $\alpha = A/(BC)^{1/2}$. Plots of log h against log v are therefore symmetrical about the log v axis and show minima at $h = 2 + \alpha$ and $v = 1$. A series of such plots for different values of α is given in Figure 1. The asymptotes to all curves are the same, and it is worth noting that the critical region for determining α is that around the minimum. Plots of Log H against Log u° for any set of experimental data obeying Equation 1 must fit one of the theoretical curves apart from a displacement of the origin. It should therefore be a relatively simple matter in practice to show whether or not Equation 1 is obeyed and if it is to determine α by curve fitting. This method of determination is superior to methods such as extrapolation of the "straight" parts of H *vs.* u° or H *vs.* $1/u^{\circ}$ plots since these place undue emphasis on values of H obtained at high or low gas velocities while ignoring the most important points which are those in the vicinity of the minimum H. A logarithmic plot is also more satisfactory for the determination of the probable error in A or α since the proportional error in u° or H can readily be accommodated by making the points of a representative size. Generally the percentage error in H and u° will be the same for all readings, and all points can be made the same size in plotting the experimental data on a logarithmic scale.

For an accurate determination of the eddy diffusion parameter A or α, two requirements should be met. Firstly the region around the minimum H should be carefully mapped so that both $H_{\min}$ and u_{opt} are accurately determinable. Secondly the position of the asymptotes on both sides of the minimum should be reasonably clear. Ideally it is desirable to cover a hundredfold range of gas velocity so that at both high and low gas velocities eddy diffusion can be assumed to play an insignificant part in peak spreading. This is some 10 times the range usually covered and a really effective experiment will put a considerable strain on the experimental technique.

When $A = 0$ Equation 4 reduces to that suggested by Giddings (*11*):

$$H = B/u + (1/A' + 1/C_g u)^{-1} \qquad (6)$$

The reduced form of this equation is written

$$h = v^{-1} + (1/\alpha' + 1/v)^{-1} \qquad (7)$$

where h and v have the same meaning as before and $\alpha' = A'/(BC)^{1/2}$ This equation is no longer symmetrical in v and $1/v$ and shows a minimum h only when $\alpha' > 1$. The minimum is then at $h = 2 - 1/\alpha'$, $v = (1 - 1/\alpha')^{-1}$. Plots of log h against log v for different values of α' are given in Figure 2. The left-hand asymptote is the same for all curves and indeed on the low velocity side there is little difference between curves for different values of α'. The right-hand asymptotes on the other hand differ and are horizontal at $h = \alpha'$. All curves for $\alpha' > 1$ show inflection points. The effect represented by A' can therefore be observed only in experiments carried out at gas velocities

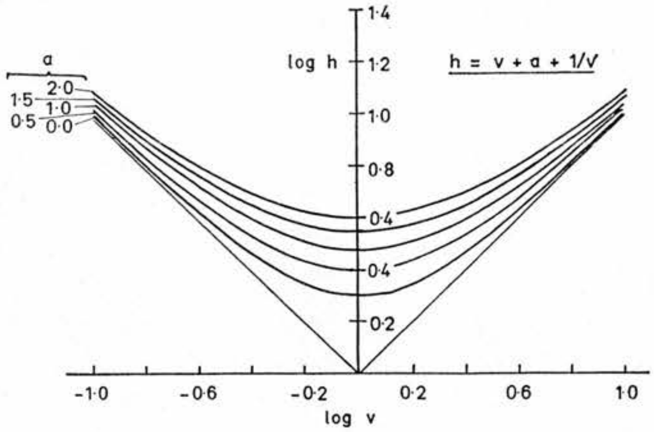

Figure 1. Logarithmic plot of reduced *HETP* against reduced linear gas velocity, $h = v + \alpha + 1/v$ with various values of α

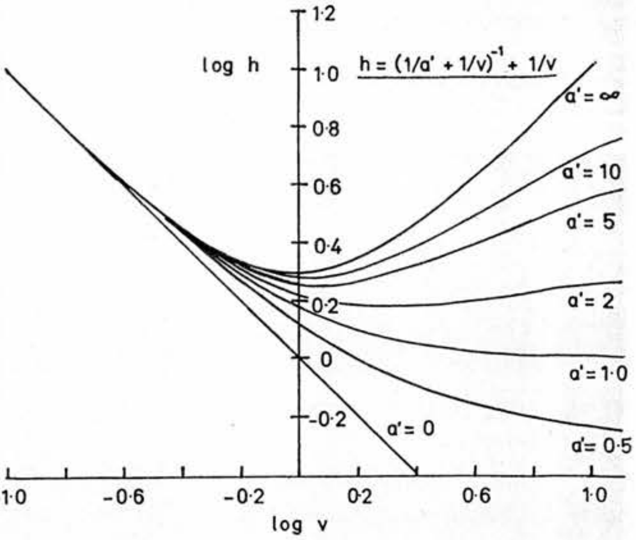

Figure 2. Logarithmic plot of reduced *HETP* against reduced linear gas velocity, $h = 1/v + (1/\alpha' + 1/v)^{-1}$ with various values of α'

considerably above those for minimum H. The curve fitting method clearly provides a general method for determining both A and A'. For the general case it would be necessary to provide theoretical curves for all possible combinations of α and α'. However a reasonable estimate of α and α' can be made by using the low velocity part of the curve to determine α and the asymmetry of the curve to determine α'.

Experimental work on the determination of A has been reviewed by Giddings (*12*). The main features of the data are their irreproducibility, the appearance of values of A much less than d_p, and the appearance of negative values of A. The view is now becoming general that A is probably close to zero for well constructed columns and that nonzero values result from imperfections in the rest of the apparatus. Littlewood (*19*) and Kieselbach (*18*) have for example shown that positive values of A can arise from a finite sample volume and from bad geometry of the column inlet and outlet. Other features which are likely to contribute to spurious eddy diffusion terms are dead volumes throughout the apparatus. Such dead volumes will normally result in tailed peaks. Both effects are likely to be more important with substances which have low retention times. In this connection it is significant that the early peaks in chromatograms are usually less symmetrical than later peaks. Negative values of A which have been reported several times (*3, 8, 19*) resulted in one case (*3*) from the use of average instead of outlet gas velocity but may also be explained by supposing a finite time constant for the injector or detector. The effect of this would be to add a finite width to any peak such that at high gas velocities an increasing proportion of the total peak width would be due to the time constant of the apparatus. Values of H at high flow rates would be too large and the dependence of H upon u too steep. Any method of analysis which laid emphasis on the points for high gas velocities (for example the extrapolation method) and assumed an *HETP* equation of form 1 would be likely to give negative values of A. In our own experiments this effect was significant. As with a finite sample volume this effect would be most serious for early peaks.

There is almost no experimental work on the possible magnitude of A'. Norem (*20*) has shown that there is a definite minimum in the *HETP vs. u* curve for air peaks in a packed column. Thus α' is likely to be at least two and probably greater than five (see Figure 2). Since $(BC)^{1/2}$ is generally of the order of d_p [Bohemen and Purnell's data (*3*) give $(BC)^{1/2}/d_p$ between 0.8 and 2.5 and values for air peaks are likely to be in the lower range], A' is probably at least five particle diameters. Unfortunately, to determine A' it is necessary to work in the high velocity region where any inadequacy in technique is likely to make the experimentally determined H too large to an increasing degree as u increases. Until the value of A' is clearly established by a number of different workers any published values must be regarded as upper limits.

EXPERIMENTAL

The main experimental difficulties in determining the spreading of air peaks in a gas chromatographic column have been noted by Norem (*20*). They are first, the difficulty of measuring peak widths accurately when they may be only some 100 mseconds, and second, the difficulty of isolating the spreading due to the column alone and eliminating that caused by external factors (injector, detector, etc.). Considerable care has to be taken to devise fast injectors and column arrangements which minimize dead space. Even so it is advisable to carry out experiments with long and short columns (*12*) and to subtract out the spreading due to the apparatus. Since the total spreading due to a number of independent or consecutive processes is given by

$$\sigma^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \ldots \qquad (8)$$

the spreading due to the column alone may be obtained from the total spreading and that due to the apparatus from the formula

$$w^2_{\text{column}} = w^2_{\text{total}} - w^2_{\text{apparatus}} \qquad (9)$$

In the present work, in spite of all precautions it was necessary to make this correction to the observed peak widths. At the highest gas velocities $w_{\text{apparatus}} = 0.44\ w_{\text{total}}$ and $w^2_{\text{column}} = 0.80\ w^2_{\text{total}}$.

We have evaluated the peak width by electronic measurement of the peak area and peak height. For this method to be reliable the peaks must be highly symmetrical. This was checked for peaks wider than 2 seconds by a $^1/_4$-second Brown recorder at a chart speed of 12 inches min.$^{-1}$ If the peaks are Gaussian the peak width is

$$w = \text{area}/\text{height} = \sqrt{2\pi}.\sigma = 2.51\sigma \qquad (10)$$

(it should be noted that w defined here differs from the usual "base width" equal to 4σ) and the number of plates in the column is

$$N = (t_R/\sigma)^2 = 2\pi(t_R/w)^2 \qquad (11)$$

Ethylene was used as solute and nitrogen was used as the carrier gas. A flame ionization detector was used because of its low detection volume and time constant. Hydrogen was added after the column at a rate of 30 ml. per min.$^{-1}$ and air was supplied at about 1000 ml. per min.$^{-1}$ The detector design was essentially that of Desty (*7*) except that a gauze basket was attached to the jet which served as the negative electrode. This increased the

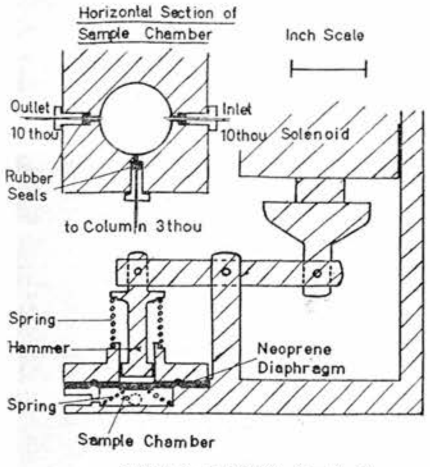

Figure 3. Details of hammer injector

(1 thou = 0.001 inch)

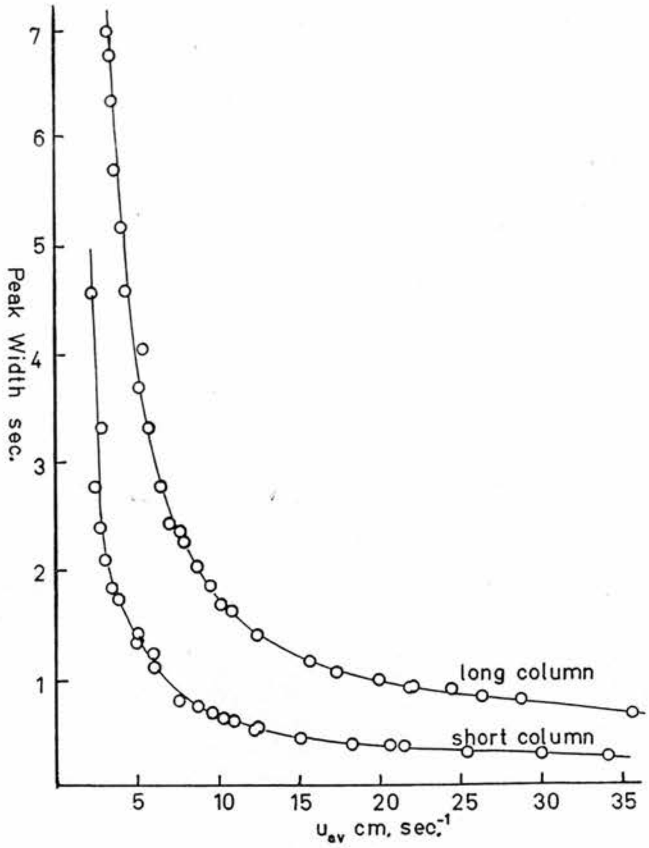

Figure 4. Variation of peak width with average linear gas velocity for long and short packed columns

linear range of the detector. The signal from the detector was supplied to an amplifier with a time constant of 10 mseconds and a most sensitive range of 5 volts per 10^{-9} amp. input. The signal was fed to an integrator and peak holding unit which stopped an electronic timer when the peak maximum was reached. The switch which started the timer also triggered the injector. Thus for each injection three parameters were recorded: retention time (seconds), peak height (volts), and peak area (volt seconds).

The injector was of the "hammer" type described by Scott (*21*). The original injector was redesigned for use with gases and details are shown in Figure 3. Ethylene was passed continuously through the injector chamber at a pressure slightly below that of the inlet to the column. This pressure was maintained by a rubber bladder containing ethylene which was mounted inside a glass bulb, itself held at a pressure slightly below that of the column by a slow leak through it from the column inlet to atmosphere. The line leading from the bladder to the injector was a piece of 0.25 mm. i.d. nylon and that from the injector to the column a 15-cm. length of 0.08 mm. i.d. nylon tubing. Because of the pressure drop between the column inlet and the injector chamber this piece of fine nylon tubing was continually purged by pure carrier gas. A small sample could be injected into the column (about 1 mm.^{3}) by energizing the solenoid which worked the hammer and momentarily compressed the gas in the chamber. The tube from the injector was led directly into the column to eliminate dead space. It was hoped that this type of injector would have a very small time constant but our results indicate that it may actually be as high as 0.2 second.

The connection of the columns to the detector was as direct as possible. With the capillary column (1664 cm. of 0.88-mm. i.d. nylon) the end was drawn down slightly and pushed well into the 1.6-mm. diameter hole leading to the 0.32-mm. diameter jet. With the packed column a piece of 0.88-mm. diameter nylon took part of the emergent gas stream to the detector while the remainder continually purged the inlet to this tube and so eliminated any stagnant backwaters. The proportion which passed to the detector could be varied by a needle valve on the rejected stream and was usually arranged so that a convenient size of sample passed to the detector. Under the best operating conditions the detector was slightly overloaded and therefore nonlinear. The effect was not great but to obtain the most reproducible results it was necessary to work to a constant peak height.

The packed column consisted of four 150-cm. lengths of 3.8-mm. diameter tubing packed with 0.50-mm. diameter glass beads. The packing was retained by 200-mesh gauze screens (*18*) held in position with glass tubing which just fitted inside the tube used for the column. The four lengths were connected together by short lengths of the 2-mm. i.d. tubing used to retain the screens.

To eliminate apparatus errors experiments were carried out with short columns, a 40-cm. length of capillary and a packed column consisting of 4- × 10-cm. lengths joined together in the same way as the 4- × 150-cm. lengths. Experiments with these columns showed that a significant part of the peak spreading was caused by factors outside the main columns. This is illustrated in Figure 4 for the packed column.

The peak widths for the short columns tend to a constant value as the velocity is increased. This suggests that the time constant of either the injector or detector was not as low as had been hoped. It is most probable that the delay occurred in the injector.

RESULTS AND DISCUSSION

The *HETP*'s derived from the corrected peak widths are plotted logarithmically in Figures 5 and 6 for the capillary and the packed columns. Values of various parameters derived from the plots are listed in Table I.

The points for the capillary column fit the theoretical curve $\alpha = 0, \alpha' = \infty$ within experimental error as expected for the Golay equation. The minimum *HETP* is 0.34 mm. compared with the theoretical value of $r/1.732 = 0.26$ mm. predicted by Golay. The somewhat higher experimental value may be due to overloading the detector. This point is being investigated. The linear gas velocity, u_{opt}, for minimum *HETP* is 11 cm. sec.$^{-1}$ From the Golay equation $u_{opt} = \sqrt{48} \times D_g/r$. Hence $D_g = 0.16$ cm.^{2} sec.$^{-1}$ This value compares with that derived from measurements on open tubes by Bohemen and

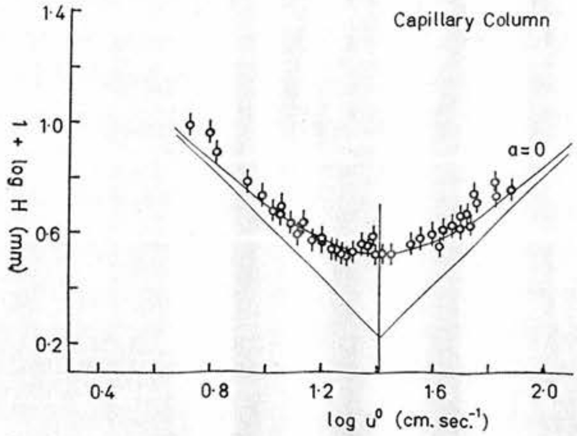

Figure 5. Logarithmic plot of *HETP* against u^0 for capillary column

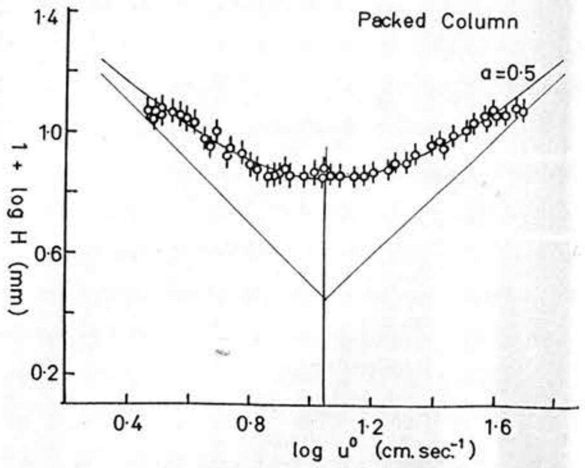

Figure 6. Logarithmic plot of *HETP* against u^0 for packed column

Purnell (*2*) for carbon dioxide in nitrogen (0.19 cm.² sec.⁻¹). For CO_2 and C_2H_4 in N_2 the Gilliland equation (*14*) gives 0.13 and 0.12 cm.² sec.⁻¹, respectively.

The plot for the packed column shows a higher degree of consistency than that for the capillary, the maximum error being about 5% in H or 2% in w. There is no evidence of asymmetry in the plot from which we may deduce that Giddings' geometrical parameter $\alpha' > 10$, and may be infinite. The classical eddy diffusion parameter α is certainly small. The best fit between the theoretical curves and the experimental data is with $\alpha = 0.5$. However, the points around the minimum are better fitted by $\alpha = 0$. There is therefore little evidence that structural inhomogeneity contributes to the *HETP* in a relatively narrow packed column (column diameter/particle diameter = 7.5). The minimum *HETP* is 0.71 mm. or $1.4 \times d_p$. Thus $A < 0.14$ mm. or $0.3 \times d_p$ and λ in the van Deemter equation is less than 0.14; $A' > 3.5$ mm. or $7 \times d_p$. The small value of A is in agreement with the results of Giddings and Robinson (*12*) and the prevailing evidence is that the eddy diffusion parameter is zero. The tortuosity factor γ in the van Deemter equation is readily determined by comparing the positions of the low velocity asymptotes for the capillary and packed columns. The value of γ depends somewhat on the values taken for α and α'. For the various reasonable combinations we obtain $\alpha = 0, \alpha' = \infty, \gamma = 0.85$; $\alpha = 0.5, \alpha' = \infty, \gamma = 0.70$; $\alpha = 0, \alpha' = 10, \gamma = 0.75$. Any of these values are acceptable and are in general agreement with previous estimates (*2, 19*). Using the value of D_g obtained from the capillary the parameter ω (Equation 4) may be evaluated for each set of α and α'. If $\alpha' = \infty$, $H_{\text{mix}} = (2 + \alpha)(2\gamma\omega)^{1/2}.d_p$; if $\alpha = 0$, $H_{\min} = (2 - 1/\alpha')(2\gamma\omega)^{1/2}.d_p$. The value of ω like γ depends on the values taken for α and α': for $\alpha = 0$, $\alpha' = \infty$, $\omega = 0.30$; $\alpha = 0.5$, $\alpha' = \infty$, $\omega = 0.23$; $\alpha = 0$, $\alpha' = 10$, $\omega = 0.36$. These values agree well with that deduced from Norem's results (*9, 20*). They indicate that a solute molecule must on the average diffuse about half a particle diameter within the time constant of the equilibration process. This compares with about one tenth of the tube diameter in a round capillary. Since the particle diameter in a packed column is about four times the diameter of the capillary which has the same linear flow resistance the solute molecule must have to diffuse about 20 times as far in the packed column as in the equivalent capillary. The whole process of gas phase mass transfer is thus about 400 times as slow. This difference emphasizes the great difference in the speed of analysis possible with the present types of packed columns when compared with capillaries and fully substantiates Golay's original suggestion. One of the present challenges in gas chromatography is to produce a packed column structure which has a higher permeability than the conventional packed column and a lower gas phase mass transfer coefficient.

LIST OF SYMBOLS

A = eddy diffusion coefficient
A' = Giddings' coupled eddy diffusion coefficient
α, α' = reduced eddy diffusion terms (Equation 5)
B = longitudinal diffusion coefficient
C = nonequilibrium coefficient
C_g, C_l = coefficients for resistance to mass transfer in gas and liquid phases
γ = tortuosity factor, $B = 2\gamma D_g$
D_g = gas phase diffusion coefficient of solute in carrier gas
D_g^o = value of D_g at column outlet
d_p = particle diameter in packed column

Table I. Column Operating Conditions and Experimental Parameters

	Packed	Capillary
Length	593 cm.	1664 cm.
Diameter of tube	0.38 cm.	0.088 cm.
Diameter of beads	0.050 cm.	...
Carrier gas	Nitrogen	Nitrogen
Solute	Ethylene	Ethylene
Temperature	18° C.	18° C.
Outlet pressure	Atmospheric	Atmospheric
$H_{\min}$	0.071 cm.	0.034 cm.
u_{opt}	11 cm. sec.⁻¹	26 cm. sec.⁻¹
α	<0.5	Zero
α'	>10	Infinite
D_g (C_2H_4 in N_2)		0.16 cm.² sec.⁻¹
Tortuosity, γ	$\alpha = 0$ $\alpha' = \infty$ 0.85	
	$\alpha = 0.5$ $\alpha' = \infty$ 0.70	
	$\alpha = 0$ $\alpha' = 10$ 0.75	
ω	$\alpha = 0$ $\alpha' = \infty$ 0.30	
	$\alpha = 0.5$ $\alpha' = \infty$ 0.23	
	$\alpha = 0$ $\alpha' = 10$ 0.36	
A and A'	<0.014 cm. >0.35 cm.	
A/d_p and A'/d_p	<0.28 >7	
$(BC)^{1/2}$	0.035 cm.	0.017 cm.
$(BC)^{1/2}/d_p$ and $(BC)^{1/2}/2r$	0.71	0.19
$H_{\min}/d_p$ and $H_{\min}/2r$	1.42	0.39

H = height of a theoretical plate ($HETP$)
$H_{\min}$ = minimum $HETP$
h = reduced $HETP$ (Equation 5)
k = column capacity coefficient = amount of solute per unit length in liquid phase divided by amount per unit length in gas phase
L = column length
λ = eddy diffusion parameter, $A = 2\lambda d_p$
N = number of theoretical plates in column
r = radius of capillary
σ = standard deviation
t_R = retention time
u = linear gas velocity
u^o = value of u at column outlet
u_{opt} = linear gas velocity at minimum $HETP$
v = reduced linear gas velocity (Equation 5)
w = peak width (Equation 10)
ω = parameter in gas phase mass transfer coefficient (Equation 4)

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