

ABSTRACT OF THESIS

Name of Candidate John W. Falconer
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Title of Thesis The High Temperature Oxidation of Propane.

Propane is the simplest hydrocarbon possessing structural properties such as secondary carbon atoms which are typical of the higher aliphatic hydrocarbons, and for this reason its oxidation has been extensively investigated. The oxidation can proceed by two distinct mechanisms, one operating at temperatures above 400°C and the other below that temperature. The low temperature oxidation has been extensively investigated, but little work has been done on the high temperature oxidation.

The work presented in this thesis consists of a kinetic and analytical investigation of the oxidation of propane in the high temperature region. The kinetic investigation has been carried out in a standard static combustion apparatus at temperatures between 400° and 460°C , and the dependence of the maximum rate and the acceleration constant on the pressures of reactants has been determined. The effect of additives on the kinetics has also been studied. The technique of Gas Phase Chromatography has been developed into a suitable quantitative method of micro-analysis of the products of hydrocarbon combustion, and the analytical investigation has been carried out almost completely by the application of this method. Analyses of suitable reaction mixtures during reaction have been made at several temperatures, and the variation in products with reactant concentration and temperature has been determined.

The oxidation in the high temperature region appears to be a two-stage reaction. In the initial stages the main product is propylene, and the acceleration can be attributed to the cracking reaction of the propyl radical which eventually gives rise to



formaldehyde, the effective branching intermediate. In the later stage of the reaction where the maximum rate is realised, the reaction mechanism is similar to one found in the low temperature region where the main chain product is a higher aldehyde, which is then responsible for the branching. At this stage the propylene concentration reaches a stationary value.

From the suggested reaction mechanisms, kinetic expressions for the maximum rate and acceleration constants have been derived, and these are in agreement with the experimental observations.

THE HIGH TEMPERATURE OXIDATION OF PROPANE.

T H E S I S

submitted for the degree of
Doctor of Philosophy

by

John W. Falconer B.Sc.

University of Edinburgh.

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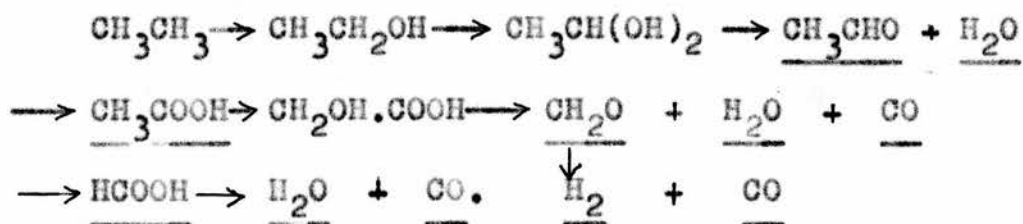
1. THE SLOW OXIDATION OF HYDROCARBONS.1.1. The Early Work.

The oxidation of hydrocarbons has been the subject of investigations by chemists for more than a century. In the early 19th century, Dalton¹, in addition to pioneering the development of Atomic Theory, carried out researches in the combustion of fuels, and identified hydrogen and carbon monoxide in the gas from burners. At about the same time, Davy carried out the first researches on ignition phenomena with a view to reducing the hazards of explosions in mines. In these he discovered the important effects of surfaces and narrow passages in controlling explosions.

However, in spite of Dalton's results, the theory which was accepted until 1860 was that of Preferential Combustion of Hydrogen, presumably based on the evidence that a flame deposits carbon when oxygen deficient mixtures are combusted. The theory became no longer tenable when Kersten² confirmed Dalton's observations by identifying hydrogen in the interconal gases of the combustion of hydrocarbons.

Armstrong³, in 1874, suggested that hydrocarbons could be oxidised by the successive hydroxylation of the C-H bonds, and this Hydroxylation Theory was expanded and developed by Bone and his co-workers⁴ during the years 1900 to 1912. In

this theory, all the intermediate compounds which had been isolated could be explained. These intermediate compounds were alcohols, aldehydes, acids, water etc., and in the case of ethane, for example, they were believed to be produced by the reactions



The importance of the Hydroxylation Theory lay in the fact that it was the first theory to introduce the concept of reaction by successive steps. This principle was extremely important, and its application led to a great advance in the understanding of oxidation mechanisms.

As more and more investigations were carried out on the combustion of hydrocarbons, it was realised that the Hydroxylation Theory had weaknesses, and the theory was criticised on several grounds. None of the investigators had been able to isolate the supposed primary intermediate, the alcohol, and although Newitt and Haffner⁵ did identify methanol in the oxidation of methane at high pressures, other criticisms were levelled by Norrish⁶ and Ubbelohde⁷. By this time it was realised that, since most of the products of the reaction contained only one atom of oxygen, the mode of

scission of the diatomic oxygen molecule was an important feature of the reaction. Ubbelohde criticised the postulate of the Hydroxylation Theory that the reaction was dissociation of the oxygen molecule into atoms



on the ground that it was not energetically plausible. It was also pointed out by Norrish that the theory could not explain the observed kinetics of the oxidation of methane. It was Bone⁸ himself who produced the evidence that invalidated his theory when he found that methanol reacted more slowly than formaldehyde, and so ought to have a higher stationary state concentration in the oxidation of methane. This latter fact was contrary to the experimental observations.

With the realisation of the defects of the Hydroxylation Theory, during the late 1920s, other workers began to advance theories. In 1927, Callendar⁹ suggested that the oxygen was incorporated into the hydrocarbon to give a peroxide and that the O-O bond was then broken. The success of the Theory of Chain Reactions in other fields led to its application to the Oxidation of Hydrocarbons. Egerton¹⁰ supported Callendar's view that peroxidation of the hydrocarbon occurred, and postulated that the oxidation proceeded by a chain reaction, the chain being an energy chain which was carried by the energy-rich peroxide molecules.

This theory could explain the action of lead tetraethyl as an antiknock by the mechanism of negative catalysis. The discovery of the existence of free radicals led to the advancement of several new mechanisms for the oxidation of hydrocarbons, and it is from that period that the most modern theories have developed directly.

In view of the considerable part that the Theory of Chain Reactions has played in developing the various theories of Hydrocarbon oxidation, it is convenient here to give a short account of its development.

1.2. The Development of Chain Theories.

The idea of a chain reaction was first advanced by Bodenstein¹¹ in 1913 to account for the high quantum yield of the hydrogen/chlorine reaction. Bodenstein proposed an ionic chain mechanism, and later, Nernst¹² suggested the more familiar homolytic chain mechanism as being a better one. In 1923 Christiansen and Kramers¹³ applied the idea to the decomposition of nitrogen pentoxide, postulating a thermal chain to explain the high rate of decomposition of nitrogen pentoxide. However, the paper was not much read, and the Chain Theory was brought into focus only when Christiansen¹⁴ published a paper which demonstrated the power of the theory by explaining the phenomenon of negative catalysis. The observation could readily be explained if one considered the

negative catalyst as merely a breaker of chains.

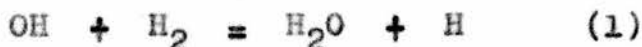
Almost immediately the Chain Theory was successfully applied to other reactions which exhibited these characteristics, such as the oxidation of aldehydes¹⁵, the oxidation of hydrocarbons in the gas phase¹⁶, the hydrogen oxygen reaction¹⁷ and the oxidation of sulphur¹⁸ in the gas phase.

Early papers all postulated thermal chains for these reactions, but the discovery of free radicals led to the advancement of free radical chain mechanisms in later work.

During the next few years, with the appearance of so many papers in the literature, it became evident that the new theories should be critically surveyed and analysed, and given some standard form. This was done by Semenov¹⁹, who had contributed extensively to the development of the theory, and the results of his survey were published in his book "Chemical Kinetics and Chain Reactions".

An important feature of Semenov's analysis was the concept of a branched chain. At this time Semenov believed that chains were carried by energy rich molecules, and not by free radicals, but the nature of the chain carrier does not affect the basic concept. In a branched chain, each chain carrier is supposed to react and produce, on the average, more than one new chain carrier. A continually increasing number of chain carriers thus results and this leads to an acceleration in the reaction rate and even explosion. This concept may be

illustrated by the consideration of two reactions from the hydrogen-oxygen reaction, where two of the reactions believed to occur are



In the first example, the reaction of the chain-carrying free radical produces another free radical, and in the second case, the reaction of one chain carrier produces two chain centres. The latter reaction is therefore a branching reaction.

The chain carriers may react in three general ways - to produce one chain carrier thus propagating the primary chain, to produce more than one chain carrier causing branching to occur, and to give no new chain carrier thus effectively breaking the chain. Now if

- δ is the probability of branching at any link
- β is the probability of chain breaking at any link
- n_0 is the number of initial chain carriers
- $w(t)$ is the velocity of the reaction
- $\Delta\tau$ is the time for which an active centre exists before entering the reaction.

Semenov deduced that the velocity of the reaction at any time t is given by

$$w(t) = Ae^{\phi t} - 1$$

which for large values of t reduces to

$$w(t) = Ae^{\phi t}$$

where

$$A = n_0 / (\delta - \beta)$$

$$\phi = (\delta - \beta) / \Delta\tau$$

If x is the amount reacted after time t , and for a gas phase reaction assuming this to be proportional to the pressure change Δp , we obtain on integrating

$$\Delta p \propto x = A/\phi \cdot e^{\phi t}$$

$$\Delta p = N \cdot e^{\phi t}$$

The value of ϕ can be obtained from a plot of $\log(\Delta p)$ against t , or alternatively, since the rate of the reaction is given by

$$d(\Delta p)/dt = \phi \cdot N \cdot e^{\phi t} = \phi \cdot (\Delta p),$$

from a plot of the rate of reaction against pressure change.

Assuming values of δ , β , and ΔT which were reasonable for free radical or energy-rich molecule reactions, Semenov showed that the velocity of the reaction might be expected to increase by a factor of the order of e every second. In order to explain observed velocities in hydrocarbons and other oxidation reactions which were very much less than this value, Semenov was forced to conclude that ΔT had to be of the order of minutes or hours, and he introduced the conception of degenerate branching to explain this slowly-developing process. He postulated that the result of initial reaction led to a relatively stable intermediate product, which accumulated in the original mixture and reacted independently, leading to the final product. The reaction of the intermediate could also create centres to start the chain of the primary reaction. In a formal way these chains could be considered as the branching of the primary chains, although such degenerate

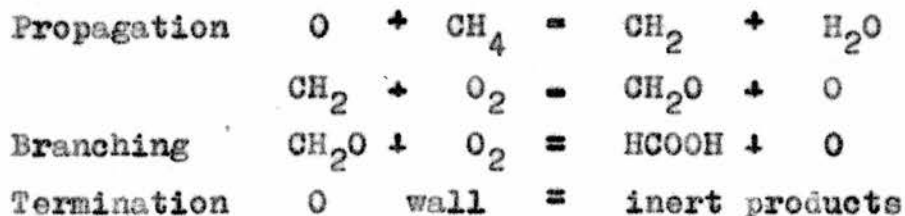
branchings occurred long after the primary chain had perished.

1.3. Recent Theories of Hydrocarbon Oxidation.

With the introduction of Chain Theory and the discovery of free radicals, came the realisation that oxidation occurred by a number of steps each of which was essentially simple in nature, entailing the making and breaking of only one or two bonds. It was obvious that the older theories could be criticised on these grounds, and several new theories were put forward which, although they differed in details, could be divided into two main types. They can be illustrated by considering the theories of Norrish⁶ and Ubbelohde⁷, both of which were advanced in 1935.

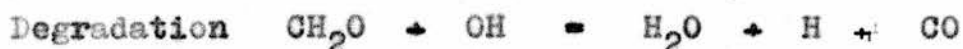
Norrish's theory is based on the belief that an aldehyde is the intermediate which gives rise to the degenerate branching, and Ubbelohde suggested that peroxides were the active intermediates.

The reaction investigated by Norrish was the oxidation of methane, and the mechanism which he advanced was the first free radical scheme involving the production of aldehydes. The chain was carried by oxygen atoms, as

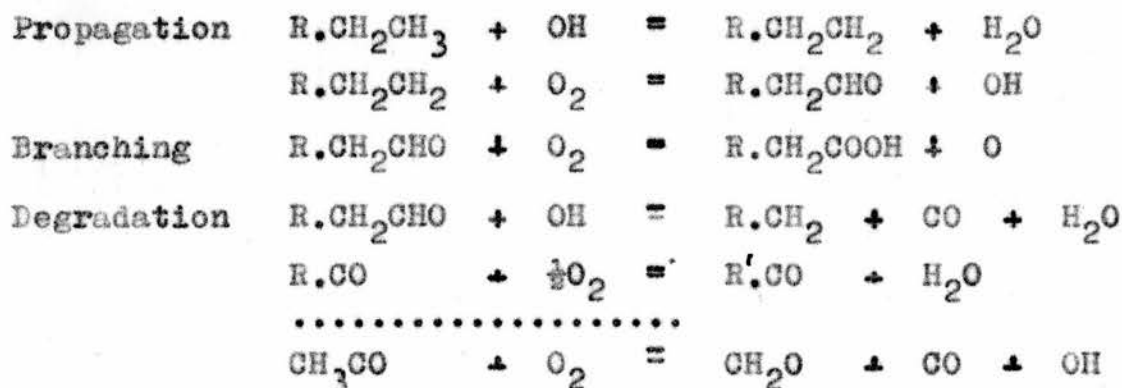


It was at first supposed that branching occurred at the

surface of the reaction vessel, but in a paper published the next year⁶, the branching was thought to occur wholly in the gas phase. The mechanism was refined after work on the oxidation of formaldehyde²⁰, and was given its final form in 1948²¹. In this later scheme, the O atom chain was replaced by an OH radical chain, and degradative reactions of the formaldehyde were introduced whereby it was removed by free radical attack without causing branching, as in the reaction

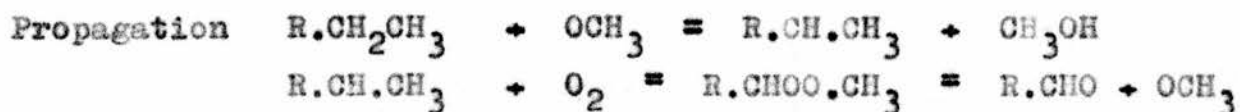


Norrish also proposed an aldehyde scheme for the oxidation of higher hydrocarbons²¹ similar to that for methane, and incorporating additional features from the work of Pope, Dykstra and Edgar²², and von Elbe and Lewis²³. The oxidation occurred by an OH radical chain, and the degradative reaction involved the successive formation and destruction of R.CO radicals. The important reactions were



Von Elbe and Lewis also included a chain carried by the OCH₃ radical instead of the OH radical, to account for the profuse

production of methanol found by Pease²⁴ in the oxidation products of propane. The formation of methanol is regarded as a sign of attack of free radicals at the secondary carbon atom.



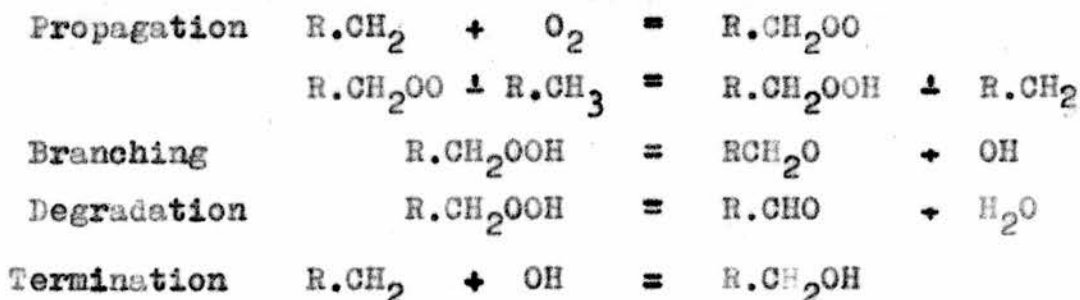
Recent work on the oxidation of methane by Walsh²⁵, and on the oxidation of acetaldehyde by McDowell and Thomas²⁶, has suggested that the branching reactions are respectively, in the case of formaldehyde



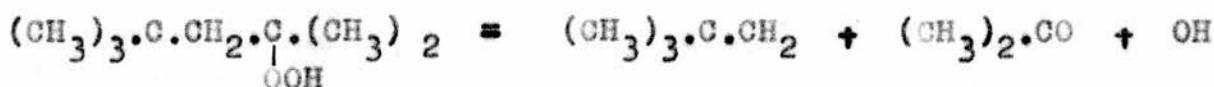
and in the case of acetaldehyde



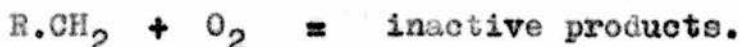
Ubbelohde⁷, suggesting that formation of oxygen atoms was unlikely because of steric factors, even although the reaction was approximately thermoneutral, proposed a chain mechanism producing peroxides. The branching reaction could then be attributed to the decomposition of the peroxides into free radicals. The important steps of Ubbelohde's scheme were the following.



The peroxide scheme has been extended by Walsh²⁷ to include a degradative reaction of the peroxide, and in the case of octane the peroxide was regarded as breaking down the following reaction



Hinshelwood²⁸ has also contributed to the development of the peroxide theory, and has suggested a chain ending step to account for the inhibiting effect of excess oxygen, as



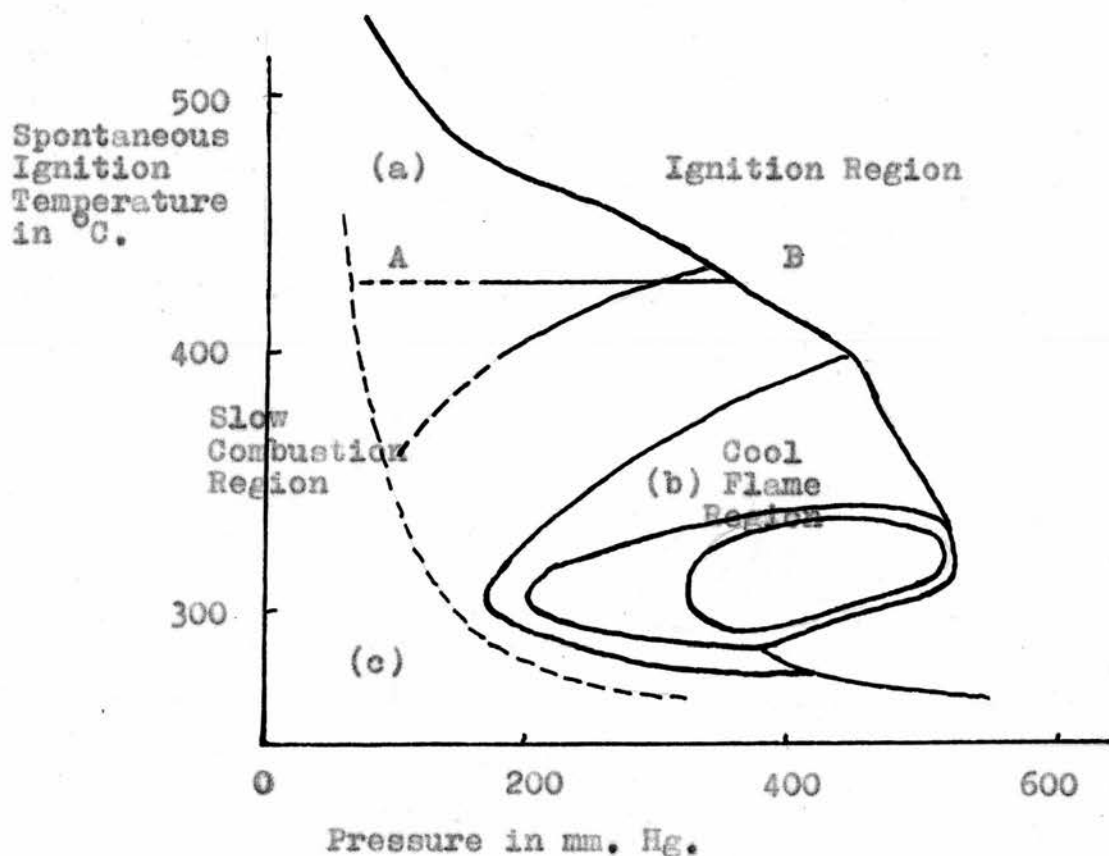
The difference between the two theories lies in the nature of the postulated branching reaction. In the case of the aldehyde chain theory, the peroxide radical $\text{R}\cdot\text{CH}_2\text{OO}$ is unstable and breaks up to give the aldehyde $\text{R}\cdot\text{CHO}$ and OH , and it is this aldehyde that gives the branching by reaction with oxygen. In the case of the peroxide theory, the $\text{R}\cdot\text{CH}_2\text{OO}$ radical is believed to be stable and to react with a hydrocarbon $\text{R}'\cdot\text{CH}_3$ giving the hydroperoxide $\text{R}\cdot\text{CH}_2\text{OOH}$ which is responsible for the branching by breaking up to give RO and OH .

2. REVIEW OF PREVIOUS WORK ON THE OXIDATION OF PROPANE.

Propane is typical of aliphatic hydrocarbons containing two or more C atoms, and its oxidation shows all the characteristics of the oxidation of these compounds. These include the degenerate branching chain mechanisms discussed

previously, a negative temperature coefficient of the reaction rate, and the occurrence of cool flames. It was the existence of these features that stimulated the interest of earlier workers in this field. The negative temperature coefficient occurs between 350°C . and 400°C . in the case of propane, and the cool flame phenomena are shown over a temperature range below this, as is recorded later. Cool flames are caused by an instability in the reaction system which causes the reaction to proceed at a greatly enhanced rate. This rapid reaction is called a cool flame and is always accompanied by the emission of a pale blue light. Since the earlier workers were influenced by the prevailing theories of hydrocarbon oxidation in the interpretation of their results, it is felt that a chronological consideration of their results would not give the best representation of the facts that are known about the reaction. Accordingly this review has been presented as a systematic consideration rather than a chronological record of the work done.

The classical investigation of the combustion of mixtures of propane and oxygen was carried out by Newitt and Thornes²⁹, who examined extensively the combustion characteristics of an equimolecular mixture over the complete combustion range of temperature and pressure. The results of the investigation are recorded in the figure, which is taken from their paper.

COMBUSTION REGIONS OF PROPANE AND OXYGEN.

It was found that the reaction could be conveniently divided into four regions of combustion; the ignition region, the region of slow oxidation at high temperatures, marked (a), the cool flame region, marked (b), and the region of slow combustion at low temperatures. In the cool flame region, up to five cool flames could be obtained, and associated with this region was the negative temperature coefficient of reaction first recorded by Pease³⁰. On going up any isobar, the rate was found to reach a maximum at about 380°C and

then fall to a minimum about 420°C . before rising again. The line AB denoted the temperature where the coefficient of reaction ^{rate} was zero. The region of combustion above this line was called the high temperature region and the region of combustion below the cool flame region was called the low temperature region.

The reaction has been studied using two types of reaction system, the static system and the flow system. Both systems have their attendant advantages and disadvantages. The flow system has the advantage that it gives relatively large amounts of reaction products which are thus more amenable to analysis, but it does not lend itself to kinetic investigation of the reaction. With a static system the reverse is true.

Investigations using flow systems have been carried out by a number of workers and their work covers the complete temperature range of slow combustion between the temperature when the reaction starts and the ignition temperature. Not all of these workers covered the complete range of temperature. The region of slow combustion at low temperatures has been investigated by Pease³⁰, Harris and Egerton³¹, Newitt and Thornes²⁹, and Norrish and Knox³²; the cool flame region by Pease, Harris and Egerton, Newitt and Thornes, Norrish and Knox, Satterfield and Wilson³³, and Kooijman³⁴; and the region of slow combustion at high temperatures by Pease,

Satterfield and Wilson, and Kooijman.

The work that has been done using static systems is not so comprehensive. The region of slow combustion at low temperatures has been investigated by Pease, the cool flame region by Newitt and Thornes, the region of negative temperature coefficient outside the cool flame region by Antonoviski and Shtern³⁵, Chernyak and Shtern³⁶, Pease, and Harris and Egerton, and a few observations on the combustion of propane and its derivatives in the high temperature region have been made by Mulcahy³⁷.

The agreement between all of these investigations is, on the whole, surprisingly good, considering the wide variety of experimental conditions and the sensitivity of the reaction to the experimental conditions. There are, however, one or two instances where results do seem to be conflicting.

The products of the reaction fall into two main types, hydrocarbons and oxygenated molecules. Of the hydrocarbons, there have been reported methane, ethane, ethylene, acetylene, propylene and, in addition, hydrogen. The oxygenated molecules comprise methanol, ethanol, formaldehyde, acetaldehyde, propionaldehyde, acids, peroxides and water. At lower temperatures, the relative amount of reacted propane producing hydrocarbon products is low, being negligible at 260°C. As the temperature is increased, the proportion of hydrocarbon in

the product increases until at 400°C , about 50% of the reacted propane appears as hydrocarbon in the product. At higher temperatures, with low oxygen concentrations, about 80 to 90% of the reacted propane appears as hydrocarbon products. The nature of the hydrocarbon product also changes as the temperature is increased. At lower temperatures relatively little ethylene is produced, the amount increasing as the temperature is increased.

The analysis of the products obtained in static experiments confirms, in general, the results obtained from the investigations using flow systems. In the former, however, discrepancies can be noted. Newitt and Thornes, in the region of negative temperature coefficient, have recorded that acetylene is produced and no ethylene, while other workers have failed to detect acetylene in any of the slow combustion reactions.

The amounts of propylene and ethylene were found to increase throughout the combustion of an equimolecular mixture, and there was general agreement that the amount of reacted propane giving hydrocarbons, relative to the amount giving oxygenated compounds, was greater at the beginning of the reaction than at the end. When the effect of the addition of propylene was investigated, however, the results of Harris and Egerton, and Chernyak and Shtern were found to be incompatible, the former recording that the advance addition of propylene had

no effect on the final product composition, and the latter recording that addition of propylene increased the final yield by just the amount added. These experiments were carried out under comparable conditions.

The information available on the kinetics of the slow combustion is rather meagre, the most extensive examination having been carried out by Pease³⁸. In this investigation, it was determined that the order of the reaction in the low temperature range was zero with respect to oxygen and was approximately 2 with respect to propane. In the high temperature range it was found that the order with respect to both oxygen and propane was between 1 and 2.

Mechanisms have been advanced for the low-temperature oxidation which explain the observed products, and from which can be deduced the observed kinetic parameters. It has been suggested that the reaction proceeds through the propyl radical, which may be either the n-propyl or the iso-propyl radical, and that the radical may react in three possible ways,

- 1) by cracking to give ethylene and a methyl radical,
- 2) by reacting with oxygen to give unsaturated hydrocarbons,
- 3) by reacting with oxygen to give oxygenated products.

The oxygenated molecules produced in the third type of reaction may be aldehydes or peroxides, either of which is known to cause an acceleration in the rate of reaction and could act as branching agents if formed. The variation in products with temperature can be adequately explained by these

three reactions, the variation in product and in rate being attributed to the change in contributions from the three reactions as the temperature is raised.

The acceleration at lower temperatures has been attributed to branching acetaldehyde or peroxide^{28,32} and the decrease in rate to an olefin-forming chain competing as the temperature is raised^{32,33}. This chain can also account for the relatively large amount of hydrogen peroxide formed in the oxidation at higher temperatures.

It has been suggested by Norrish²¹ that the rise in the rate at higher temperatures above the region of negative temperature coefficient was possibly due to some other branching reaction such as formaldehyde oxidation as in the case of methane.

Summarising, the oxidation has been investigated by flow methods over the whole of the range of slow combustion and by static methods up to 420°C. The kinetics of the slow oxidation have been determined in the low temperature range and at 400°C., and a scheme has been advanced that explains the mechanism in the low temperature range.

No investigation either of the products or the kinetics has been undertaken in the high temperature range in a static system.

3. THE AIM OF THE RESEARCH.

Previous work has shown that the products from the oxidation of propane are a complex mixture of hydrocarbons, oxygenated hydrocarbons, hydrogen peroxide and water. The analysis of such a mixture is difficult, and considerable ingenuity has had to be employed to obtain quantitative estimates of all the products. At higher temperatures in a static system, the pressure of reactant required to give measurable rates is usually considerably less than atmospheric pressure, and the amount of product available for analysis is correspondingly smaller. This was probably the reason why investigations in the high temperature region were confined to flow systems, where appreciable quantities of products could be obtained. The amount of product available from a combustion in a static apparatus in the high temperature range is of the order of 1000 μ -mole, and to determine the minor components of such a mixture quantitatively, some method of micro-analysis must be employed. The methods available in the literature, apart from requiring a diversity of apparatus, mostly suffer from some disadvantage, such as inability to distinguish unsaturated hydrocarbons, or necessity of a separate run for the determination of each component, or time required for a full analysis being inconveniently long.

The recent developments in gas phase chromatography

suggested that it would be worth-while to develop the technique as a quantitative method of micro-analysis for the products of hydrocarbon oxidation.

The aim of the research was to investigate the oxidation of propane in the high temperature region using a static reaction system, in which a thorough investigation of the kinetic characteristics could be made. By the development of gas phase chromatography into a suitable analytical technique, an investigation of how the products of the reaction varied with the experimental conditions could also be made.

From the data thus obtained, it was hoped that the mechanism of the oxidation of propane in the high temperature region could be established.

The reader will be able to judge for himself the extent to which these aims have been realised.

EXPERIMENTAL TECHNIQUE

1. THE APPARATUS AND PROCEDURE.

1.1. The Kinetic Apparatus.

The kinetic apparatus was a static combustion apparatus of conventional design constructed of pyrex glass, and is illustrated in figure 1.1. The pumping system consisted of a two-stage vertical annular jet type of mercury vapour pump, backed by a Hyvac Rotary Oil pump. A McLeod Gauge was employed for measurement of the pressure during the evacuation, and it was found that the pressure could be reduced to 10^{-5} mm. of mercury after 30 minutes pumping. The purified reactants were stored in 5-litre reservoirs, and any required mixture was made up by measuring the reactants into the 500 cc. mixing vessel. The sharing ratio between the mixing vessel and the reaction vessel plus the Bourdon Spoon Gauge was known. The reaction vessel was made of tubular pyrex glass 5.5 cm. in diameter, and was of capacity 522 cc. It was cleaned with chromic acid and thoroughly rinsed with distilled water before being sealed on to the apparatus.

The measurement of the pressure change during the reaction was made with a Bourdon Spoon Gauge made of pyrex glass and fitted with an optical lever arrangement. The deflection of the pointer was thus magnified and could be read on a metre long scale, a pressure change of 1 mm. mercury giving a deflection of 7.93 mm. on the scale. The deflection was linear with respect to the pressure over the pressure range

used. The Bourdon Gauge was connected to the reaction vessel by means of 2 mm. internal diameter capillary tubing, which was maintained at 100°C by means of a heating coil to prevent condensation of any product which might diffuse into the capillary tubing.

The reaction vessel was housed in a furnace, and was surrounded by a copper jacket to promote uniform heating. The furnace consisted of a silica tube, 66 cm. long by 9.2 cm. internal diameter, which was heated by three independent windings of nichrome wire of resistances 150, 100 and 150 ohms respectively, the whole being suitably lagged and insulated. The temperature along the reaction vessel was made constant to within $\pm 1^{\circ}\text{C}$ by varying the voltages through the windings, and the mean temperature could be controlled to $\pm 1^{\circ}\text{C}$ by fitting a voltage stabiliser to the power supply.

The temperatures were measured by means of a thermocouple which had been standardised, in conjunction with a Doran Thermocouple Potentiometer.

1.2. The Materials.

Oxygen was obtained from a cylinder, and was quoted as being 99.5% pure, the remainder being mainly argon. It was drawn through a liquid oxygen trap to remove any condensable impurities, and then allowed to leak into a 5 litre reservoir.

Propane was obtained from two sources. The analytical

experiments were carried out with 99.8% propane which contained 0.2% butane and was not purified further. It was kindly gifted by B.P. Research laboratories, Sunbury-on-Thames. The kinetic investigation was carried out using propane that contained 1% ethane and 0.1 to 0.2% propylene. This standard of purity was obtained by passing commercial propane through three bubblers which contained respectively 1) concentrated sulphuric acid containing 0.6% W/W of silver sulphate, 2) concentrated sodium hydroxide, and 3) concentrated sulphuric acid containing silver sulphate. The propane was then passed through a charcoal column saturated with bromine, and finally passed through a phosphorus pentoxide column. This propane was then distilled, liberal initial and final portions being discarded, and the middle fraction being retained.

Carbon Dioxide was distilled from commercial cardice, liberal initial and final fractions being discarded, and the middle fraction being retained.

Propylene was prepared by dehydrating isopropanol with phosphorus pentoxide, the gas evolved being scrubbed with a 10% solution of sodium hydroxide and then distilled from -80°C to -183°C , the middle fraction being retained.

Monomeric Formaldehyde was prepared by the method of Spence and Wild⁴². The apparatus consisted of three parts, a distilling flask, a separator and a trap, the last being

connected to the vacuum line. The separator consisted of a bundle of three U-tubes the upper parts of which were heated to 120°C and the lower parts cooled to -80°C . Commercial paraformaldehyde, which had been dried over concentrated sulphuric acid in a vacuum dessicator, was heated to 110°C in the distillation flask under vacuum. During this, the condensing vessels were heated by means of a blow-pipe flame to prevent the condensation of water. The trap was then cooled to -183°C , the separator to -80°C , and the tap to the pump closed. As the distillation proceeded, the oilbath temperature was gradually raised to 120°C , and when sufficient monomer had been collected, the oil-bath was removed and the trap carefully sealed off. Alternate removal and replacement of the liquid oxygen container brought all the formaldehyde to the foot of the trap which was then sealed on to the line in position. The function of the separator was to alternately heat and cool the gases whereby the water was completely removed. (Slightly wet formaldehyde polymerises readily).

Acetaldehyde and Propionaldehyde were prepared by trapping the vapour of the commercial aldehydes and using the middle fraction.

Hydrogen was obtained from a cylinder and was not purified further.

Methane was obtained from a cylinder and was not purified further. It contained 0.8% hydrogen.

Ethane was obtained from a cylinder and was not purified further. It contained 1.2% ethylene.

Ethylene was obtained from a cylinder and was not purified further. It contained 0.2% ethane.

Carbon Monoxide was prepared by dropping formic acid into concentrated sulphuric acid heated to 100°C in vacuum. The carbon monoxide evolved was purified by passing through two traps at -183°C .

1.3. The Analytical Apparatus and Procedure.

The apparatus used for the analysis is illustrated in figure 1.3.1. The removal of the products for analysis was effected by first isolating the reaction vessel from the Bourdon Gauge, and then connecting it to an evacuated sampling vessel cooled with liquid oxygen in the central finger. The tubing connecting the reaction vessel to sampling vessel was heated to prevent condensation of the products. For the purpose of detailed analysis, the original sample was divided into three fractions:-

Fraction 1, containing the gases uncondensable at -183°C

Fraction 2, containing the gases uncondensable at -80°C

Fraction 3, containing the products condensable at -80°C .

The first two fractions were pumped off by means of a Toepler Pump, and their volume, pressure and temperature were

measured. The amount of product in the complete sample was known, and the amount in fraction 3 was obtained by difference. The calibrated volumes of the Toepler Pump bulbs were determined by weighing the amount of mercury required to fill them to the calibration marks. The pressure in the Toepler bulbs was measured on the adjoining manometer, and the temperature was also measured.

The mixture to be analysed was introduced into the by-pass sampling U-tube of the chromatography apparatus which provided for reproducible dosage of samples of known volume and pressure, the volume being that of the U-tube and the pressure being recorded on a manometer.

The four Gas Phase Chromatography columns which were required for a complete analysis were connected to a manifold, which allowed the appropriate column for the fraction being analysed to be selected immediately.

The temperature of each column was controlled by an electrically-heated jacket, which consisted of an inner glass tube of diameter about 25 mm. wound with nichrome heating tape, the whole being placed in an outer glass tube to thermostat it. The voltage to the jackets was supplied by a voltage stabiliser through a variac transformer. By this means the column temperature was controlled to $\pm 1^{\circ}\text{C}$.

The flow rate of carrier gas through the column was determined by the pressure head at the entrance to the column

and this was accurately controlled by means of water column bubblers, one of suitable height being used for each column. Minor fluctuations in the pressure were smoothed by a buffering vessel, which also served as a "backing volume" when a sample was being introduced into the column.

The first three columns utilised Gas/Solid Chromatography and the fourth column, Gas/Liquid Chromatography. The respective packings for the four columns were 1) Activated Charcoal, 2) Silica Gel, 3) Silica Gel and 4) Dinonyl Phthalate on Firebrick. The packings were prepared as follows: Activated charcoal was prepared by drying and sieving the commercial charcoal "Sutcliffe and Speakman, 207B", the fraction of mesh B.S.S. 52-72 being taken. Silica Gel was prepared by drying and sieving commercial silica gel "B.D.H. 25-72 mesh", the fraction of mesh 52-72 mesh being taken. Firebrick was prepared by crushing commercial firebrick, and drying and sieving the particles, the fraction of 52-72 mesh being taken. The dinonyl phthalate was deposited on the firebrick by dissolving it in methylene dichloride, making a slurry of the firebrick in the solution, and evaporating off the solvent. The proportion by weight of dinonyl phthalate to firebrick was 20/100.

All of the columns were packed by filling the glass tube

with the packing, and then pressing the tube against the spindle of a rotary oil pump, the vibration which ensued giving uniform packing.

A description of the columns and the conditions under which they were operated is given in the following table.

Column Number	1	2	3	4
Diameter (mm.)	9	4	4	4
Length (cm.)	85	190	90	500
Temperature °C.	20	35	89	100
Flow Rate (cc/min.)	46.5	35.0	35.0	14.5
Fraction analysed	1	2(a)	2(b)	3

After leaving the column, the carrier gas passed into the measuring cell of the Thermal Conductivity Detector and from there to a flow meter. The thermal conductivity detector is illustrated in figure 1.3.2, and consisted of a solid copper block with two channels drilled in it. Each channel had a tungsten filament stretched along its axis, of resistance approximately 13 ohms, and the carrier gas from the columns was allowed to stream over the filaments. The measuring cell was balanced by another cell through a constant flow of carrier gas passed.

The two cells of the detector were part of a Wheatstone Bridge, whose output was measured by a sensitive moving coil galvanometer. The electrical circuit for the detector is

shown in figure 1.3.3. The voltage across the bridge was set at 6.5 volts by means of rheostat 1 and a standard cell. Rheostat 2 was used to control the sensitivity of the galvanometer, and rheostat 3 to adjust the output of the bridge.

To carry out an analysis, the flow rates of carrier gas passing through both cells of the detector were set and the bridge was adjusted so that a zero or near-zero signal was obtained on the galvanometer. The gas flow was then directed through the introductory U-tube and the sample swept into the column. Components of the mixture travelled at different rates through the column and thus separated into bands, pure carrier gas issuing between the component bands. The passage of such a band through the detector caused a change in the filament temperature, proportional to the concentration of the foreign vapour, which resulted in an unbalance of the bridge. This was recorded by the galvanometer and when the galvanometer deflection was plotted against time, a trace was obtained which consisted of a number of peaks, one for each component of the mixture, as illustrated in figure 1.3.4.

A calibration graph for each component of the products was obtained in the following way. A sufficiently dilute mixture of the component in nitrogen was made, and aliquots of this mixture were passed through the appropriate column

and the height of the galvanometer deflection measured. In this way a graph of Peak Height against μ -mole of product was obtained. A typical calibration graph is shown in figure 1.3.5, and it can be seen that the dependence of the peak height on the amount of product is almost linear. The error in making a determination was estimated to be about 2%.

Unfortunately, it was not possible to obtain a quantitative analysis of fraction 3 using Gas/Liquid Chromatography, since formaldehyde and peroxide tend to polymerise or decompose on the column. However, a semi-quantitative picture of the fraction was given by the chromatogram. To obtain a quantitative measure of the formaldehyde, peroxide and methanol, fraction 3 was removed from the apparatus, dissolved in water and examined by the following methods.

1.3.6. Analysis of Formaldehyde.

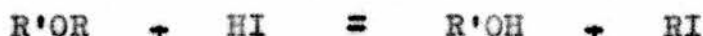
Formaldehyde was determined by the method of Bricker and Johnson³⁹. A solution of chromotropic acid was prepared by dissolving 2.5 gm. of dry powder in 25 ml. water, filtering off any insoluble material. Since the colour of the reagent altered on standing, a new reagent blank was run each day.

1 ml. of the solution of fraction 3 was placed in a B14 test-tube, and to it was added 0.5 ml. of chromotropic acid solution, and then 5 ml. concentrated sulphuric acid with

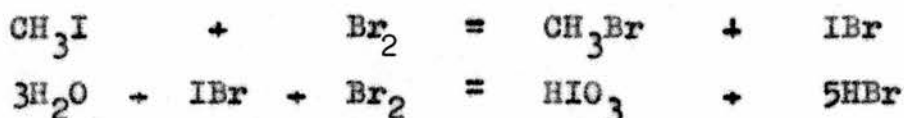
continuous shaking. The test-tube was stoppered and then placed in a beaker of boiling water for 30 minutes. After cooling, the contents were diluted to 50 ml., and the optical density of the coloured solution was determined at 570 m μ . against the reagent blank. From this reading the amount of formaldehyde could then be obtained from a calibration graph.

1.3.7. Analysis of Methanol.

The methanol was determined by the method of Scott and Furman⁴⁰, using a modified Zeisel procedure based on the reaction



The volumetric work is based on the equations



The iodate was determined by iodine titration.

The apparatus used is shown in figure 1.3.7. 3 ml. of fraction 3 solution were added to a mixture of 3 ml. AR phenol and 5 ml. constant boiling hydriodic acid contained in the flask. The mixture was boiled for 30 minutes during which time a slow stream of carbon dioxide was passed through the system. By this method all the methoxyl was converted into methyl iodide, which was carried over by the stream of gas. Any iodine or hydriodic acid carried over was removed by scrubbing the gases in a 1/1 mixture of 5% cadmium sulphate and 5% sodium thiosulphate solutions. The methyl iodide was absorbed in approximately 10 ml. of a 10% solution of sodium

acetate in glacial acetic acid containing a few drops of bromine. At the end of 30 minutes the absorption tube was disconnected and its contents transferred to a 250 ml. conical flask containing 1 gm. of sodium acetate. The volume was made up about 150 ml. and 1 ml. formic acid added to discharge the excess bromine. When the colour had completely disappeared, 10 ml. of dilute sulphuric acid followed by 1 gm. of potassium iodide was added. The iodine liberated was finally titrated with N/100 sodium thiosulphate contained in a micro-burette. A blank experiment was carried out using the reagents alone, and subsequent determinations corrected by this amount.

1.3.8. Analysis of Peroxide.

The total peroxide was determined by the oxidation of ferrous to ferric, the latter being determined colorometrically as the thiocyanate as described by Egerton et al.⁴¹.

5 gm. ammonium thiocyanate and 5 gm. ferrous sulphate were dissolved in 100 ml. water containing 1 ml. concentrated sulphuric acid, and the solution freed from red colour by shaking with amyl alcohol. 1 ml. of this reagent solution was added to 3 ml. of the solution fraction 3, when the colour developed instantly, and was stable for at least 2 hours. The optical density of the coloured solution was determined at 450 m μ . against a reagent blank and from this reading the amount of peroxide could then be obtained from a calibration graph.

1.3.9. Examination of Fraction 3 by Chromatography.

The amount of the condensable fraction from an average run was of the order 500 μ -moles, and it was shown that less than 10% of this amount consisted of typical condensable products of hydrocarbon combustions such as alcohols, aldehydes and peroxides etc., the remaining 90% being water. Since these oxygenated products were present in such small amounts and were in solution in water, they were not amenable to investigation. The formaldehyde, methanol and peroxide were determined quantitatively as previously described, and a semi-quantitative picture of the rest of the fraction was obtained by analysing the mixture by Gas/Liquid Chromatography. Fraction 3 was distilled from the sampling vessel into the introductory U-tube by heating the former with hot water and cooling the latter with liquid oxygen. The sample was then introduced as vapour into the stream of carrier gas by directing the stream of carrier gas through the U-tube which was heated with hot water. It was observed that some of the sample condensed in the glass tubing before entering the column, and it was mainly for this reason that the analyses were not quantitative.

A typical chromatogram of the condensable products from the combustion of 100 mm. propane and 50 mm. oxygen at 435°C is shown in figure 1.3.9, and as can be seen, peaks were present at 7.5, 13.5, 19.0, 21.5, 25.0 and 29.0 minutes

respectively. The variation in the shape of the peak at 21.5 minutes suggested that it was probably compounded of two peaks at 21 and 22 minutes.

The chromatograms of substances that could possibly be products of the reaction were obtained, and from this calibration, some attempt was made to identify the peaks in the chromatogram of the products. The elution times of standard substances are given in the following table and illustrated in figure 1.3.9.

<u>Substance</u>	<u>Elution Time</u>
Acetaldehyde	13.5 minutes
Methyl formate	14.5 minutes
Methanol	16.5 minutes
Dimethyl formal	19.0 minutes
Dimethyl acetal	20.5 minutes
Propionaldehyde	22.0 minutes
Ethyl formate	22.5 minutes
Methyl acetate	23.0 minutes
Ethanol	25.0 minutes
Isopropanol	28.5 minutes

It will be seen that the peak at 13.5 minutes could be attributed to acetaldehyde or methyl formate, or possibly both. The peak at 19 minutes could be dimethyl formal, and those between 20 and 23 minutes could be any of dimethyl acetal, propionaldehyde, ethyl formate or methyl acetate. The peak at 25 minutes in the chromatogram of the products is unlikely

to be ethanol, since the latter was found to "tail" rather badly, while the former is quite well defined. The peak at 29 minutes could possibly be isopropanol.

An attempt was made to isolate these peaks and to identify them by infra-red spectroscopy, but owing to further complications, limited success was obtained. In order to obtain sufficient product for infra-red examination, the condensable products at -80°C from ten combustions of 100 mm. propane and 50 mm. oxygen were collected and then chromatogrammed together. The column then appeared to be overloaded, since no distinct peaks were found between 19 and 25 minutes, the products appearing as one large peak. In addition a new peak was found at 17 minutes which was presumably due to a new product formed by the reaction of the existing products in the sampling vessel. However, the peaks at 7 to 8 minutes, 13 to 15 minutes, 16 to 18 minutes, ^{19 to 25} and 25 to 30 minutes were trapped out separately and examined as vapours by infra-red spectroscopy.

The peak at 7 to 8 minutes was identified as a saturated hydrocarbon, and the spectrum of the peak at 13 to 15 minutes was identical with that of acetaldehyde, showing that this peak contained only acetaldehyde. The peak at 15 to 18 minutes could not be identified, but the infra-red spectrum contained strong carbonyl absorption at 1745 and 1760 cm^{-1} , and also strong absorption in the 830 to 1400 cm^{-1} range. This type of spectrum is sometimes attributed to peroxides and to

epoxy compounds.

The peak at 19 to 25 minutes was obviously a mixture, but the spectrum gave a strong carbonyl absorption at 1740 cm^{-1} , which was possibly compounded of several carbonyl peaks. There was a definite inflection in the carbonyl peak at 1755 cm^{-1} , which could be attributed to propionaldehyde, and in addition, absorption maxima at 1420, 1370, 1215 and 1155 cm^{-1} . The spectra of the other possible products of the reaction mentioned above were also examined, and the carbonyl absorption found in the spectrum of product could not be attributed to any of these.

The compound that was eluted at 29 minutes was found to contain carbon-hydrogen and carbonyl absorption in its spectrum.

From a height of the peaks in the chromatograms and an estimate of the sensitivity of the detector to these products, a semi-quantitative estimate of the amounts of the condensable products was calculated. This showed that the maximum pressure attained by any of the products was of the order of 0.5 mm. in the reaction vessel.

1.4. The Kinetic Procedure.

Since the reaction rate was sensitive to the state of the walls of the vessel, a standard procedure was employed before each reaction was carried out. This consisted of pumping for 15 minutes with only the backing pump, followed by 15 minutes pumping with the mercury vapour pump. The initial pumping had to be done with only the backing pump, since ethane, one of

the products of the reaction which would be retained in the trap before the mercury vapour pump, has a vapour pressure of the order 10^{-2} mm. mercury at -183°C , and the apparatus could not then be pumped below this value.

The first few runs of the day were found to give erratic behaviour, the rate of reaction for a given mixture increasing with each run. After three or four runs, the rates were found to be reproducible, presumably because the walls of the reaction vessel had to undergo some "aging process". Therefore before any effect of the variation of pressure etc. was investigated, a typical reaction was repeated until the maximum rate of reaction was constant, after which it was assumed that the walls of the reaction vessel were in a "steady state", and that the effects of variations could then be investigated.

The distribution ratio of gas on connecting the mixing vessel and the evacuated reaction vessel plus Bourdon Gauge was determined, and mixtures were made up by adding to the mixing vessel from the storage reservoirs the calculated amounts of reactants that would give the required final mixture composition. After the standard pumping procedure, the mixing vessel and the reaction vessel were connected, and the reaction was assumed to start when the gas mixture entered the reaction vessel. This was registered by a kick on the Bourdon Gauge. The reaction mixture was given 15 seconds to equilibrate, after

which the tap connecting the reaction vessel and the mixing vessel was closed. After 30 seconds the shorting tap on the Bourdon Gauge was closed, and readings of the pressure change were taken at suitable time intervals.

A typical plot of the pressure change against time is shown in figure 1.4.1, and is of the characteristic sigmoid form. It has been shown by Semenov that the pressure rise during the initial part of the reaction can be expressed in the mathematical form $\Delta p = N.e^{\phi t}$, where ϕ is the acceleration constant. The value of ϕ may be obtained by plotting $\ln(\Delta p)$ against time, or alternatively as has already been shown, by plotting reaction rate against pressure change Δp . Each of these plots gives a straight line of slope ϕ . Since there is some error in measuring the value of Δp at zero time, the latter method of determining ϕ is preferable, since it is unaffected by errors in Δp . A typical plot of rate against pressure change is given in figure 1.4.2, and as expected consists of a straight line.

The kinetic parameters that were examined in this investigation were the maximum rate and the acceleration constant.

1.5. The Analytical Procedure.

When analyses were carried out, a sample was obtained by first isolating the reaction vessel from the Bourdon Gauge, and then connecting it to the evacuated sampling vessel, which was cooled with liquid oxygen in the central finger. 75 to 95% of the reaction mixture was thereby removed, and two minutes were allowed for equilibrium to be reached after which the sampling

vessel was isolated from the reaction vessel. From the Bourdon reading and the initial pressure, the pressure of the reaction mixture before removal of the sample was obtained, and the final pressure after sampling in the reaction vessel was determined by connecting it to a manometer. The temperature, volume and pressure of the sample were then known, and the amount of the sample could be calculated.

As has already been mentioned, this sample was divided into three fractions for the purpose of detailed analysis. Fraction 1 contained the gases uncondensable at -183°C , fraction 2 the gases uncondensable at -80°C , and fraction 3 the gases condensable at -80°C . Fractions 1 and 2 were pumped off by the Toepler Pump, and their volume temperature and pressure measured. The amount of fraction 3 was obtained by difference.

A typical example of the calculation of an analysis is the following analysis.

Analysis of the Products of the Combustion of 100 mm. Propane and 50 mm. Oxygen at 435°C .

Initial reading of Bourdon Gauge	=	2.55 cm.	
Reading of Gauge when sample taken	=	15.40 cm.	
Bourdon deflection	=	12.85 cm.	
Change in pressure	=	16.2 mm.	
Final pressure of the reaction mixture	=	166.2 mm.	= M
Pressure on manometer to reaction vessel after sampling	=	14.1 mm.	
Final pressure in reaction vessel after sampling	=	15.6 mm.	
Pressure of sample	=	150.6 mm.	
Volume of reaction vessel	=	522 cc.	
Temperature of sample	=	435°C .	
Number of moles in sample	=	1782 μ -moles	= T

<u>Fraction 1.</u> Pressure of fraction	= 233.4 mm.
Volume of fraction	= 23.91 cc.
Temperature of fraction	= 21.0°C.
Number of moles in fraction	= 303.8 μ -moles = F
Pressure of aliquot in introductory vessel	= 181.7 mm.
Temperature of introductory vessel	= 20.0°C.
Volume of introductory vessel	= 14.31 cc.
Number of moles in aliquot	= 142.7 μ -moles = A

The pressure of product X in the reaction mixture is given by the formula $p = (\mu_x \times F \times M) / (A \times T)$, where μ_x is the number of micromoles of product X found in the aliquot.

	Peak Height	μ -mole (μ_x)	p
H ₂	8.0 cm.	1.96	.39 mm.
O ₂	31.2 cm.	98.0	19.8 mm.
CO	7.2 cm.	39.2	7.8 mm.
CH ₄	4.4 cm.	6.0	1.2 mm.

<u>Fraction 2.</u> Pressure of fraction	= 190.1 mm.
Volume of fraction	= 97.83 cc.
Temperature of fraction	= 22°C.
Number of moles in fraction	= 1011. μ -moles = G

Fraction 2(a).

Pressure of aliquot in introductory vessel	= 320.3 mm.
Volume of introductory vessel	= 14.31 cc.
Temperature of introductory vessel	= 20.0°C.
Number of moles in aliquot	= 254.5 μ -moles = A'

The pressure of product X in the reaction mixture is given by the formula $p = (G \times \mu_x \times M) / (A' \times T)$

	Peak Height	μ -mole (μ_x)	p
C ₂ H ₆	0	0	0 mm.
CO ₂	4.1 cm.	2.04	.76 mm.
C ₂ H ₄	5.4 cm.	13.1	5.0 mm.

Fraction 2 (b).

Pressure of aliquot in storage vessel = 119.2 mm.

Pressure of aliquot + nitrogen in storage vessel = 636.4 mm.

Fraction 2 contains only ethane, carbon dioxide, ethylene, propane and propylene.

Amount of aliquot of fraction 2 analysed = 254.5 μ moles

Amount found in fraction 2(a) = 15.14 μ moles

\therefore Amount present in fraction 2(b) = 239.4 μ moles

Therefore the percentage of fraction 2(b) in fraction 2 =
94% = K

(i) Pressure of aliquot of solution in nitrogen = 100.8 mm.

(ii) " " " = 99.0 mm.

	Peak Height	μ -mole	C	mean C	p
(i) C ₃ H ₈	48.8 cm.	10.86	.779	.776	68.7 mm.
C ₃ H ₆	7.0 cm.	3.08	.221	.224	19.8 mm.
(ii) C ₃ H ₈	50.0 cm.	11.13	.773		
C ₃ H ₆	7.5 cm.	3.28	.227		

In this case the pressure of the product is given by the formula $p = (M \times G \times K \times C) / T$

Fraction 3.

Number of moles in fraction = T - G - F = 1782 - 1011 - 303.8 = 467.2 μ -moles = B

The pressure of the condensable products is given by the formula $p = (M \times B) / T = 43.7$ mm.

Summarising these results

		<u>Material Balances</u>	
		Initial	Estimated
P	= 16.2 mm.		
O ₂	= 19.8 mm.		
C ₃ H ₈	= 68.7 mm.		
H ₂	= 0.39 mm.	C Balance 300	285
CH ₄	= 1.2 mm.	H Balance 800	781
C ₂ H ₆	= 0 mm.	O Balance 100	93
C ₂ H ₄	= 5.0 mm.		
C ₃ H ₆	= 19.8 mm.		
CO	= 7.8 mm.		
CO ₂	= 0.76 mm.		
Condensables	= 43.7 mm.		

A qualitative estimate of fraction 3 was obtained by chromatogram.

A quantitative estimate of the formaldehyde, methoxyl and peroxide was obtained by replacing the introductory U-tube with a B19 test-tube and distilling fraction 3 into the test-tube as before. The test-tube was removed and 10 ml. distilled water pipetted into it before it was allowed to warm up. The solution kept stoppered in a freezing mixture before examination, to prevent decomposition or evaporation of the products before examination. Aliquots of this solution were analysed as described previously.

1.6. Remarks regarding the Kinetic and Chromatographic Apparatus.

The apparatus in which the kinetic experiments were carried out is of a form well-known in the investigations of hydrocarbon combustion. The Bourdon Spoon Gauge provides a relatively simple and effective method of measuring the pressure change, the optical lever enabling readings to be made at a glance. The main error introduced in its use is that pressure changes cannot be determined until about 30 seconds after the entry of the reactants into the reaction vessel, and there is also the disadvantage that there is some "dead space" in the Bourdon Gauge and in the tubing to the vacuum line. By use of capillary tubing this latter error can

be reduced to a negligible amount. The disadvantage in the Bourdon Gauge of the delay in measuring the pressure change is amply compensated by the other features such as robustness, sensitivity, ease of reading and constancy of volume over a wide pressure range.

The analytical technique used in the investigation has considerable advantage over those used previously, in that a complete quantitative analysis of the gaseous products and a qualitative picture of the condensable products can be obtained from the combustion products of one run in a matter of two to three hours. This compares very favourably with the times and conditions required for complete analyses using other techniques. There is now available in the literature a considerable volume of information^{43,44 & 45} to which reference can be made when constructing a chromatography apparatus, and the importance of the column parameters such as flow rate of carrier gas, column temperature and particle diameter is now fully appreciated. It must be pointed out however, that at the beginning of this research when the apparatus was constructed, little was known of the theoretical significance of the effect of these variables, and that the apparatus was constructed with reference to empirical observations. It is interesting to note that the column parameters finally chosen, e.g. the particle diameter of the packing, % liquid phase and flow rate are of the order that the theory predicts give the most efficient separation.

In the literature it is recorded that while the peak area is linearly dependent on the amount of sample, this is not so for peak height. The work reported in the literature has, however, been carried out with samples of the order of 1000 μ -moles, whereas the amounts in the present work were of the order of 100 μ -moles. In this range the peak height does vary almost linearly with the amount of substance, with a slight decrease in sensitivity at high quantities.

EXPERIMENTAL RESULTS.

The oxidation of propane has been investigated kinetically and analytically. The kinetic investigation consisted of a study of the maximum rate and acceleration constant under varying conditions of temperature and reactant pressure. The effect of additives on these parameters was also investigated, the nature of the additives being suggested by the analytical results.

In the analytical investigation, the gaseous products were examined thoroughly at different temperatures, but, because of technical difficulties, the condensable products were less extensively studied.

The experiments were carried out over a considerable period of time, and the results have been given in logical rather than chronological order to facilitate discussion.

The kinetic experiments are described first, and these include an account of the effects of additives. This section is followed by the results from the analytical experiments, and finally, a description of the condensable products is given.

2.1. The Dependence of the Maximum Rate on the Conditions.

The dependence of the maximum rate on the pressures of the reactants was determined at 400° and at 460°C, using appropriate variations of the pressure of the reactants at each of these temperatures. The orders of the reaction with respect to the reactants were determined by plotting the logarithm of the maximum rate against the logarithm of the appropriate pressure, the order being given by the slope of the line obtained.

It was noted that the results tended to become irreproducible in oxygen-rich mixtures, when the ratio of propane to oxygen was smaller than 2/1, and results from these mixtures should therefore be examined with this reservation.

Table 2.1.1 and the corresponding graph 2.1.1 show that the order of the maximum rate with respect to the total pressure at 400°C is 3.92 ± 0.1 , these experiments being carried out with a 2/1 mixture of propane to oxygen.

The dependence of the maximum rate on the oxygen pressure is shown in the tables and figures of section 2.1.2. These illustrate the irreproducibility of results with oxygen-rich mixtures which had been mentioned previously. With very rich mixtures, the results are completely irreproducible, and the reproducibility increases as the ratio of propane to oxygen becomes greater than 1/1. Several attempts were made to improve the results of section 2.1.2.(c) where the propane

pressure is very low at 90 mm., but better reproducibility than that recorded could not be obtained. Although the results are irreproducible, they do show the tendency of the order of the maximum rate with respect to oxygen to decrease at high oxygen concentrations. In the parts of the plots where the results are reproducible, an order of 1.61 ± 0.2 is obtained in section 2.1.2 (a) and of 1.65 ± 0.2 in section 2.1.2 (b). Thus under the conditions when the reaction is reproducible, the order of the maximum rate with respect to oxygen is 1.63 ± 0.2 .

In the tables and graphs of section 2.1.3 are recorded the results of experiments in which the pressure of propane was varied. In these experiments the ratio of the propane pressure to the oxygen pressure seldom falls below 1, and is more frequently near 2, and therefore the reproducibility of the results is greatly increased. When the oxygen pressure is constant at 120 mm., the order of the maximum rate with respect to propane is 2.64 ± 0.2 , when the oxygen pressure is 80 mm., the order is 2.5 ± 0.2 , and when the oxygen pressure is 50 mm., the order is 2.6 ± 0.2 . As a result of these determinations, it may be said that the order of the maximum rate with respect to the propane pressure is 2.6 ± 0.1 at 400°C .

Thus, summarising the results for the dependence of the maximum rate on the pressure at 400°C ,

the order with respect to the propane pressure - 2.6 ± 0.1

the order with respect to the oxygen pressure = 1.63 ± 0.2

the order with respect to the total pressure = 3.9 ± 0.1 ,

and the expression for the maximum rate may be written as

$$\text{approximately } \rho = k(\text{C}_3\text{H}_8)^{2.5}(\text{O}_2)^{1.5}$$

The occurrence of fractional indices in the order of a reaction is frequently, in the case of gas-phase reactions at least, an indication that there is a term involving the total pressure in the rate expression. In addition, the reaction at 460°C does show a definite inert gas effect, as shown in section 2.1.8, and therefore the expression $\rho = k(\text{C}_3\text{H}_8)^2(\text{O}_2)(P)$ was examined, where (P) was taken as $(\text{C}_3\text{H}_8 + \text{O}_2)$. To test the validity of this expression, a plot of $\rho/(\text{C}_3\text{H}_8)$ against $(\text{C}_3\text{H}_8)(\text{O}_2)(P)$ was constructed, and allowing for the observed irreproducibility of some points, the experimental results were found to fit this expression, as shown in figure 2.1.4.

The order of the maximum rate with respect to the reactants was also investigated at 460°C , where slightly different results were found. The table and figure of section 2.1.5 show that the order of the maximum rate with respect to the total pressure of a 2/1 mixture of propane and oxygen is unchanged at 3.95 ± 0.1 at 460°C , but the following section 2.1.6, shows that the dependence of the maximum rate on the propane pressure has fallen. In section 2.1.6, the order of the maximum rate with respect to propane pressure was investigated at oxygen pressures of 20 mm., 50 mm., and 120 mm.

respectively. Although the results are quite reproducible, in the second instance when the pressure of oxygen was 50 mm., the results with propane-weak mixtures tend to lie off the straight line drawn through the remainder of the points. The order of the maximum rate of the propane pressure in the case when the oxygen pressure was 20 mm. was 2.05 ± 0.1 , and when the oxygen pressure was 50 mm. was 1.98 ± 0.1 . When the oxygen pressure was 120 mm., the ratio of the propane pressure to the oxygen pressure was always much less than 1, but even so, the results were still relatively reproducible, and the unexpected order of 3.53 ± 0.3 was obtained for the maximum rate dependence on propane.

The order of the maximum rate with respect to the oxygen pressure was also determined at three different pressures of propane, namely 60 mm., 90 mm. and 120 mm. In the first two instances the reproducibility was not good, as was expected because of the low propane to oxygen ratios, but the results did show that the oxygen dependence did have a definite trend. At 60 mm. and 90 mm. of propane, both of the logarithmic plots, as seen in section 2.1.7, are curved, with the line having a gradient of approximately 2 when the propane and oxygen pressures are comparable. At higher oxygen pressures the maximum rate tends to become independent of the oxygen pressure. In the investigation with 120 mm. propane, the order is found to be 1.8 ± 0.2 . Therefore, in the reaction at high

temperatures, the order of the maximum rate with respect to oxygen tends to have the value just under 2 at high propane to oxygen ratios, with the order falling as the oxygen pressure is increased.

The dependence of the maximum rate on the pressure on inert gas was also investigated at 460°C, and the results are shown in section 2.1.8. These indicate that there is a definite pressure effect, the rate increasing linearly with the pressure.

Thus, summarising the results for the dependence of the maximum rate on the pressure at 460°C, in propane rich mixtures,

the order with respect to the propane pressure = 2.0 ± 0.1

the order with respect to the oxygen pressure = 1.8 ± 0.2

the order with respect to the total pressure = 3.95 ± 0.1

and the expression for the maximum rate with propane rich mixtures may be expressed as approximately $\rho = k(C_3H_8)^2(O_2)^2$. Although at first sight this expression is a simple one, since the reaction does show a strong inert gas effect at this temperature, the true order of the maximum rate with respect to the propane and oxygen pressures alone is probably fractional, the true expression being of the form

$$\rho = k(C_3H_8)^{1.5}(O_2)^{1.5}(C_3H_8 + O_2).$$

This expression is rather more complicated than the one found at 400°C, and a possible explanation is suggested later.

There follows now the tables which show the dependence of the maximum rate on the conditions. In the tables the

pressure changes are given in Bourdon centimetres, and the maximum rates in Bourdon centimetres/minute. The sensitivity of the Bourdon Gauge was 1 cm. mercury = 7.93 Bourdon cm. The nomenclature that is used is

ρ = maximum rate in Bourdon cm./minute

Δp = pressure change in Bourdon cm.

p = pressure of reactant in mm.

2.1.1. The Dependence on the Total Pressure.

Propane pressure/oxygen pressure = 2/1 ; $T = 400^{\circ}\text{C}$.

Run No.	p	$\log p$	ρ	$\log(\rho)$	Δp
4	150	2.18	1.74	0.24	27
2	180	2.26	2.85	0.45	29
5	210	2.32	5.49	0.74	37
1	240	2.38	11.0	1.04	43
3	270	2.44	19.08	1.30	48
6	300	2.48	24.7	1.39	-

$$\text{Order } n = 3.92 \pm 0.2$$

2.1.2. The Dependence on the Oxygen Pressure.

(a) Propane pressure = 150 mm. ; $T = 400^{\circ}\text{C}$.

Run No.	p	$\log p$	ρ	$\log(\rho)$	Δp
3	48	1.68	4.1	0.61	28.5
7	72	1.86	8.3	0.92	36.6
5	98	1.99	12.9	1.11	47.1
2	148	2.17	24.5	1.39	72.5
1	150	2.18	25.0	1.40	71.7
6	195	2.29	20.0	1.30	83.3
4	245	2.39	25.0	1.40	91.3

$$\text{Order } n = 1.61 \pm 0.2$$

2.1.2.

(b) Propane pressure = 200 mm. ; T = 400°C.

Run No.	p	log p	ρ	log(ρ)	Δp
6	29	1.46	3.34	0.52	24
4	50	1.70	7.4	0.87	30
7	70	1.85	12.3	1.09	36
5	91	1.96	23.8	1.38	47
2	115	2.06	30.2	1.48	72
8	117	2.07	32.4	1.51	75
1	120	2.08	34.3	1.54	70
9	146	2.17	48.2	1.69	79
3	203	2.31	35.2	1.55	ca.100

Order n = 1.65 \pm 0.2

(c) Propane pressure = 90 mm. ; T = 400°C.

Run No.	p	log p	ρ	log(ρ)	Δp
3	90	1.95	3.9	0.59	41
5	120	2.08	5.6	0.75	49
2	160	2.20	5.5	0.74	53
7	160	2.20	7.4	0.87	54
1	160	2.20	5.2	0.72	52
6	210	2.32	7.6	0.88	56
4	270	2.41	7.7	0.89	55

2.1.3. The Dependence on the Propane Pressure.

(a) Oxygen pressure = 120 mm. ; T = 400°C.

Run No.	p	log p	ρ	log(ρ)	Δp
8	90	1.95	2.0	0.30	-
6	120	2.08	8.3	0.92	48
1	151	2.18	9.7	0.99	-
2	151	2.18	10.8	1.03	58
3	150	2.18	9.8	0.99	-
5	181	2.26	18.3	1.26	63
7	210	2.32	20.0	1.30	69
4	239	2.40	44.0	1.64	69

Order n = 2.64 \pm 0.2

2.1.3.

(b) Oxygen pressure = 80 mm. ; T = 400°C.

Run No.	p	log p	ρ	log(ρ)	Δp
3	80	1.94	2.0	0.30	-
1	120	2.08	5.2	0.72	44
2	120	2.08	5.5	0.74	44
5	159	2.20	8.2	0.91	40
4	201	2.30	13.0	1.11	40
6	240	2.38	23.2	1.37	42

Order n = 2.5 \pm 0.2

(c) Oxygen pressure = 50 mm. ; T = 400°C.

Run No.	p	log p	ρ	log(ρ)	Δp
3	120	2.08	2.0	0.30	27.3
5	160	2.20	4.0	0.60	31.0
7	198	2.30	8.3	0.92	-
1	200	2.30	8.6	0.94	35.3
2	201	2.30	8.0	0.90	34.8
4	240	2.38	14.7	1.17	36.5
6	272	2.44	15.6	1.19	34.0

Order n = 2.6 \pm 0.22.1.5. The Dependence on the Total Pressure.

Propane pressure/oxygen pressure = 2/1 ; T = 460°C.

Run No.	p	log p	ρ	log(ρ)	Δp
4	92	1.97	2.1	0.33	19
1	120	2.08	4.6	0.68	26
3	150	2.18	10.6	1.03	33
5	180	2.25	24.6	1.39	39
2	212	2.33	45.0	1.65	49

Order n = 3.95 \pm 0.1

2.1.6. The Dependence on the Propane Pressure.

(a) Oxygen pressure = 20 mm. ; T = 460°C.

Run No.	p	Log p	ρ	log(ρ)	Δp
2	80	1.90	2.5	0.40	12.3
5	100	2.00	3.9	0.59	12.1
3	120	2.08	5.4	0.74	12.0
1	140	2.14	6.0	0.84	12.0
6	140	2.14	7.8	0.89	12.0
7	150	2.18	8.8	0.94	12.0
4	160	2.20	10.6	1.03	11.8

Order n = 2.05 \pm 0.1

(b) Oxygen pressure = 50 mm. ; T = 460°C.

Run No.	p	log p	ρ	log(ρ)	Δp
3	59	1.77	5.6	0.75	24.5
7	69	1.83	7.6	0.88	23.9
5	93	1.97	11.8	1.07	23.8
1	98	1.99	12.0	1.08	24.1
2	98	1.99	11.5	1.07	23.3
6	110	2.04	15.0	1.19	23.9
4	121	2.08	18.5	1.27	23.9
8	128	2.11	21.0	1.32	23.9
9	148	2.17	28.5	1.45	24.0

Order n = 2.02 \pm 0.2

(c) Oxygen pressure = 120 mm. ; T = 460°C.

Run No.	p	log p	ρ	log(ρ)	Δp
2	30	1.48	4.8	0.38	36.0
6	40	1.60	8.8	0.94	-
4	45	1.65	10.0	1.00	49.0
1	60	1.78	26.0	1.41	49.0
7	60	1.78	40.0	1.60	-
5	70	1.85	53.5	1.73	51.0
3	80	1.90	65-75	1.88	51.5

Order n = 3.53 \pm 0.3

2.1.7. The Dependence on Oxygen Pressure.

(a) Propane pressure = 60 mm. ; T = 460°C.

Run No.	p	log p	ρ	log(ρ)
7	40	1.60	5.7	0.76
5	60	1.78	9.3	0.97
3	77	1.87	17.5	1.24
6	100	2.00	17.5	1.24
1	120	2.08	17.5	1.24
2	120	2.08	22.5	1.35
8	120	2.08	15.8	-
4	142	2.15	30.0	1.48

Order n approached 2 at low oxygen pressures.

(b) Propane pressure = 90 mm. ; T = 460°C.

Run No.	p	log p	ρ	log(ρ)	Δp
3	30	1.48	5.8	0.76	37.5
9	40	1.60	11.0	1.04	-
5	49	1.69	17.5	1.24	53.8
1	58	-	19.0	-	-
2	58	1.77	19.0	1.28	37.1
6	74	1.87	24.0	1.38	-
4	90	1.95	23.0	1.36	20.3
8	90	1.95	25.0	1.40	-
7	104	1.98	28.0	1.45	-

Order n = approx. 2 at low oxygen pressures.

(c) Propane pressure = 120 mm. ; T = 460°C.

Run No.	p	log p	ρ	log(ρ)	Δp
7	20	1.30	7.5	0.86	19.3
2	30	1.48	13.5	1.13	25.0
5	40	1.61	25.0	1.40	30.8
4	50	1.70	35.0	1.54	39.5
1	60	1.78	48.3	1.68	42.0
6	60	1.78	47.5	1.68	43.0
3	70	1.86	72.5	1.86	49.0

Order n = 1.8 \pm 0.2

2.1.8. The Dependence on Pressure of Carbon Dioxide.

Propane Pressure = 100 mm., Oxygen pressure = 50 mm.;

T = 460°C.

Run No.	p_{CO_2}	ρ
1	0	15.8
2	0	15.8
4	0	15.8
6	0	16.0
8	0	15.8
7	27	17.0
3	48	20.0
9	72	21.0
5	100	24.0

2.2. The Kinetics of the Acceleration Constant.

The dependence of the acceleration constant on the pressures of the reactants was determined at 400°C and at 460°C. The order of the acceleration constant with respect to each reactant, and the total pressure, was obtained by plotting the logarithm of the acceleration constant against the logarithm of the corresponding pressure, the order being given by the slope of the line drawn through these points.

As mentioned previously, the acceleration constant was obtained from a plot of the rate against the pressure change, this method being the one least affected by experimental errors. In some cases this plot did not give a straight line as predicted by Semenov's Theory, but consisted of two linear portions (for example see figure 2.2.6 (i)) the latter being of greater

slope, indicating an increase in the acceleration as the reaction proceeded. Where these two slopes occur, they are referred to as the initial and the final acceleration constants respectively. The significance of this two-stage nature will be discussed later.

The earlier acceleration constant has quite different kinetic dependencies from the later one in that it is almost independent of the oxygen pressure. The later acceleration constant has kinetic dependencies which are similar to those associated with the low temperature reaction, and therefore one may tentatively identify the later acceleration constant with that of the low temperature reaction, and the initial acceleration constant with that of some reaction introduced at high temperatures.

It was found that at 400°C almost all the plots of rate against pressure change gave graphs that contained only one linear portion, with the exception of a few in section 2.2.2. At 460°C , on the other hand, the distinction of two linear portions was often quite marked. For this reason the examination of the "initial" acceleration constant has been confined to the higher temperature.

Table 2.2.1 and the corresponding graph 2.2.1 show that the order of the acceleration constant with respect to the total pressure of a 2/1 mixture of propane and oxygen at 400°C was found to be 3.5 ± 0.4 . The dependence of the oxygen pressure at 400°C is illustrated in section 2.2.2, and was

found to be 1.6 ± 0.2 , and the dependence of propane pressure recorded in section 2.2.3, to be 2.5 ± 0.2 .

Summarising the investigations at 400 C.,

the order with respect to propane pressure = 2.5 ± 0.2

the order with respect to oxygen pressure = 1.6 ± 0.2

the order with respect to total pressure = 3.5 ± 0.4

and the dependence of the acceleration constant on the pressure at 400°C may be written $\phi = k(C_3H_8)^{2.5}(O_2)^{1.5}$.

The existence of a total pressure effect will lower these values and give an expression nearer the form of

$$\phi = k(C_3H_8)(O_2)(P) \text{ where } (P) = (\gamma C_3H_8 + O_2).$$

In the investigation at 460°C, the unusual "initial" and "final" acceleration constants were found in some of the runs, and where possible its dependence on the pressure conditions was examined.

Table 2.2.4 gives the variation in both the "initial" and the "final" acceleration constants with the variation in the total pressure of a 2/1 mixture of propane and oxygen at 460°C. The "initial" acceleration constant was found to have an order of 1.9 ± 0.3 , and the "final" acceleration constant an order of 2.4 ± 0.3 with respect to the total pressure.

The dependence of the acceleration constant on the propane pressure at 460°C is shown in section 2.2.5, where two investigations with different oxygen pressures were carried out. With 20 mm. of oxygen, only the "final" acceleration constant was observed, and it had an order of 1.9 ± 0.2 with

respect to the propane pressure. With 50 mm. of oxygen, both acceleration constants were observed, the "initial" having an order of 1.9 ± 0.2 , and the "final" one an order of 1.6 ± 0.2 with respect to the propane pressure.

The dependence on the oxygen pressure at 460°C is shown in section 2.2.6, the propane pressure being 120 mm. It was in this particular investigation that the two linear portions were most distinct, and the plots of rate against pressure change, from which the acceleration constants were obtained, are shown in figure 2.2.6.(1). The "initial" acceleration has an order of 0.2 ± 0.1 , and the "final" one an order of 1.1 ± 0.2 with respect to the oxygen pressure.

Summarising the results at 460°C , we have for the "initial" acceleration constant

the order with respect to propane pressure = 1.9 ± 0.2

the order with respect to oxygen pressure = 0.2 ± 0.1

the order with respect to the total pressure = 1.9 ± 0.3

and for the "final" acceleration constant

the order with respect to the propane pressure = 1.75 ± 0.2

the order with respect to the oxygen pressure = 1.1 ± 0.2

the order with respect to the total pressure = 2.4 ± 0.3

A dependence on the total pressure is probably present, and therefore the expressions for the acceleration constants are probably of the form:

$$\phi_i = (C_3H_8)(O_2)^0(P)$$

$$\phi_f = (C_3H_8)(O_2)(P)$$

where (P) is a total pressure term of the form ($\gamma C_3H_8 + O_2$).

The significance of these observations is discussed later.

There now follows the tables which show the dependence of the acceleration constant upon the conditions. In the tables the rates are given in Bourdon cms./minute, the pressure changes in Bourdon cm., and the nomenclature is

- ϕ = acceleration constant
- ϕ_i = initial acceleration constant
- ϕ_f = final acceleration constant
- p = initial reactant pressure in mm.

2.2.1. The Dependence on the Total Pressure.

Prepane pressure/oxygen pressure = 2/1 ; T = 400°C.

Run No.	p	log p	ϕ	log ϕ
4	153	2.18	0.12	1.08
2	178	2.26	0.18	1.26
5	210	2.32	0.29	1.46
1	240	2.38	0.43	1.63
3	274	2.44	1.10	0.04
6	300	2.48	1.77	0.25

$$\text{Order } n = 3.5 \pm 0.4$$

2.2.2. The Dependence on the Oxygen Pressure.

Propane Pressure = 200 mm. ; T = 400°C.

Run No.	p	log p	ϕ	log ϕ
6	30	1.48	0.18	1.25
4	50	1.70	0.39	1.59
7	70	1.85	0.51	1.71
5	90	1.96	1.17	0.07
1	120	2.07	1.60	0.20

Order n = 1.6 ± 0.2 2.2.3. The Dependence on the Propane Pressure.

Oxygen Pressure = 50 mm. ; T = 400°C.

Run No.	p	log p	ϕ	log ϕ
3	120	2.08	0.12	1.08
5	160	2.20	0.22	1.35
1	200	2.30	0.42	1.63
4	240	2.38	0.67	1.83
6	272	2.44	0.89	1.95

Order n = 2.5 ± 0.2 .2.2.4. The Dependence on the Total Pressure.

Propane Pressure/Oxygen Pressure = 2/1 ; T = 460°C.

Run No.	p	log p	ϕ_1	log ϕ_1	ϕ_f	Log ϕ_f
4	92	1.96	.16	1.21	.16	1.16
1	120	2.08	.26	1.42	.26	1.42
3	151	2.18	.40	1.61	.54	1.73
5	181	2.26	.42	1.62	.74	1.87
2	212	2.33	.77	1.88	1.20	0.08

Order n_1 = 1.9 ± 0.3 Order n_f = 2.4 ± 0.3 .

2.2.5. The Dependence on the Propane Pressure.

(a) Oxygen pressure = 20 mm. T = 460°C.

Run No.	p	log p	ϕ	log ϕ
2	80	1.90	.20	1.31
5	100	2.00	.31	1.49
3	120	2.08	.43	1.64
1	140	2.14	.51	1.71
6	140	2.14	.64	1.80
7	150	2.18	.69	1.84
4	160	2.20	.78	1.89

Order $n = 1.9 \pm 0.2$.

(b) Oxygen pressure = 50 mm. T = 460°C.

Run No.	p	log p	ϕ_i	log ϕ_i	ϕ_f	log ϕ_f
3	59	1.77	0.19	1.27	0.43	1.64
7	69	1.83	0.26	1.42	0.49	1.69
5	93	1.97	-	-	0.71	1.85
2	98	1.99	0.47	1.67	0.78	1.89
6	110	2.04	0.57	1.75	0.87	1.94
4	121	2.08	0.64	1.87	0.99	0.00
8	128	2.11	0.80	1.93	1.25	0.10
9	148	2.17	1.00	0.00	1.38	0.14

Order $n_i = 1.9 \pm 0.2$ Order $n_f = 1.6 \pm 0.2$.2.2.6. The Dependence on the Oxygen Concentration.

Run No.	p	log p	ϕ_i	log ϕ_i	ϕ_f	log ϕ_f
7	20	1.30	0.4	1.60	0.48	1.68
5	40	1.61	0.5	1.70	0.73	1.86
4	50	1.70	0.5	1.70	1.05	0.02
1	60	1.78	0.5	1.70	1.59	0.17
3	70	1.86	0.6	1.78	1.68	0.23

Order $n_i = 0.2 \pm 0.1$ Order $n_f = 1.1 \pm 0.2$.

3. The Effect of Additives on the Kinetics of the Reaction.

The importance of intermediate compounds in determining the rate of reaction has been recognised for a considerable time in the theories of the oxidation hydrocarbons, and investigation of the effects of the addition of possible intermediate compounds often gives information as to the nature of the reaction mechanism. The function of these intermediate compounds is to act as a radical source, and one of the more important details upon which the addition of such a radical source can shed light, is the nature of the degradation reaction, that is, the non-branching reaction by which the intermediate is removed. If this reaction is of the type



where XH is the intermediate and R. and X. are radicals, it is possible, by the addition of suitable intermediate, to produce a "negative induction period"⁴⁶ where the reaction starts off at more than the maximum rate and slows down to give the maximum rate of the reaction when no additive has been introduced. Acetaldehyde is such a radical source, and we were therefore interested in ascertaining what effect the addition of it had on the reaction rate.

The curious behaviour of propylene, as is demonstrated later in the analytical results, suggested that it might play an important role in the oxidation, especially as it is a

well-known inhibitor of chain reactions⁴⁷. The effect of the addition of propylene was therefore also investigated.

The effect of propylene on the acceleration constant is shown in figure 3.1. The mixture which was examined was 100 mm. propane and 50 mm. oxygen, and in these runs the propylene was not added, but was substituted for the same amount of propane. The initial mixture was thus similar, with respect to the propylene concentration, to one produced after a considerable degree of reaction. In a typical run where the propylene concentration was 10 mm., the composition of the initial mixture was 90 mm. propane, 10 mm. propylene and 50 mm. oxygen. As can be seen in figure 3.1., the initial linear portion of the plot was partially removed by the substitution of 5 mm. propylene, and was completely removed by the substitution of 10 mm. propylene. In the plot of the acceleration constant in the run with 10 mm. propylene there was no initial part and the single straight line that was obtained corresponded to the "final" acceleration constant. Substitution of larger amounts of propylene increased the value of the acceleration constant.

In a series of runs at high pressure of propane and with varying amounts of oxygen, a series of acceleration constant plots with two distinct linear portions was obtained. Figure 3.2 shows that by substitution of suitable amounts of

propylene for propane, the initial straight line parts of these plots could be removed. The plots illustrated were obtained from runs with 120 mm. propane and 50, 60 and 70 mm. of oxygen respectively. When 8, 10 and 12 mm. propylene (amounts comparable with those present when the acceleration constant altered) were substituted for propane in the initial mixtures, the initial acceleration constant was not found in the respective mixtures with 50, 60 and 70 mm. oxygen. Thus in propane rich mixtures, the amount of propylene produced initially was proportional to the amount of oxygen in the initial mixture.

Because of the observed effect of propylene in accelerating the reaction, this latter observation might account for the increase in order with respect to oxygen as the temperature is raised.

The effect of the addition of aldehydes was also investigated, using formaldehyde, acetaldehyde and propionaldehyde. In order to keep the rate of reaction under control under the accelerating conditions produced by aldehydes, the pressures of the reactants that were investigated were reduced to 80 mm. propane and 40 mm. oxygen. The aldehydes were premixed with the reactants in the mixing vessel a few minutes before reaction.

Figures 3.3 and 3.4 show the effect of addition of varying amounts of formaldehyde and acetaldehyde respectively.

The induction period was reduced and the maximum rate slightly increased by the addition of both formaldehyde and acetaldehyde, the latter being the more effective. In neither case, however, even with the addition of 10 mm. of aldehyde, did the reaction start off at maximum rate.

In view of the fact that propylene obviously played an important role in the reaction, especially in the later stages, the effect of the addition of aldehydes to mixtures containing propylene was investigated.

The aldehydes were added to reaction mixtures containing 65 mm. propane, 15 mm. propylene and 40 mm. oxygen, and figures 3.5, 3.6 and 3.7 show the effect of the addition of varying amounts of formaldehyde, acetaldehyde and propionaldehyde respectively. These curves show that the addition of propylene made the reaction rate much more sensitive to the amount of aldehyde added, the addition of 8 mm. of formaldehyde, and 4 mm. of acetaldehyde or propionaldehyde almost removing the induction period.

When the amount of propylene substituted was increased to 20 mm., the reaction mixture then consisting of 60 mm. propane, 20 mm. and 40 mm. oxygen, the effect of the addition of acetaldehyde is shown in figure 3.8. The addition of 4 mm. of acetaldehyde removed the induction period completely, the reaction starting off at maximum rate. Addition of larger amounts of acetaldehyde led to the production of a "negative

induction period", where the reaction started off at greater than maximum rate and then slowed down to give the maximum rate. This effect is shown in the curves where 6 mm. and 8 mm. of acetaldehyde were added.

The theoretical implications of these results are discussed later.

4. ANALYTICAL RESULTS.

Reaction mixtures were analysed at successive stages in the reaction for oxygen, propane, propylene, ethane, ethylene, methane, hydrogen, carbon monoxide, carbon dioxide, formaldehyde, methoxyl and peroxide. The sampling and fractionation of the sample have already been described.

Since each sample taken for analysis involved a separate experiment, a study of the progress of the reaction in time required in principle a high degree of reproducibility in the reaction curves. This was achieved by carrying out several runs until the rate of reaction reached a steady state and any additional variation was allowed for in the following way. A complete pressure-time curve for a particular reaction mixture was obtained. Samples for analysis were then removed after a given pressure rise rather than after a given time. In plotting yields against time the original Δp versus time curve was used to obtain the time for any given pressure rise. This involved the assumption that the pressure change gave a measure of the stage of reaction, which was confirmed by the results.

The results are expressed in mm. partial pressure in the reaction vessel at the reaction temperature. The formaldehyde, methoxyl and peroxide were determined in only one series of runs, and in that series accounted for less than 2% of the carbon balance.

4.1. Material Balances.

Material balances were constructed for each series of runs by comparing the amounts of elements in the reactants and in the products.

In making these calculations, it was assumed that the condensable fraction contained only water (except in the series where the formaldehyde, methoxyl and peroxide were determined, when they were included in the material balances). This assumption was justified by the observations that

a) the carbon content of these products was almost always less than 1% of the total carbon in the mixture and was never more than 2% of the total carbon. The error in the hydrogen and oxygen balances introduced by the assumption of formaldehyde and methanol to be water was negligible.

b) the amounts of peroxides determined analytically were always less than 1 mm., and the assumption of the product to be water introduced no large error.

c) the chromatogram of fraction 3 showed that although there were several other products present, they were present in amounts less than 1 mm. of each product.

A hydrocarbon was found in the chromatogram of fraction 3 and this indicated that some of fraction 2 remained dissolved in the products condensable at -80°C . The amount of hydrocarbon detected was found to depend on the efficiency of fractionation by the Toepler pump. To get perfect separation

the time of pumping was inconveniently long and so a balance had to be struck between efficiency and time of pumping. The amount of hydrocarbon dissolved was approx. proportional to the amount of fraction 3, and in the later stages of the reaction was equivalent to about 2% of the total carbon. No estimate of this hydrocarbon was made when making up the element balances.

The material balances calculated with these assumptions all agreed to within 10%, and in many cases were much better. The differences in the material balances could be attributed to the above assumptions and also to several processes that were observed in the reaction system. These were

- 1) the formation of polymers on the walls of the tubes leading from the reaction vessel. A brown polymer was observed at the exit from the reaction vessel, and a white polymer along the tubes through which the sample passed. From previous observations recorded in the literature³³, these were believed to be a hydrocarbon and a formaldehyde polymer respectively;

- 2) the attack on the mercury of the Toepler pump by the products of the reaction. This could be the reason why the amount of peroxide isolated was always less than 1 mm., and why the oxygen balance was sometimes rather low.

The tables and graphs of section 4.2.1 show the variation in concentration of the products and reactants throughout the

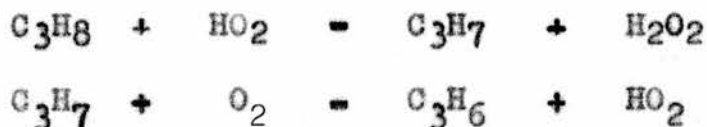
the reaction of 100 mm. propane and 50 mm. oxygen at 435°C. To show the variations in the rate of production of the various products more clearly, the pressure change of the product or reactant is plotted against the total pressure change. This latter plot shows a number of interesting features.

The pressure change of the reactants, propane and oxygen, follow the total pressure change quite closely, showing that the rate of change of pressure gives a measure of the rate of reaction, as determined by the rate of removal of reactants.

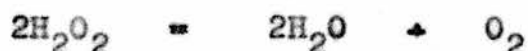
The main gaseous products of the reaction are methane, ethylene, carbon monoxide and propylene, and small amounts of ethane, hydrogen and carbon dioxide are also formed.

The nature of the reaction varies with the extent of the reaction, since in the initial stages propylene is formed fairly quickly, and at maximum rate has a stationary concentration.

In the initial stages of the reaction almost all the propane that is removed appears as propylene with the disappearance of approximately 1 mole of oxygen, and only small amounts of the other gaseous products are formed. A possible mechanism by which this could occur is



The decomposition of the hydrogen peroxide on the walls of the reaction vessel as



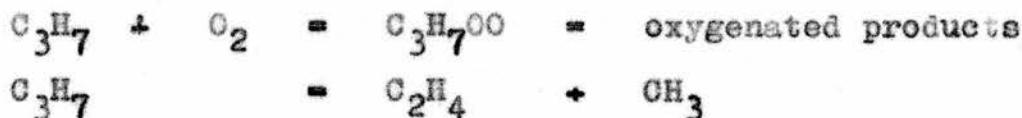
regenerates oxygen and thus explains why the amount of oxygen reacted is rather less than the amount of propylene produced. After about 30% reaction when the concentration of propylene has reached an appreciable value, the rate of production of propylene falls off until, at 60% reaction, it reaches a stationary value. Presumably the propylene is removed by some reaction, and at 60% reaction, when its concentration is stationary, the rate of production of propylene equals the rate of removal of propylene. The nature of the reaction that removes the propylene leads to considerable discussion, but since there appears to be no change in the nature of the other products of the reaction, it is reasonable to postulate that the reaction gives rise to the same radical as propane, namely the propyl radical, and the reaction by which the propylene is removed may be



This reaction is the reverse of a reaction advanced previously, so that the interesting feature of a free radical equilibrium is suggested. The probability of this happening is discussed later.

The initial rates of production of ethylene and carbon monoxide are quite small compared with that of propylene, but

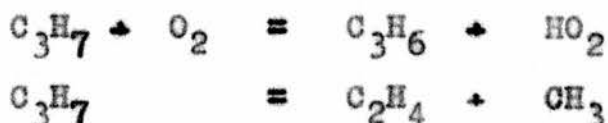
once the rate of production of propylene falls off, these rates increase, with the rate of production of carbon monoxide being greater than the rate of production of ethylene. It is suggested that these products may be formed by the alternative reactions of the propyl radical such as



methane and carbon monoxide being produced by the subsequent reaction of the products of these initial reactions.

The methoxyl and formaldehyde concentrations follow the pressure change curve quite closely over most of the reaction, and although the peroxide determinations are not very reproducible, they seem to indicate that the peroxide concentration rises to a maximum and then falls to almost zero at the end of the reaction.

Sections 4.2.2 and 4.2.3 show the effect of reducing the initial oxygen concentration from 50% to 10% and then to 2% of the propane concentration. The most marked change is the increase in the rate of production of ethylene relative to the rate of production of propylene. This suggests that the reaction producing propylene is of higher order with respect to the oxygen concentration than the one producing ethylene, which is in agreement with the reactions suggested previously, namely



The relative rate of production of carbon monoxide also falls.

Sections 4.2.4 and 4.2.5 give the analysis of reaction mixtures of 100 mm. propane and 50 mm. oxygen at 445° and 475°C respectively. As is shown in figure 4.3 increase in the temperature has the effect of increasing the amounts of methane and ethylene formed and the amount of propane reacted, while the amounts of carbon monoxide, propylene and total condensable products are little affected. The total pressure change also increases slightly. These effects suggest that there is an increase in the cracking reaction relative to the oxidation reactions as the temperature is raised.

The unusual variation in the propylene concentration and also the appearance of the two acceleration constants at higher temperatures indicate that there may be some connection between these two observations, and the effect of replacing some of the propane in the initial reaction mixture with propylene to various extents was investigated. The results are shown in sections 4.2.6, 4.2.7, and 4.2.8, and the most obvious observation in this set of investigations is that propylene appears to have an equilibrium concentration in the region of 25 mm. under these conditions, and that the propylene concentration tends to move towards that value throughout the reaction. The graph numbered 4.4 shows the effect of the replacement of propane by propylene on the other

products of the reaction. The amounts of methane and ethylene are unaffected, whereas the amount of carbon monoxide produced is substantially increased. There is also a decrease in pressure change and total pressure of condensable products as the amount of propane replaced by propylene is increased.

From these results it can be deduced that the substitution of propylene for propane in the initial mixture makes reactions producing carbon monoxide more probable, without affecting the rate of production of ethylene and methane.

There now follows the tables of analyses in which are shown the effects which have just been discussed. The tables are all illustrated in the corresponding figures. The pressures of products and reactants are given in mm. at the temperature of the reaction vessel to facilitate the examination of the results. The element balances are given in mm. atoms and the times of sampling are in minutes except where otherwise stated.

Table 4.2.1. Products from 100 mm. propane and 50 mm. oxygen at 435°C.

Run No.		D	F	A	C	E	B
Δp	0	5.1	10.5	16.2	22.3	27.8	33.4
Time	0	2.26	2.84	3.17	3.44	3.69	5.0
O_2	50	41.0	30.7	19.8	8.7	0.38	0.
C_3H_8	100	87.4	79.0	68.3	60.5	55.0	52.4

Table 4.2.1. (contd.)

Run No.	D	F	A	C	E	B
H ₂	- 0.1	0.2	0.4	0.6	0.8	1.1
CH ₄	- 0.4	0.6	1.2	1.8	3.9	6.1
C ₂ H ₆	- 0.2	-	-	0.2	0.3	0.6
C ₂ H ₄	- 1.3	3.0	4.9	4.9	10.4	11.6
C ₃ H ₆	- 10.2	15.7	19.3	20.6	22.0	21.5
CO	- 1.3	3.77	7.77	12.2	16.8	19.4
CO ₂	- .17	.39	.76	.83	1.46	1.66
Condensables	- 14.1	30.1	43.7	58.0	65.3	70.0
C Balance	300 298	295	282	272	275	273
H Balance	800 797	800	775	752	763	765
O Balance	100 98	96	93	90	86	93

The formaldehyde, methoxyl and peroxide were determined in a separate series of runs.

Run No.	6	12	3	7	2	9
Δ P	2.3	3.4	7.2	11.0	14.7	18.5
Time	1.70	1.98	2.54	2.88	3.09	3.27
CH ₂ O	0.06	0.06	0.15	0.18	0.33	0.60
CH ₃ OH	-	0.34	1.0	0.89	0.87	1.50
H ₂ O ₂	0.20	0.38	0.33	0.47	-	0.5
Run No.	5	10	4	8	11	1
Δ P	22.2	25.6	26.8	30.8	33.3	34.3
Time	3.44	3.59	3.66	3.85	4.25	5.0
CH ₂ O	0.66	0.55	0.79	1.04	0.75	0.83
CH ₃ OH	2.24	2.20	2.24	2.28	2.2	2.12
H ₂ O ₂	0.42	1.09	0.42	0.44	0.14	0.01

Table 4.2.2. Products from 95.5 mm. propane and 9.5 mm. oxygen at 435°C.

Run No.	0	B	D	C	E	A
Δp	0	2.02	3.78	5.68	7.25	8.95
Time	0	2.60	3.82	5.35	6.30	8.2
O_2	9.5	7.3	4.5	2.4	0.9	0.
C_3H_8	95.5	90.0	86.0	84.1	80.7	78.7
H_2	0	0.02	0.05	0.07	0.15	0.25
CH_4	0	0.5	0.7	1.0	1.6	2.4
C_2H_6	0	-	0.1	-	0.1	0.15
C_2H_4	0	1.0	1.9	2.6	4.5	5.5
C_3H_6	0	3.6	6.6	8.4	9.3	10.5
CO	0	0.2	0.3	0.5	1.1	1.4
CO_2	0	0.04	0.08	0.08	0.09	0.18
Condensables	0	5.0	8.3	11.2	13.8	15.0
C Balance	287	283	283	284	282	283
H Balance	764	757	755	760	754	756
O Balance	19	20	18	17	17	17

Table 4.2.3. Products from 99.1 mm. propane and 1.9 mm. oxygen at 435°C.

Δp	0	3.0
O_2	1.9	0
C_3H_8	99.1	94.1
H_2	0	0.13
CH_4	0	0.97
C_2H_6	0	0
C_2H_4	0	2.02
C_3H_6	0	3.1
CO	0	0.21
CO_2	0	0
Condensables		3.6

Table 4.2.3. (contd.)

C Balance	297	297
H. Balance	793	791
O Balance	3.8	3.8

Table 4.2.4. Products from 100 mm. propane and 50 mm. oxygen at 445°C.

The propane used in this series of runs contained 1.4% ethane.

Run No.	0	F	C	G	E
Δp	0	3.3	5.2	5.6	10.8
Time	0	1.45	1.85	1.94	2.52
O_2	50	45.3	40.0	-	30.4
C_3H_8	98.6	87.6	86.3	81.3	74.1
H_2	0	0.03	0.10	-	0.3
CH_4	0	0.3	0.50	-	0.9
C_2H_6	1.4	1.4	1.4	1.5	1.3
C_2H_4	0	1.16	2.07	2.56	4.11
C_3H_6	0	8.0	10.4	11.5	17.7
CO	0	0.34	1.72	-	4.85
CO_2	0	0.1	0.2	-	0.6
Condensables	0	9.8	12.9	-	26.6
C Balance	299	290	290	-	292
H Balance	797	778	797	-	781
O Balance	100	101	95	-	93
Run No.		A	D	B	H
Δp		16.8	22.7	28.4	33.7
Time		2.96	3.27	3.44	5.0
O_2		18.5	7.3	0	0
C_3H_8		66.1	54.9	50.4	47.9

Table 4.2.4 (contd.)

Run No.	A	D	B	H
H ₂	0.5	0.7	0.9	1.3
CH ₄	1.7	2.7	5.2	7.7
C ₂ H ₆	1.5	1.9	1.4	1.9
C ₂ H ₄	7.15	10.5	14.2	14.0
C ₃ H ₆	19.3	22.2	21.6	19.6
CO	7.9	13.4	17.4	19.7
CO ₂	0.9	1.4	1.6	1.9
Condensables	43.5	57.7	66.1	70.0
C Balance	284	274	271	263
H Balance	776	753	753	742
O Balance	90	88	87	93

Table 4.2.5. Products from 100 mm. propane and 50 mm. oxygen at 475°C.

Run No.	O	F	D	B	E	C	A
Δp	0	9.2	16.4	22.8	28.1	33.8	39.8
Time (secs)	0	44.0	55.5	61.1	64.6	68.3	100
O ₂	50	36.5	25.2	13.9	8.6	1.8	0
C ₃ H ₈	100	81.7	70.6	60.7	55.0	47.4	43.6
H ₂	0	0.2	0.5	0.7	0.9	1.1	1.8
CH ₄	-	1.0	1.9	2.8	4.4	5.5	9.4
C ₂ H ₆	-	0.1	0.2	0.2	0.2	0.3	1.2
C ₂ H ₄	-	3.2	7.6	9.6	13.4	18.0	20.6
C ₃ H ₆	-	12.6	18.0	22.6	22.9	21.5	22.8
CO	-	2.1	6.0	9.5	12.6	16.3	19.3
CO ₂	-	0.2	-	0.6	0.9	1.2	1.3
Condensables	-	21.9	37.6	54.0	60.6	72.7	71.0
C Balance	300	296	293	282	279	276	273
H Balance	800	796	788	781	783	751	757
O Balance	100	97	95	93	91	95	93

Table 4.2.6. Products from 90 mm. propane, 10 mm. propylene and 50 mm. oxygen at 435°C.

Run No.		C	D	E	B	A
Δp	-	7.3	12.9	18.2	23.7	32.6
t	-	2.55	3.19	3.56	3.93	5.25
O ₂	50	36.1	23.8	14.6	5.0	-
C ₃ H ₈	90	76.2	68.3	57.6	55.2	52.4
H ₂	-	0.2	0.4	0.5	0.6	1.0
CH ₄	-	-	0.9	1.6	2.6	6.3
C ₂ H ₆	-	-	-	-	-	0.50
C ₂ H ₄	-	2.1	4.1	6.0	8.2	12.1
C ₃ H ₆	10	19.0	21.1	22.2	23.6	23.3
CO	-	3.6	9.7	12.4	17.1	21.8
CO ₂	-	0.5	0.8	1.5	1.9	2.0
Condensables	-	21.4	37.6	47.5	62.2	67.6
C Balance	300	297	288	267	287	280
H Balance	780	775	769	720	777	773
O Balance	100	98	97	92	93	94

Table 4.2.7. Products from 80 mm. propane, 20 mm. propylene and 50 mm. oxygen at 435°C.

Run No.		C	B	D	E	A
Δp	0	6.6	12.2	17.5	23.3	28.8
Time	-	2.14	2.75	3.13	3.50	5.0
O ₂	50	34.4	22.2	12.2	4.0	0
C ₃ H ₈	80	67.6	61.6	55.5	49.0	45.6
H ₂	0	0.2	0.4	0.5	0.7	0.9
CH ₄	0	-	1.0	1.9	3.5	5.2
C ₂ H ₆	0	-	-	-	0.5	0.5
C ₂ H ₄	0	2.5	4.7	6.6	8.7	13.1
C ₃ H ₆	20	24.9	26.7	27.3	26.6	25.7
CO	0	5.0	10.0	15.9	21.0	24.2
CO ₂	0	0.7	1.3	1.7	2.3	2.9

Table 4.2.7 (contd.)

Run No.	O	C	B	D	E	A
Condensables	0	22.6	35.0	49.8	60.5	61.8
C Balance	300	288	287	281	270	273
H Balance	760	746	747	742	731	720
O Balance	100	98	92	93	94	92

Table 4.2.8. Products from 60 mm. propane, 40 mm. propylene and 50 mm. oxygen at 435°C.

Run No.	O	C	B	D	A
Δp	0	7.1	13.5	19.8	25.9
Time	-	1.59	1.93	2.22	5.0
O ₂	50	29.8	13.0	1.9	0
C ₃ H ₈	60	49.7	44.4	38.3	36.9
H ₂	0	0.2	0.4	0.6	0.9
CH ₄	0	1.0	1.8	3.7	5.8
C ₂ H ₆	0	-	-	-	0.6
C ₂ H ₄	0	3.7	6.3	9.0	11.3
C ₃ H ₆	40	39.4	37.5	35.0	32.1
CO	0	7.1	15.2	23.6	27.4
CO ₂	0	0.7	1.6	2.2	2.8
Condensables	0	26.7	44.9	57.1	58.6
C Balance	300	284	287	267	267
H Balance	720	707	704	683	677
O Balance	100	95	89	89	92

4.5. Examination of Fraction 3 by Chromatography.

The methods that were used in the chromatographic investigation of fraction 3 are described in section 1.3.9. Of the several peaks that were found in the chromatogram only one,

that of acetaldehyde, was positively identified by its infra-red spectrum, most of the remaining components possessing spectra with carbonyl absorptions. The amounts of these other products produced were very small, and in addition complete separation was not obtained in the chromatogram. These two factors together made investigation of fraction 3 by this method rather unsatisfactory, and no attempt was made to pursue this examination further. However, the chromatogram of fraction 3 did give some qualitative information about the nature of the condensable fraction.

The chromatogram of the condensable products from the combustion at 475°C was very similar to that of the products from the combustion at 435°C , in that the same peaks were present. The amounts of the products was rather less, as would be expected.

The chromatogram of fraction 3 from the products of combustion of 60 mm. propane, 40 mm. propylene and 50 mm. oxygen at a point about maximum rate is shown in figure 4.5. The amounts of products were rather more than from the combustion of propane alone, and in addition, a compound which was eluted at 17 minutes was present. The compound at 19 minutes was now one of the major condensable products.

The variation in the amounts of these products throughout the reaction could also be followed in the chromatograms of the samples.

The height of the acetaldehyde peak was found to reach

a maximum at the maximum rate of reaction, and then to fall until it finally reached a concentration of a fifth of its value at maximum rate.

The peak at 17 minutes, and also, in the combustions with propane alone, the peak at 19 minutes appeared only when there was a relatively large amount of condensable products, and never became very large. They might therefore be attributed to compounds formed by the reaction of the products in the sampling vessel.

The remainder of the peaks increased throughout the reaction, but it is quite possible that any variation in one of the peaks would be masked by the superposition of peaks from other products.

DISCUSSION.

In the part of the thesis which follows the experimental results recorded in the previous sections are discussed and a reaction mechanism which can account for them is suggested.

In the first section of the discussion is given the thermal data from which the heats of reaction of the majority of the reactions are calculated. The next section consists of a discussion of the reactions by which the products are formed, and also of the reactions which give rise to branching.

In the final section the important reactions of the proposed mechanism are considered and from them are derived theoretical expressions for the kinetic parameters, the acceleration constant and maximum rate. These expressions are then compared with the experimental ones.

1. Thermal Data.

The thermal data which have been used in calculating the energy changes in the reactions advanced are given in the following tables. In general, a chemical reaction takes place only if it results in a decrease in the free energy of the system, but unfortunately the free energy changes for the majority of the reactions possible in the oxidation of propane are not known. The heat of reaction is usually the most easily obtainable thermodynamic quantity, and in general, the enthalpy changes have been taken as rough approximations to the free energy changes, and regarded as a rough criterion of whether or not a reaction can take place. Which of a number of possible competitive reactions will take place in a system will depend not on the free energy or the enthalpy changes, but on the activation energy. Swarc⁴⁸ has shown in the case of the reaction of sodium atoms, that the activation energy of the reaction is proportional to the exothermicity of the reaction, the proportionality factor being 0.3. In the reaction of free radicals with hydrocarbons it is unlikely that the same proportionality of the activation energy to the exothermicity will exist, since the reaction complexes will not show the same features with different radicals. Nevertheless, the enthalpy change of a reaction does give some estimate of the possibility of its occurring.

The heats of formation of the molecules tabulated have been

taken from "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds" by Rossini et al., and from "Circular 500 Selected Values of Chemical Thermodynamic Properties, 1952". The heats of formation of free radicals have been taken from these tabulated in "Gas Kinetics" by Trotman-Dickenson.

The heat of dissociation of the H-O₂ bond has been the subject of some speculation, and values from 55 ± 10 K-cals. by Walsh⁴⁹, to the value 36 K-cals. by Evans Hush and Uri⁵⁰ have been advanced. However, the most reliable experimental observation has been carried out by Foner and Hudson⁵¹ and this gave ^{an} intermediate value of 47.2 K-cals.

Using this value the heat of formation of the HO₂ radical can be calculated to be 5 K-cals. This value has been adopted in the following discussion.

In the following table the Heats of Formation are given in K-cals./mole at 25°C and 1 atmosphere pressure.

Compound	Heat of Formation	Radical	Heat of Formation
CH ₄	-17.9	CH ₃	32.5
C ₂ H ₆	-20.2	C ₂ H ₅	25.2
C ₃ H ₈	-24.8	n C ₃ H ₇	22
C ₂ H ₄	+12.5	iso C ₃ H ₇	17
C ₃ H ₆	+ 4.9	C ₃ H ₅	30
CH ₃ OH	-48.3	OH	10.1
C ₂ H ₅ OH	-56.7	HO ₂	5
CH ₂ O	-28.8	CH ₃ O	- 1
CH ₃ CHO	-44	C ₂ H ₅ O	- 8

Compound	Heat of Formation	Radical	Heat of Formation
C_2H_5CHO	-46	CHO	+ 6
CO	-26.4	CH_3CO	- 6
CO_2	-94		
H_2O_2	-32.6		
H_2O	-57.8		

2. THE MECHANISM OF THE REACTION.

2.1. Discussion of the Products.

In the reactions that follow, the heats of reaction will be given in K-cals. In the case of reactions involving the propyl radical, the heat of reaction of the n-propyl radical will be given and then the heat of reaction of the iso propyl radical in brackets after it.

The numbers that are given to the reactions are those from the complete reaction scheme which is given later.

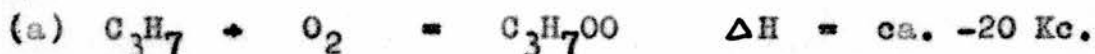
Previous work has led to the hypothesis that the oxidation of propane proceeds by way of the initial formation of the propyl radical which may subsequently react by three possible routes -

- a) $C_3H_7 + O_2 = \text{Oxygenated Products } \Delta H = \text{ca. } -40 \text{ Kc.}$
 b) $C_3H_7 + O_2 = C_3H_6 + HO_2 \quad \Delta H = -12 \text{ } (-7) \text{ Kc.}$
 c) $C_3H_7 = C_2H_4 + CH_3 \quad \Delta H = 23 \text{ } (28) \text{ Kc.}$

Among the oxygenated products is one which may produce degenerate branching. The unusual features of the oxidation such as cool flames and negative temperature coefficient of reaction rate, can be explained by the postulate that the nature

of either the branching or chain propagating reaction depends on the temperature. The reaction occurring at temperatures below 300°C is believed to be mainly reaction (a) while reaction (b) becomes increasingly important as the temperature is raised until it predominates between 400 and 500°C. Finally, reaction (c), which has a higher activation energy than the other two, only becomes important at higher temperatures, becoming appreciable at about 400°C, and then increasing in importance until it is the main reaction above 500°C.

The nature of reaction (a) has been investigated by Bell et al.⁵² and almost certainly the first step is the addition of the oxygen molecule to the radical to form the propyl peroxy radical



As has been mentioned in the introduction, there has been considerable controversy over the fate of this radical, one school maintaining that it was sufficiently stable to react with a hydrocarbon or some other molecule to give a hydroperoxide molecule, and the other school suggesting that it was unstable and decomposing before reaction to give an aldehyde and a free radical. Certainly the formation of a hydroperoxide has been demonstrated in the oxidation of tetralin and cumene in the liquid phase⁵⁸, but hydroperoxides have only been isolated in gas phase oxidation at temperatures

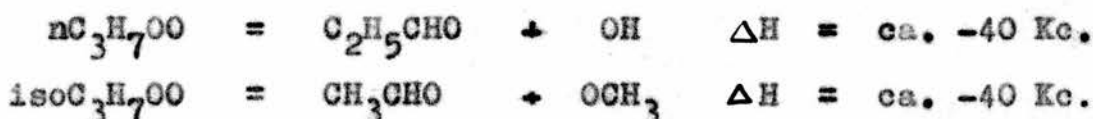
about 200°C, by Bell et al.⁵² in the hydrogen bromide catalysed oxidation of a number of hydrocarbons. However only tertiary hydroperoxides were isolated and they were unable to obtain even small amounts of primary or secondary hydroperoxides from ethane and propane.

It is unlikely then, that under the conditions of this investigation, hydroperoxides will be stable intermediates in the oxidation of propane. It has been postulated by Norrish^{21,53} that the free radical breaks down to give an aldehyde and a smaller free radical, and Lewis and von Elbe²³ have suggested that the iso-propyl radical is formed, and that the corresponding iso-propyl peroxy radical breaks down to give acetaldehyde and methoxyl radical.

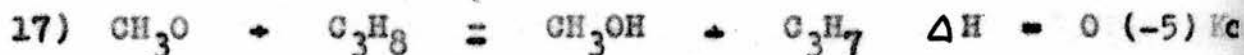
So far, no mention has been made of the identity of the propyl radical, whether it is the n-propyl or the iso-propyl radical. Knox⁵⁴, in the investigation of the attack of chlorine atoms on propane, has shown that both primary and secondary C atoms are attacked, and that the difference in activation energies for attack at these positions is 450 cal. The P factors were also shown to be of comparable magnitude, the ratio for attack at secondary to attack at primary being 1.65 to 1. Although HO₂ radicals do not have the same reactivity as chlorine atoms, the difference in activation energies for attack by HO₂ radicals on the primary and secondary C atoms is unlikely to be much greater than that for

attack by chlorine atoms. Therefore one may expect both n-propyl and iso-propyl radicals to be produced in the reaction.

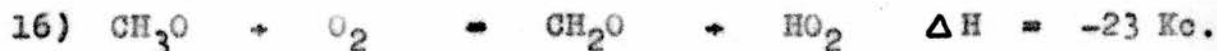
The reactions of the corresponding propylperoxy radicals if they decompose on formation are



Acetaldehyde has certainly been identified in the products of the reaction, and indications have been found that propionaldehyde is also present. In the investigations at lower temperatures, where the preponderance of the iso-propyl radical over the n-propyl radical is greater because of its lower activation energy of formation, considerable quantities of methanol and acetaldehyde have been isolated. This is especially true of the work of Pease²⁴, who obtained almost quantitative production of methanol and acetaldehyde in the combustion of propane in oxygen-weak mixtures. This reaction can also explain the small amounts of methanol as determined by the Zeisel method, found in the products of this investigation. The methanol is produced by the reaction of the methoxyl radical with a propane or a product molecule

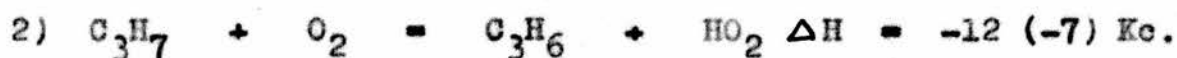


The methoxyl radical may also react with oxygen as



and this reaction probably accounts for the low yield of methanol.

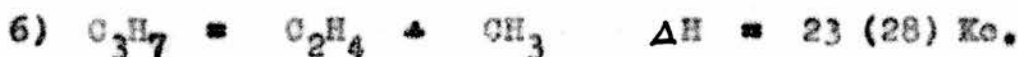
The formation of propylene from both n-propyl and iso-propyl radicals by the abstraction of an H atom by oxygen is an exothermic reaction, and gives the most convenient explanation of the formation of the olefine. In the initial stages of the reaction as is illustrated in figure 4.2.1, propylene is formed from propane in almost a 1 to 1 ratio, with the disappearance of almost 1 molecule of oxygen, and a chain reaction that can explain these observations is



These two reactions constitute a chain reaction which is carried by the HO_2 radical. In addition to explaining the formation of propylene, the chain reaction can also give a convenient explanation of the large amounts of hydrogen peroxide sometimes found in the reaction products. Kooijman and Ghijsen³⁴ have shown that high yields of hydrogen peroxide can be obtained between 400° and 460°C , and other workers³⁰ have shown that the amount of hydrogen peroxide isolated depends inversely on the efficiency of the surface of the reaction vessel in catalysing its heterogeneous decomposition. In this investigation, although some peroxide was isolated, the amount determined was relatively small, and this may be due to decomposition of the peroxide in the reaction vessel or in the sampling vessel. Decomposition of hydrogen peroxide

in the reaction vessel with the regeneration of some oxygen explains why the amount of oxygen removed initially is less than the amount of propane.

Reaction 6, the cracking of the propyl radical to produce ethylene and the methyl radical, is endothermic in the case of both n-propyl and iso-propyl radicals, as



It is therefore not surprising that the production of ethylene only becomes predominant at relatively high temperatures above 450°C. The methyl radical formed in the above reaction may react a) with oxygen giving formaldehyde and a hydroxyl radical or b) with propane to form methane and a propyl radical, as



These reactions explain why the methane concentration is low in the initial stages of the reaction, and then begins to rise when the oxygen has been exhausted, as is shown in figure 4.2.1.

When the amount of oxygen in the reaction mixture is reduced from 50% to 10% of the propane pressure, the most marked change is the increase in the rate of production of ethylene as compared with the rate of production of propylene, the relative increase in the rates being by a factor of three, as is shown in figure 4.2.2. This figure also shows that the relative rate of production of carbon monoxide falls, and of methane increases, as the oxygen concentration is decreased.

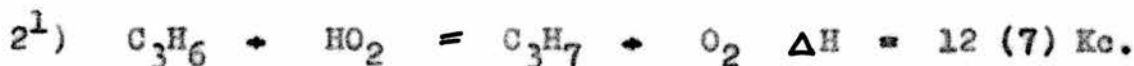
When the oxygen in the reaction mixture is reduced from 10% to 2%, the increase in the rate of ethylene production relative to the rate of propylene production is also very marked, the relative rate going up by a factor of 2.4.

The increase in the rate of production of ethylene relative to that of propylene as the percentage of oxygen in the initial reaction mixture is reduced indicates that the propylene is formed by a reaction of higher order with respect to oxygen than is the ethylene. This confirms the suggested reactions for the production of the two species, which are



An unusual feature of this investigation has been the observation that the propylene concentration reaches a stationary value. We therefore conclude that at that stage of the reaction, the propylene is being removed by some reaction at the same rate as which it is being formed. The products of the reaction have been examined with propylene concentrations both above and below the stationary concentration (see figures 4.2.6, 4.2.7, 4.2.8) and there seems to be little change in the nature of the gaseous products of the reaction. This observation suggests that the propylene reacts by the same reaction route as propane, namely by way of the propyl radical. The conclusion is rather a surprising one, for it means in effect that an equilibrium is set up in the free

radical reaction,



An alternative reaction of propylene with HO_2 is the formation of the allyl radical



The latter reaction would seem much more likely, since it is considerably more exothermic and would be expected at first sight to have a lower activation energy. However, the exothermicity of the latter reaction is due in some part to the resonance energy of the allyl radical and in some part to the heat of formation of the hydrogen peroxide molecule, and the activation energy is probably of the same order as that of the former reaction. It is interesting to note that in the investigation of the oxidation of propylene, Bawn and Skirrow⁵⁵ suggested that the HO_2 radical added to the double bond of the propylene. Only in this way could the relatively high yield of acetaldehyde with respect to formaldehyde which they obtained, be explained.

There is no direct experimental evidence of the formation or reaction of the allyl radical, but the brown polymer that was deposited at the exit of the reaction vessel after a considerable period of operation could possibly have been produced by polymerisation of allyl radicals, as was found by Satterfield and Wilson³³.

When, in the investigation of the combustion of 100 mm.

propane and 50 mm. oxygen, 10 mm. propylene are substituted for 10 mm. propane in the initial mixture, very little change is noticed in the final products of the reaction, but interesting changes occur in the rates of production of the products. This is illustrated in figure 4.2.6.

The concentration of propylene still reaches a stationary value, but the rates of production of carbon monoxide and ethylene remain constant throughout the reaction, and do not show the increase in rate of production at about 30% reaction which is found with only propane and oxygen as the initial reactants. In this case also, the rate of production of methane increases when the oxygen concentration falls.

The same effects are found when larger amounts of propane are replaced in the initial mixture by propylene, as is seen in figures 4.2.7 and 4.2.8. These figures also show that propylene has an equilibrium concentration of about 25 mm. in this particular set of experimental conditions, and when varying amounts are substituted in the initial mixture, the concentration does tend toward this value as the reaction proceeds. Figure 4.4 shows that as propane is replaced by propylene in the initial mixture, the total pressure change and the amount of total condensable product falls, and that while little change in the final concentration of ethylene and methane occurs, the final concentration of carbon monoxide is appreciably increased.

From these results it may be seen that in the initial stages of reaction of a propane/oxygen mixture, the main reaction is one which produces propylene and that only small amounts of methane, ethylene and carbon monoxide are produced. As the propylene concentration builds up, it begins to be removed from the reaction mixture and so tends towards a stationary state concentration. At the same time as the rate of propylene production falls off, the rates of production of carbon monoxide and of ethylene increase, the former being greater than the latter. One may therefore link the reaction removing propylene with the one producing carbon monoxide. The connection between these two observations can be found in the reactions suggested above.

The variation in the reaction products as the temperature is increased is shown in figure 4.3. The amounts of carbon monoxide, propylene and total condensable products remain unchanged, but there is an increase in the amounts of ethylene and methane produced, and in the amounts of propane reacted. The total pressure change is also increased.

If one assumes that all the ethylene comes from the cracking of the propyl radical, it can be calculated from the relative amounts of ethylene to propylene at the different temperatures, that the difference in activation energy of the reactions by which these products are produced is 18 K-cals. The activation energy of the cracking reaction has been reported by

Bywaters and Steacie⁵⁶ as 18 K-cals., but this value does not agree with the calculated ΔH of the reaction of 23 (28) K-cals.

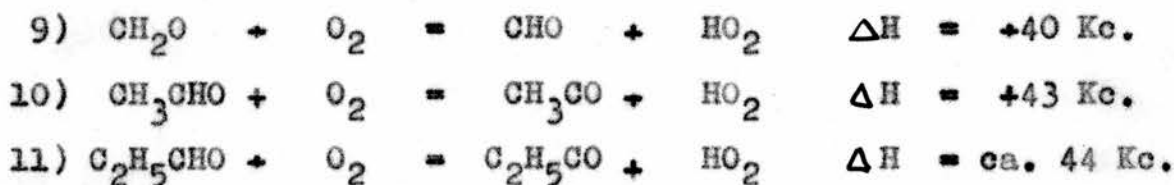
2.2. Discussion of the Branching Mechanism.

Semenov¹⁹ has shown that the oxidation of hydrocarbons occurs by a degenerately branching chain mechanism, and that the intermediate product responsible for the branching must have a lifetime of the order of minutes before entering the branching reaction. Norrish⁵⁷ has shown that if the intermediate fulfils these conditions, it must attain a pressure of the order of millimetres during the course of the reaction. There is some controversy as to the identity of this branching intermediate in combustions at lower temperatures - whether it is an aldehyde or a peroxide molecule. There is general agreement, however, that at the high temperatures employed in this investigation, peroxides other than hydrogen peroxide have a very short lifetime, of the order of much less than 1 second, and therefore they cannot be responsible for the degenerate branching that is observed. On the other hand, aldehydes are thermally stable molecules at these temperatures, and addition of them to the reaction system does reduce the induction period, and it is therefore reasonable to suggest that aldehydes are possible branching intermediates in the oxidation.

Now, formaldehyde and acetaldehyde have been identified in the products, and it has been shown that propionaldehyde may

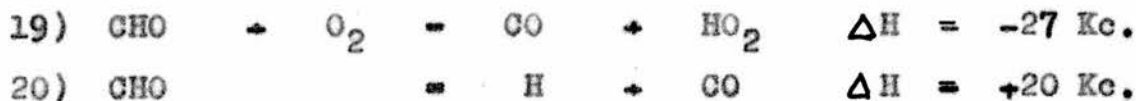
also be present. Although the amounts of these products that have been determined are less than the amount that has to be added to remove the induction period, the aldehydes that are present must act as branching intermediates and therefore at least a considerable part of the branching can be attributed to these aldehydes. It is possible that the unidentified products found in the condensable fraction may be derivatives of aldehydes, and the amount of aldehyde actually present in the product may be more than the amount determined. If this were the case almost all of the branching could be attributed to the aldehydes.

Walsh²⁵, from an investigation of the oxidation methane, and McDowell and Thomas²⁶, from an investigation of the oxidation of acetaldehyde, have suggested that the branching reactions of formaldehyde and acetaldehyde are respectively,



By analogy the last reaction may be taken as the branching reaction of propionaldehyde.

The formyl radical that is produced may either react with oxygen or decompose to give H and CO, as



The H atom produced in the latter reaction could possibly,

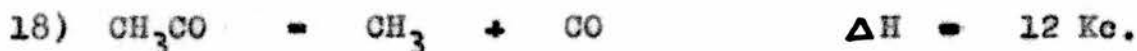
by reaction with propane or a product molecule, be the source of the small amount of hydrogen found in the products, as in the equation



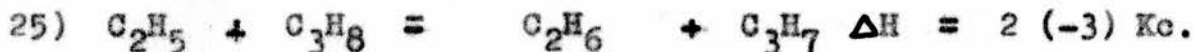
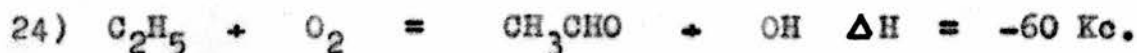
The formyl radical may possibly give rise to the small amount of carbon dioxide found in the products, by the reaction



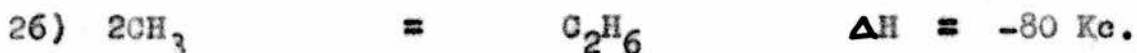
The acetyl and propionyl radicals produced from the respective aldehydes are unstable at temperatures above 150°C , decomposing to give



The ethyl radical may subsequently react according to the reactions



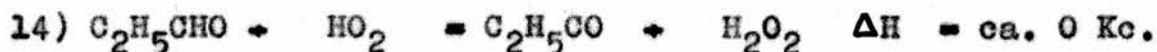
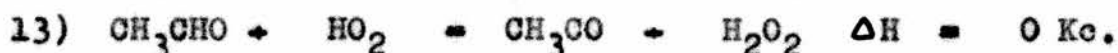
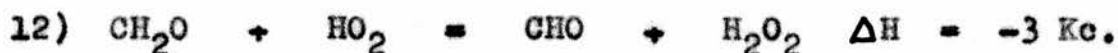
The latter reaction could possibly be the source of the small amount of ethane detected towards the end of the reaction. An alternative source may be the dimerisation of methyl radicals



Both of these reactions would occur to any extent only in absence of oxygen.

In addition to reacting with oxygen to give branching of the reaction chain, aldehydes also suffer degradative reactions

by attack of free radicals, as



Once the reaction has started, the free radicals are produced by the branching reactions, and therefore there is a proportionality between the concentration of aldehydes and the concentration of free radicals. The degradative reaction of the aldehydes is thus second order with respect to the free radical concentration, and it is this quadratic destruction that controls the maximum rate of reaction. The differential equation for the free radical concentration is of the form

$$dn/dt = k_0 + k_1 n - k_2 n^2$$

where k_0 is associated with the initiating reaction producing the initial number of centres, $k_1 n$ is associated with the centres produced in the branching reaction, and $k_2 n^2$ is associated with the reaction that removes the aldehydes without branching.

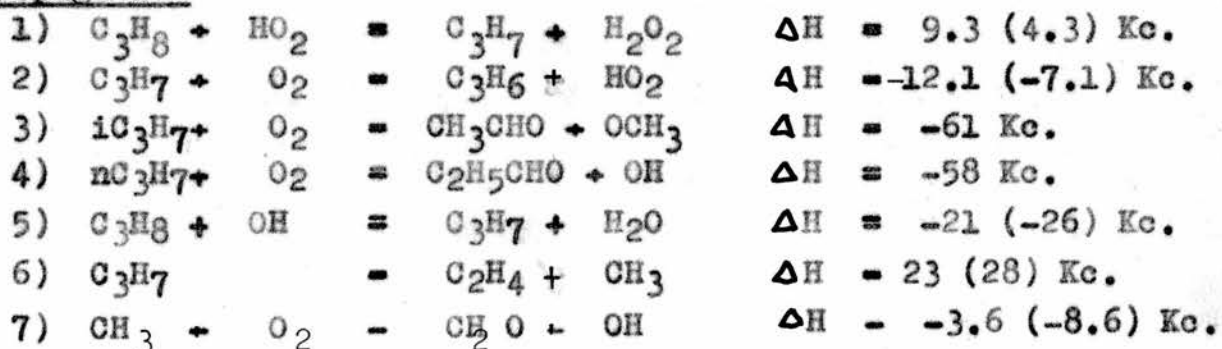
If the free radical concentration is made greater than the stationary state value at maximum rate, by addition of say acetaldehyde the rate of attack on the branching intermediate is increased and its concentration is reduced to the value at "maximum rate". This is the effect which has been demonstrated in the addition of aldehydes to various

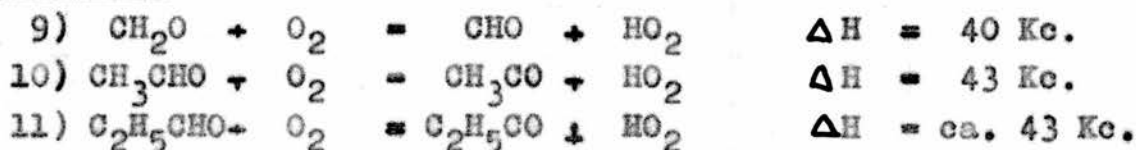
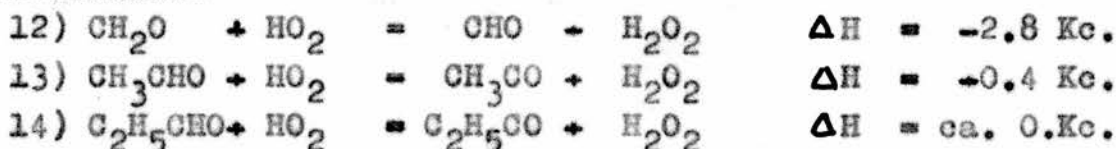
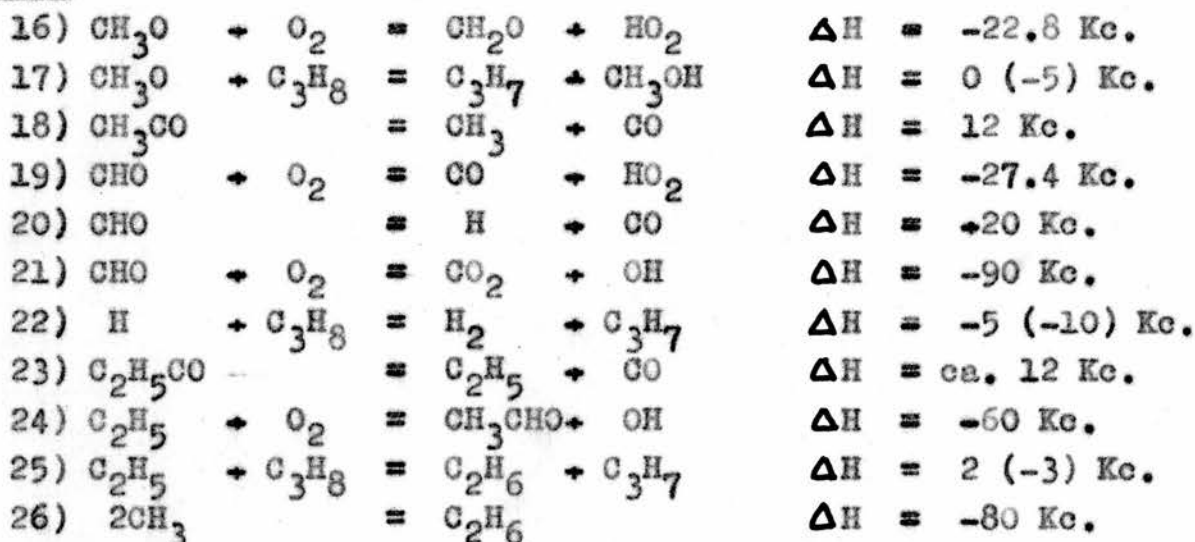
reaction mixtures, illustrated in figures 3.3 to 3.8. The effect is somewhat complicated by the superimposed propylene effect, but when one considers the investigation with 60 mm. propane, 20 mm. propylene and 40 mm. oxygen in section 3.8, the curves that are obtained by addition of varying amounts of acetaldehyde fully bear out these theoretical predictions. The addition of 4 mm. acetaldehyde completely removes the induction period, the reaction starting off at maximum rate, and the addition of 6 mm. and 8 mm. of acetaldehyde causes the reaction to start off at a rate greater than the expected maximum rate, after which the rate slows down to the expected maximum rate. These facts comprise very strong evidence that the reactions suggested above form the mechanism by which the combustion is carried out.

The analytical and the kinetic evidence both point to the fact that the role played by propylene in the oxidation of propane is an important one, and from these observations some suggestions can be made as to the nature of this role.

On the basis of the analysis of the reaction products, the following basic scheme appears feasible.

Propagation



BranchingDegradationTerminationAlso

It appears from the analytical results that two distinct mechanisms occur in the oxidation of propane, one predominating in the initial stages of the reaction, and the other in the region of maximum rate. In the initial stages of the reaction, the main product of the reaction chain is propylene, and in the later stages the propylene concentration is constant. Initially the propyl radical may react by three types of reactions, and in the later stage only two of these reactions are effectively possible. The role of the propylene then is

to block one of the reaction streams of the propyl radical and to force it to react by the other two routes.

3. Discussion of the Kinetic Expressions.

The investigation of the maximum rate in section 2.1 and of the acceleration constant in section 2.2 have shown that at 400°C the maximum rate of reaction is given by the expression

$$\rho = k(C_3H_8)^2(O_2)(P)$$

where (P) is a term involving the total pressure of the reaction system and was taken as $(C_3H_8 + O_2)$, and that the acceleration constant is given by a similar expression. This type of expression for the maximum rate is typical of the kinetic expressions obtained in low temperature investigations. When the temperature is raised to 460°C, the total order of the reaction remains the same at 4, but the order with respect to oxygen increases and the order with respect to propane diminishes, so that the rate expression for the maximum rate is of the form

$$\rho = K.(C_3H_8)^{1.5}(O_2)^{1.5}(P)$$

The appearance of these fractional orders suggests that the reaction becomes more complicated under these conditions, and this suggestion is confirmed by the analytical results. Further proof is obtained from an investigation of the acceleration constant of the reaction, when two acceleration constants are obtained. One is found at the beginning of the reaction and has been called the "initial" acceleration constant

and the one that occurs later the "final" acceleration constant.

The analytical results suggest that these acceleration constants may be attributed to two different mechanisms, and this is supported by the observation that they have different kinetics. The initial acceleration constant is given by the expression

$$\phi = k(\text{C}_3\text{H}_8)^{1.9}(\text{O}_2)^{0.2}$$

and the final acceleration constant by the expression

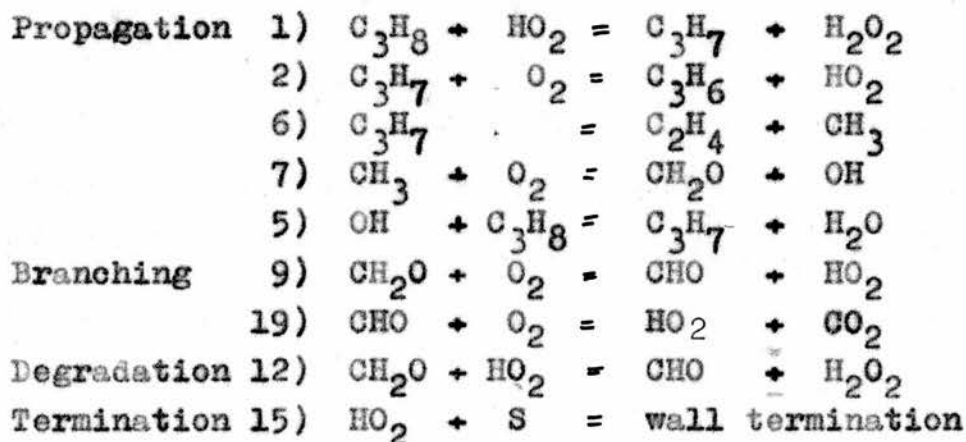
$$\phi = k(\text{C}_3\text{H}_8)^{1.75}(\text{O}_2)^{1.9}$$

The kinetic evidence bears out the analytical observations in suggesting that two mechanisms occur in the oxidation of propane at high temperatures, the one occurring in the initial stages of reaction, and the one occurring in the region of maximum rate. In the initial reaction, the main reaction is the production of propylene with the production of small amounts of ethylene and carbon monoxide also occurring. In this mechanism the branching may possibly be attributed to the reaction of the formaldehyde produced from the reaction of the methyl radical with oxygen. In the reaction at maximum rate, since the propylene concentration remains steady, the reactions for the production and removal of propylene may be omitted from the reaction scheme, and the large amounts of carbon monoxide relative to ethylene show that the reaction by way of aldehyde is an important reaction.

These simplified schemes may then be written down and the kinetic relationships derived as in the following sections.

3.1. The Kinetics of the Initial Reaction.

In the initial stages of the reaction the product of the main chain reaction is propylene, and since the amounts of ethylene and carbon monoxide produced are almost equal the branching may be attributed mainly to the reaction of formaldehyde which is produced eventually as a result of the cracking reaction of the propyl radical. The termination reaction is probably removal of HO_2 radicals at the wall, and the main reactions of the simplified scheme may be written, selecting the appropriate equations from the complete scheme given earlier, as



To obtain a kinetic expression for the acceleration constant, defined as the rate of production of new chains per primary chain, from this reaction scheme, one has to consider the amount of branching intermediate produced by the chain and the rate at which it reacts to give a branching reaction.

The amount of formaldehyde produced per chain is $[\alpha[\text{C.L.}] - 1]$, where $[\text{C.L.}]$ is chain length, and α is the fraction of C_3H_7 radicals that react by cracking rather than by having a hydrogen atom abstracted. For large values of the chain length the expression reduces to $\alpha[\text{C.L.}]$. The value of the acceleration constant is the rate at which this formaldehyde reacts with oxygen, giving two free radicals and may be expressed as

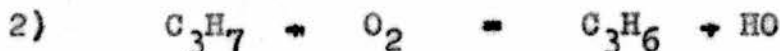
$$\phi = 2k_9 \cdot \alpha \cdot [\text{CL}][\text{O}_2].$$

The chain length is defined as the rate of propagation divided by the rate of termination of chains and is expressed

$$[\text{C.L.}] = \frac{k_1[\text{C}_3\text{H}_8][\text{HO}_2]}{k_{15}[\text{HO}_2]} = \frac{k_1[\text{C}_3\text{H}_8]}{k_{15}}$$

$$\text{giving } \phi = \frac{2k_9 k_1 \cdot \alpha \cdot [\text{C}_3\text{H}_8][\text{O}_2]}{k_{15}}$$

Now the two competing reactions of the propyl radical in this simple scheme are



$$\text{and } \alpha = \frac{R_6}{R_2 + R_6} = \frac{k_6[\text{C}_3\text{H}_7]}{k_2[\text{C}_3\text{H}_7][\text{O}_2] + k_6[\text{C}_3\text{H}_7]} = \frac{k_6}{k_2[\text{O}_2] + k_6}$$

The analytical results, for example section 4.2.1, show that in the initial stages of reaction, the rate of reaction 2 (as measured by the rate of production of propylene) is some 10 times the rate of reaction 6 (as measured by the rate of

production of ethylene).

That is, $k_2[O_2] \doteq 10 \times k_6$

so that k_6 is small in comparison with $k_2[O_2]$ and the expression for α then may be simplified to

$$\alpha = \frac{k_6}{k_2[O_2]}.$$

Substituting in the expression for the acceleration constant gives

$$\phi = \frac{2k_1k_6k_9}{k_2k_{15}} \cdot \frac{[C_3H_8][O_2]}{[O_2]}$$

It was shown in section 2.1.4 that the reaction has a definite dependence on the total pressure, and the expression for reaction 15 must therefore include a term to allow for the effect of the total pressure on the diffusion of radicals to the wall, as

$$k_{15} = k_{15}^0/[P] \quad \text{where } [P] = [\gamma C_3H_8 + O_2]$$

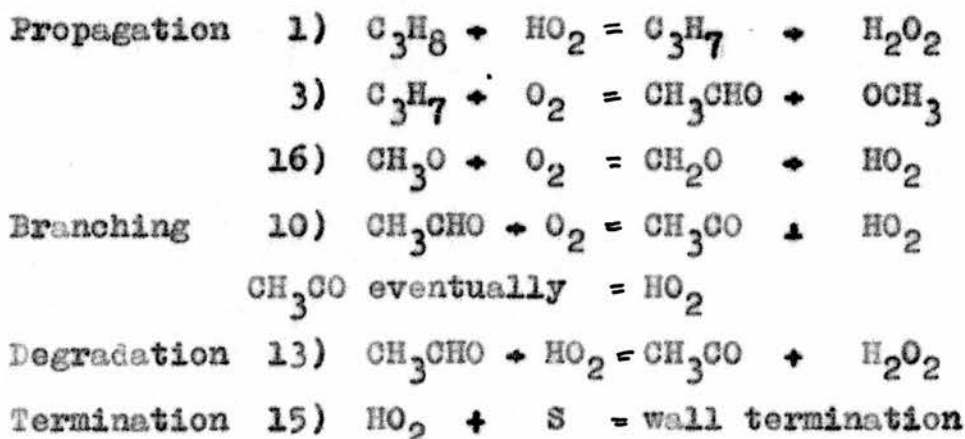
so that $\phi = k[C_3H_8][\gamma C_3H_8 + O_2]$.

This expression is in quite good agreement with experimental determinations which give the expression $\phi_1 = k[C_3H_8]^{1.8}[O_2]^{0.2}$ for the dependence of the initial acceleration constant on the pressure of the reactants.

The maximum rate corresponding to this reaction mechanism is never experimentally realised, since the reaction mechanism alters after the initial stages of reaction.

3.3.2. The Kinetics of the Final Reaction.

In the "final" reaction which is defined as the reaction that occurs during the region in which the maximum rate of reaction is reached, the propylene concentration is at a stationary value and therefore the propane is removed by the reactions other than those that produce propylene. These reactions give rise to both formaldehyde and higher aldehydes, but since the amount of carbon monoxide is appreciably higher than the amount of ethylene, a considerable amount of reaction must occur by way of the higher aldehydes. Since these higher aldehydes are more active in accelerating the reaction than formaldehyde, the simplifying assumption is made that all the branching may be attributed to acetaldehyde. This assumption is necessary to make the derivation of the kinetic expression a manageable operation. Selecting the appropriate reactions from the main scheme, the mechanism is



At maximum rate a stationary state is set up, and we have

$$(1) \quad 0 = \frac{d[\text{HO}_2]}{dt} = -k_1[\text{C}_3\text{H}_8][\text{HO}_2] + k_3[\text{C}_3\text{H}_7][\text{O}_2] + 2k_{10}[\text{A}][\text{O}_2] - k_{15}[\text{HO}_2].$$

$$(2) \quad 0 = \frac{d[\text{C}_3\text{H}_7]}{dt} = k_1[\text{C}_3\text{H}_8][\text{HO}_2] - k_3[\text{C}_3\text{H}_7][\text{O}_2]$$

$$(3) \quad 0 = \frac{d[\text{A}]}{dt} = k_3[\text{C}_3\text{H}_7][\text{O}_2] - k_{10}[\text{A}][\text{O}_2] - k_{13}[\text{A}][\text{HO}_2]$$

Adding (1) and (2) gives

$$(4) \quad 0 = 2k_{10}[\text{A}][\text{O}_2] - k_{15}[\text{HO}_2]$$

$$\therefore [\text{A}] = \frac{k_{15} \cdot [\text{HO}_2]}{2k_{10} [\text{O}_2]}$$

from (2)

$$[\text{C}_3\text{H}_7] = \frac{k_1[\text{C}_3\text{H}_8][\text{HO}_2]}{k_3[\text{O}_2]}$$

Substituting these expressions in equation (3) gives

$$(5) \quad 0 = \frac{k_1 k_3 [\text{C}_3\text{H}_8][\text{HO}_2][\text{O}_2]}{k_3 [\text{O}_2]} - \frac{k_{10} k_{15} [\text{HO}_2][\text{O}_2]}{2k_{10} [\text{O}_2]} - \frac{k_{13} k_{15} [\text{HO}_2]^2}{2k_{10} [\text{O}_2]}$$

$$\therefore [\text{HO}_2] = \frac{2k_{10}}{k_{13} k_{15}} \left[k_1 [\text{C}_3\text{H}_8] - \frac{k_{15}}{2} \right] [\text{O}_2].$$

At maximum rate

$$\begin{aligned} - \frac{d[\text{C}_3\text{H}_8]}{dt} &= k_1 [\text{C}_3\text{H}_8][\text{HO}_2] \\ &= \frac{2k_1 k_{10} [\text{C}_3\text{H}_8]}{k_{13} k_{15}} \left[k_1 [\text{C}_3\text{H}_8] - \frac{k_{15}}{2} \right] [\text{O}_2] \end{aligned}$$

The second term in bracket corresponds to the removal of propane by branching reaction and this is small compared with the amount removed by the main chain, and the expression

reduces to

$$-\frac{d[C_3H_8]}{dt} = \frac{2k_1k_{10}}{k_{13}k_{15}} [C_3H_8]^2 [O_2].$$

As mentioned previously, the strong inert gas effect suggests that the termination is controlled by diffusion of HO_2 radicals to the wall and is inversely proportional to the pressure, giving for the termination reaction

$$k_{15} = k_{15}^0/[P] \quad \text{where } [P] = [\gamma C_3H_8 + O_2]$$

The maximum rate is therefore given by the expression

$$\rho = k[C_3H_8]^2 [O_2][\gamma C_3H_8 + O_2].$$

which is in good agreement with the experimental expression that is obtained at $400^\circ C$ where

$$\rho = k[C_3H_8]^2 [O_2][C_3H_8 + O_2]$$

the coefficient γ being taken as 1.

It was shown that when the temperature is raised to $460^\circ C$, the experimental expression is rather more complex, being of the form

$$= k[C_3H_8]^{1.5} [O_2]^{1.5} [P].$$

and a possible explanation of this may be found in the analytical results which indicate that at higher temperatures the contributions from other reaction mechanisms are increased, these other mechanisms having different kinetics.

As has been shown previously²⁰ the expression for the acceleration constant is

$$\phi = k_b [\alpha [\text{C.L.}] - 1]$$

In this case $\alpha = 2$ and $[\text{C.L.}] = \frac{k_1 [\text{C}_3\text{H}_8] [\text{HO}_2]}{k_{15} [\text{HO}_2]}$ giving

$$\begin{aligned} \phi &= \frac{2k_1 k_{10} [\text{C}_3\text{H}_8] [\text{O}_2]}{k_{15}} \\ &= \frac{2k_1 k_{10} [\text{C}_3\text{H}_8] [\text{O}_2] [P]}{k_{15}^0} \\ &= k [\text{C}_3\text{H}_8] [\text{O}_2] \quad (\text{C}_3\text{H}_8 + \text{O}_2) \end{aligned}$$

Here the agreement with the experimental observations is not good, the latter giving

$$\phi_f = k [\text{C}_3\text{H}_8]^{1.75} [\text{O}_2]^{1.9}.$$

However, since a considerable amount of reaction has occurred before this reaction mechanism comes into play, the initial concentrations are considerably altered, and it is to be expected that agreement is not too good between the experimental and theoretical values.

This investigation has been confined almost entirely to reaction mixtures weak in oxygen, but kinetic observations have shown that the maximum rate does tend to become independent of the oxygen pressure at high oxygen pressures. This effect has been recorded previously in other investigations of combustions - for example it was found in the oxidation of butanone by Bardwell and Hinshelwood⁵⁹, in the oxidation of cyclopropane by McEwan and Tipper⁶⁰ and in the oxidation of methanol by Bell and Tipper⁶¹. It has been shown in the analytical results of this investigation that the nature of

the reaction is affected by the relative amount of oxygen present, and in the absence of analytical data with oxygen rich mixtures, any discussion of this effect must necessarily be very speculative. For this reason discussion of this feature is deferred until the relevant analytical data is available.

The main point that has arisen from the present investigation is that the oxidation of propane in the high temperature region is a two stage reaction. This has been reflected in both the analytical and kinetic results. The plots of acceleration constants at higher temperatures have shown two distinct linear portions, and these have been associated with two different reaction mechanisms. The analytical results also show that the nature of the reaction products depends on the stage of the reaction. In the initial stages propylene is the main product and only small amounts of ethylene and carbon monoxide are produced, whereas in the later stages of the reaction, the propylene concentration is stationary and the rates of production of ethylene and carbon monoxide are increased, the latter being the greater. In addition, in the initial reaction, the relative rates of production of propylene and ethylene are strongly dependent on the oxygen concentration, indicating that they are of different order with respect to oxygen.

To explain the stationary concentration of propylene at maximum rate, a free radical equilibrium between propyl and oxygen on the one hand and propylene and HO_2 on the other has been advanced. The substitution of propylene for propane increases the amount of carbon monoxide produced without increasing the amount of ethylene, and therefore the amount of intermediate product giving rise to carbon monoxide is increased. This intermediate product is probably a higher aldehyde.

In the initial reaction the branching can probably be attributed to the cracking reaction of propyl, since this eventually gives rise to formaldehyde, the branching intermediate. The branching in the later stages is probably controlled mainly by the reaction of the higher aldehydes, acetaldehyde and propionaldehyde. The fact that the maximum rate is kinetically determined, and is not simply due to a fall off in the acceleration caused by consumption of the reactants, is confirmed by the addition of acetaldehydes to suitable reactant mixtures, when a negative induction period is obtained. This effect shows that it is the quadratic destruction of the branching intermediate that controls the maximum rate.

The reaction shows a strong inert gas effect with carbon dioxide, the rate increasing with the pressure of inert gas, and this indicates that the termination reaction is removal

of HO_2 radicals at the surface of the reaction vessel.

The kinetic expressions for the variation of the two acceleration constants with pressure of reactants are quite different, which is further proof that they are associated with different reactions. The initial acceleration constant is almost independent of the oxygen pressure, whereas the later one does show a dependence on the oxygen pressure, being of a form similar to that associated with the low temperature reaction.

SUMMARY.

Propane is the simplest hydrocarbon possessing structural properties such as secondary carbon atoms which are typical of the higher aliphatic hydrocarbons, and for this reason its oxidation has been extensively investigated. The oxidation can proceed by two distinct mechanisms, one operating at temperatures above 400°C and the other below that temperature. The low temperature oxidation has been extensively investigated, but little work has been done on the high temperature oxidation.

The work presented in this thesis consists of a kinetic and analytical investigation of the oxidation of propane in the high temperature region. The kinetic investigation has been carried out in a standard static combustion apparatus at temperatures between 400° and 460°C , and the dependence of the maximum rate and the acceleration constant on the pressures of reactants has been determined. The effect of additives on the kinetics has also been studied. The technique of Gas Phase Chromatography has been developed into a suitable quantitative method of micro-analysis of the products of hydrocarbon combustion, and the analytical investigation has been carried out almost completely by the application of this method. Analyses of suitable reaction mixtures during reaction have been made at several temperatures, and the variation in products with reactant concentration and temperature has been determined.

The oxidation in the high temperature region appears to be

a two-stage reaction. In the initial stages the main product is propylene, and the acceleration can be attributed to the cracking reaction of the propyl radical which eventually gives rise to formaldehyde, the effective branching intermediate. In the later stage of the reaction where the maximum rate is realised, the reaction mechanism is similar to one found in the low temperature region where the main chain product is a higher aldehyde, which is then responsible for the branching. At this stage the propylene concentration reaches a stationary value.

From the suggested reaction mechanisms, kinetic expressions for the maximum rate and acceleration constants have been derived, and these are in agreement with the experimental observations.

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University of Edinburgh.

June, 1957.

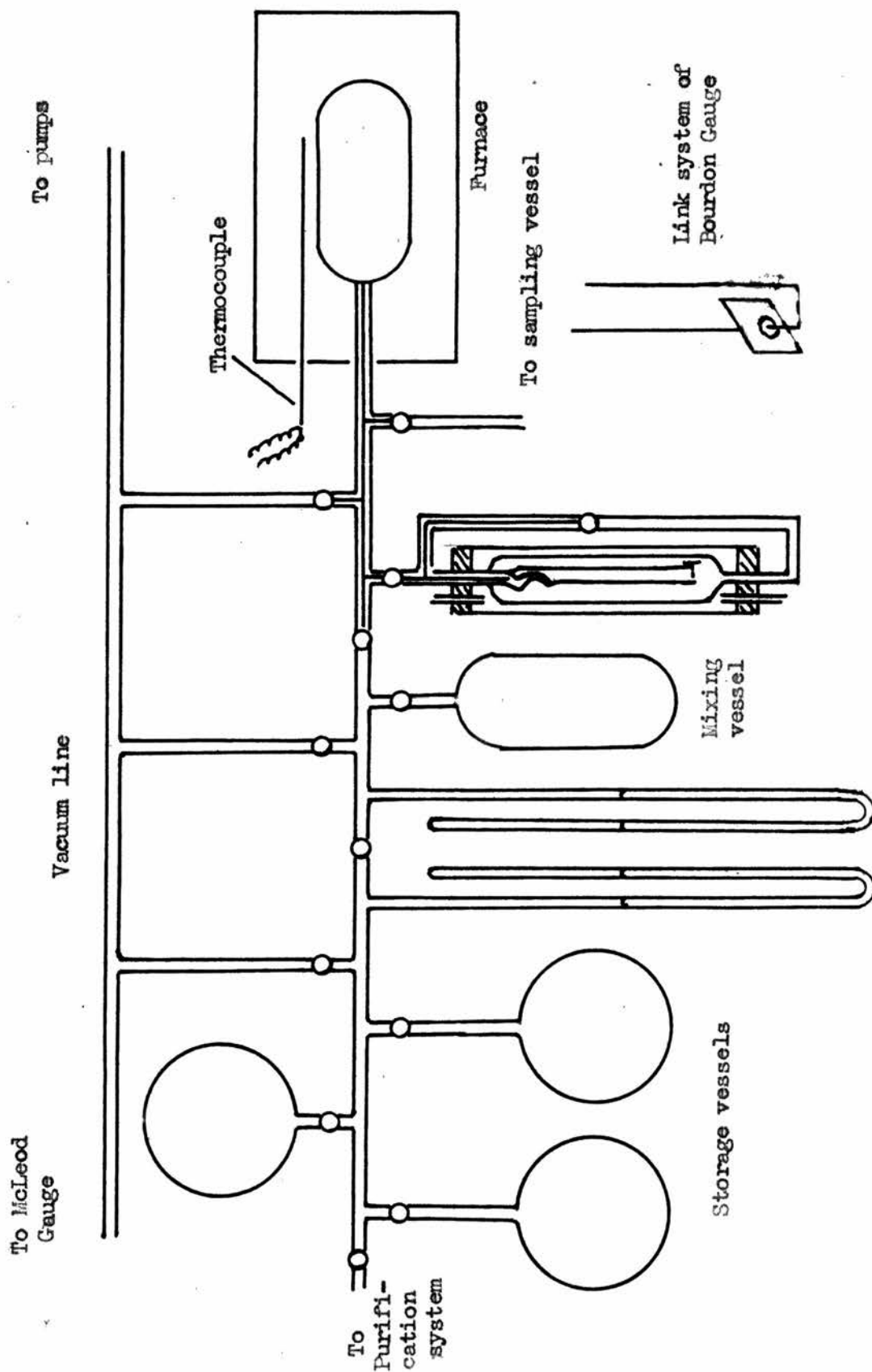


Figure 1.1. The Kinetic Apparatus.

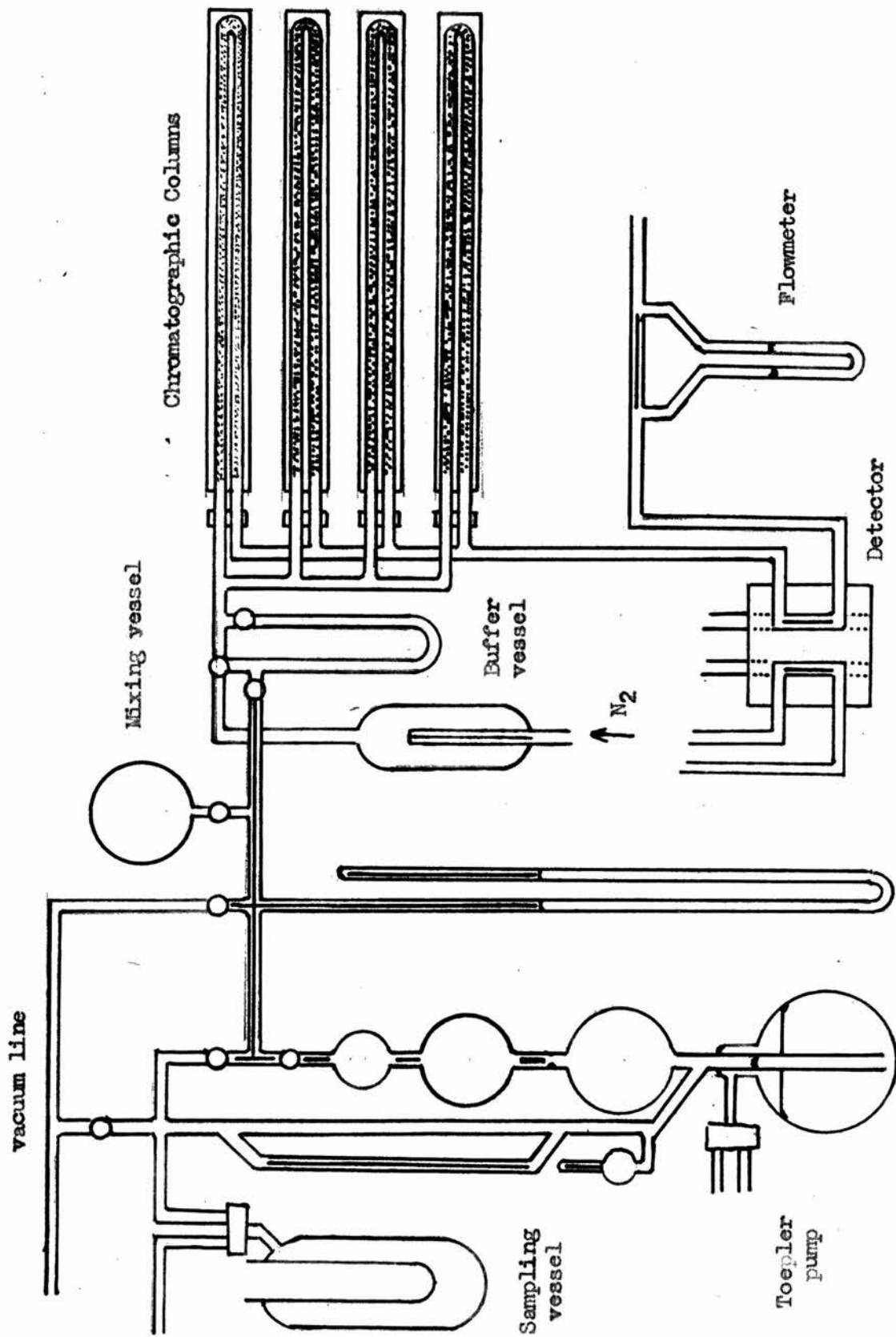
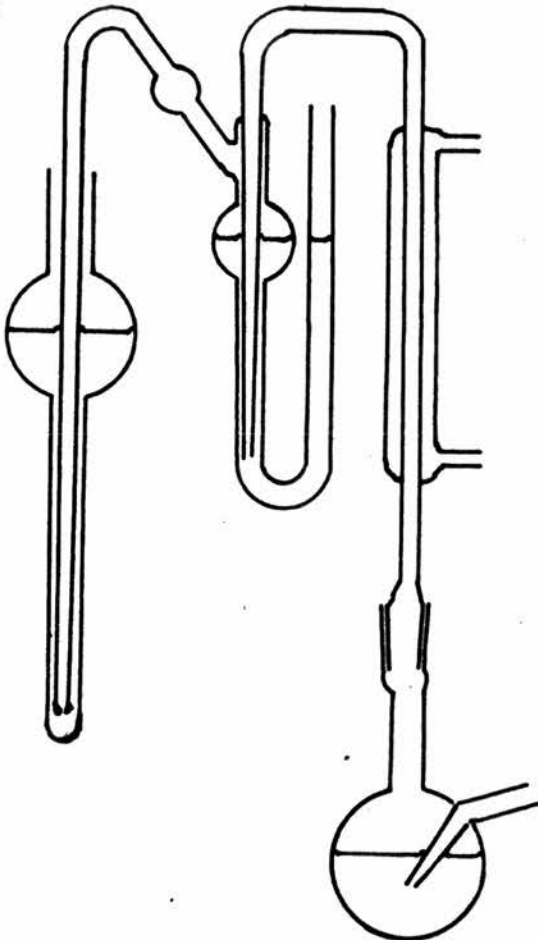
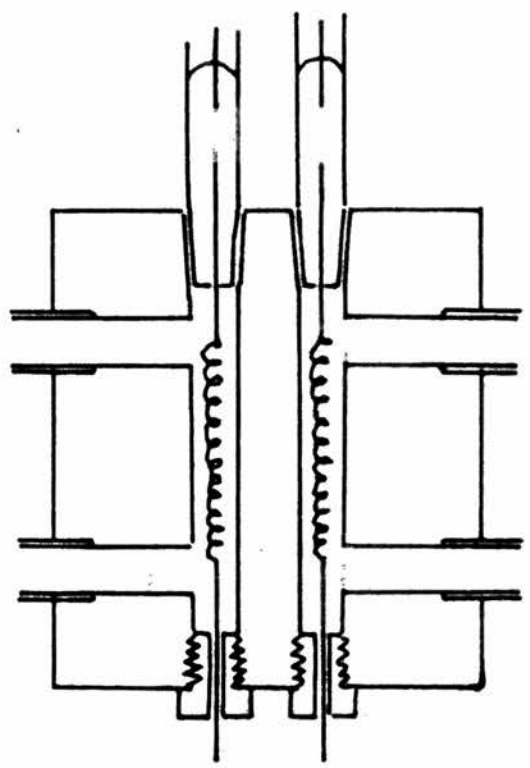


Figure 1.3.1. The Analytical Apparatus.



Zeisel Apparatus.

Figure 1.3.7.

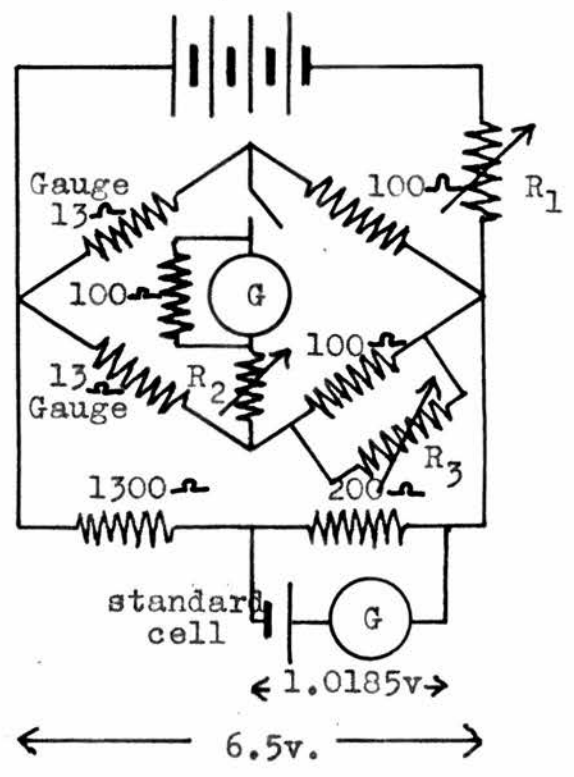


Thermal Conductivity Detector.

Figure 1.3.2.

Electrical Circuit
of Detector.

Figure 1.3.3.



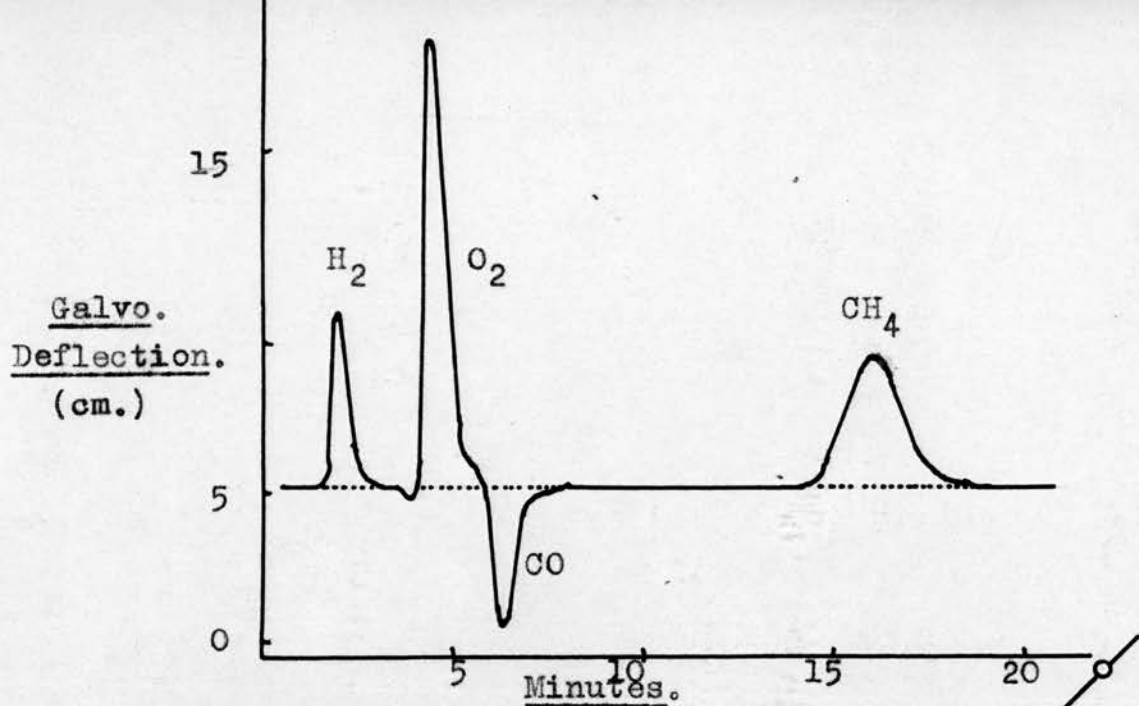


Figure 1.3.4. Chromatogram of Fraction 1.

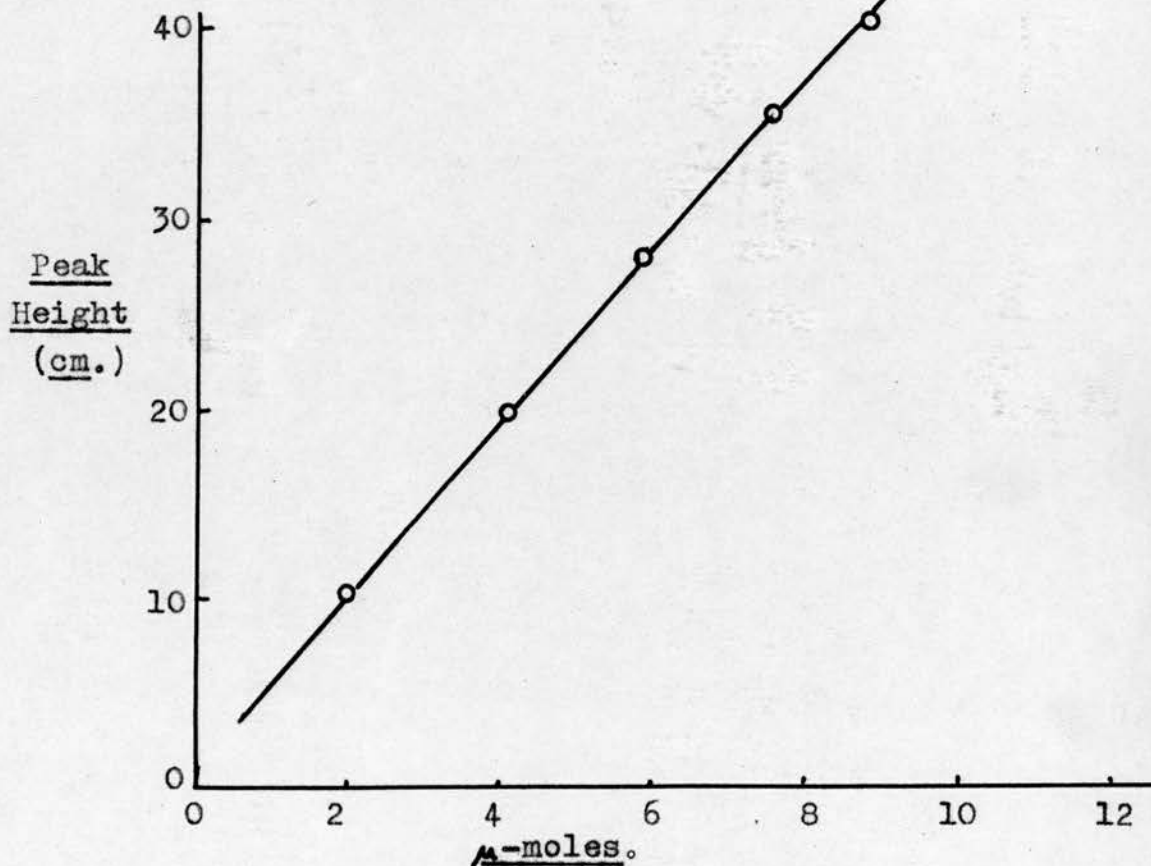


Figure 1.3.5. Calibration Graph for Propane.

Galvo.
Deflection.

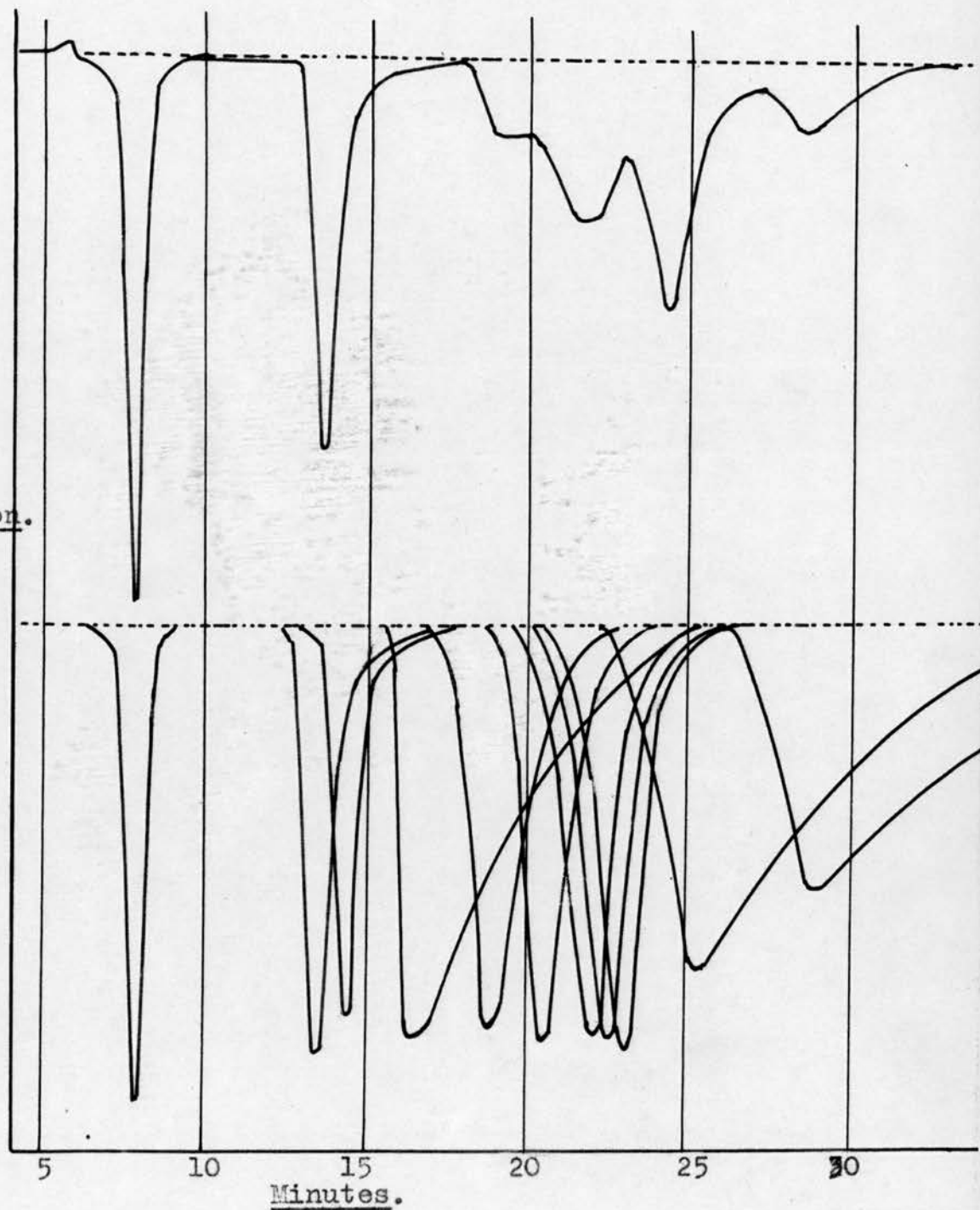


Figure 1.3.9. Chromatograms of Fraction 3 and of Standards.

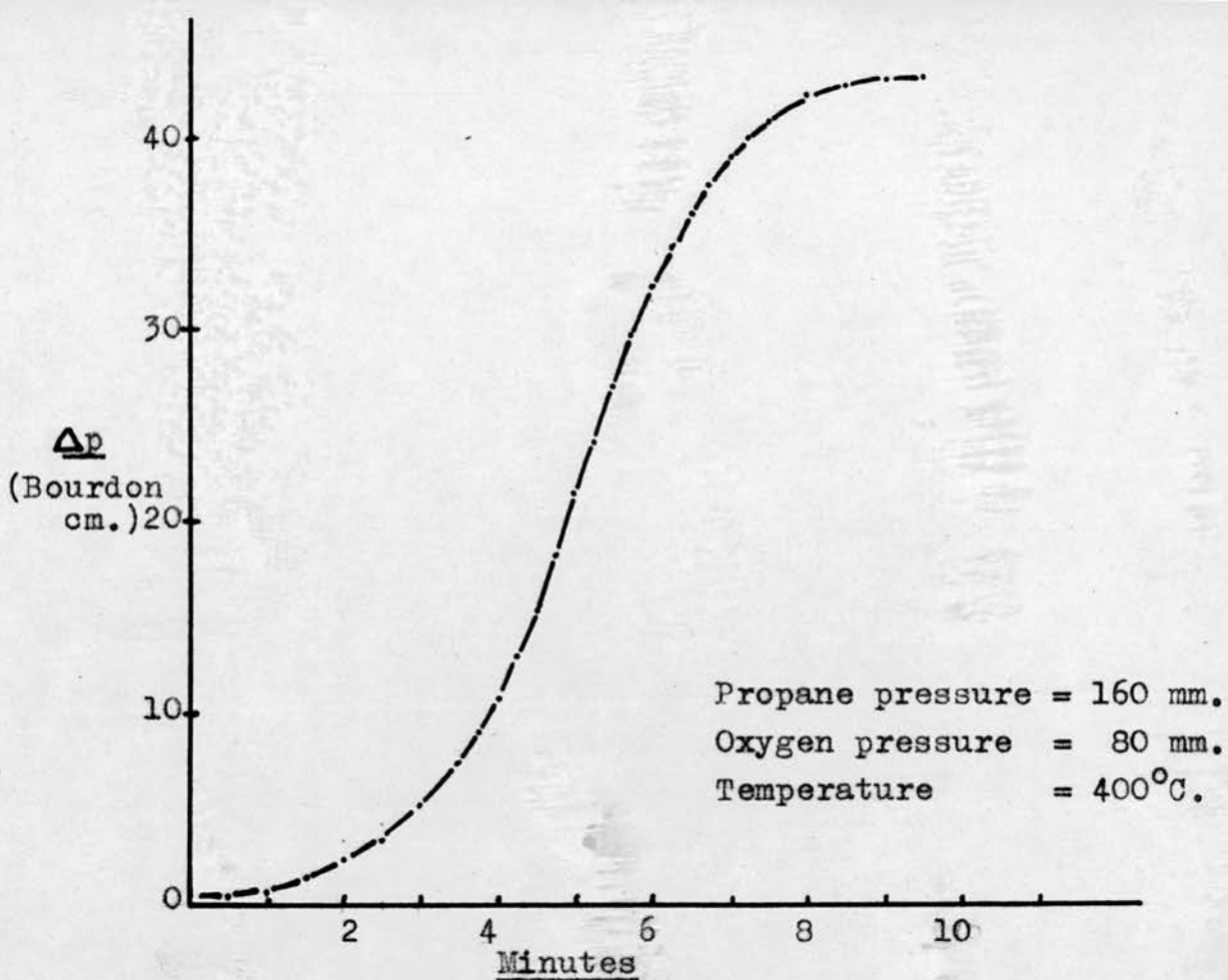


Figure 1.4.1. A Typical Curve of p against Time.

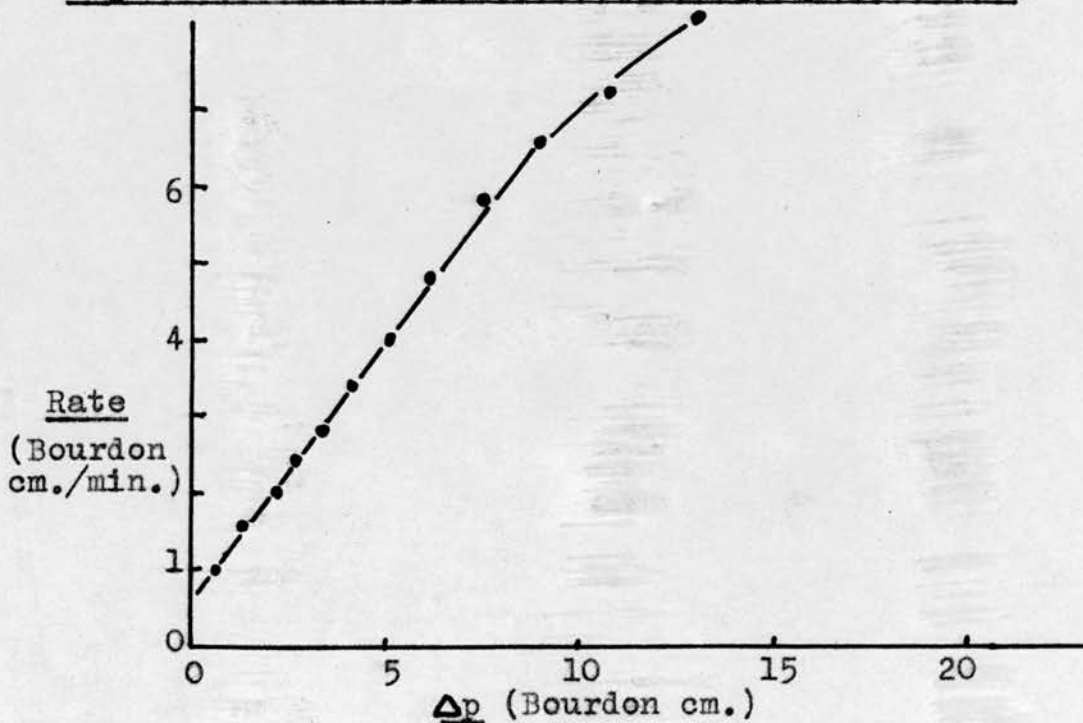


Figure 1.4.2. A Typical Curve of Rate against p .

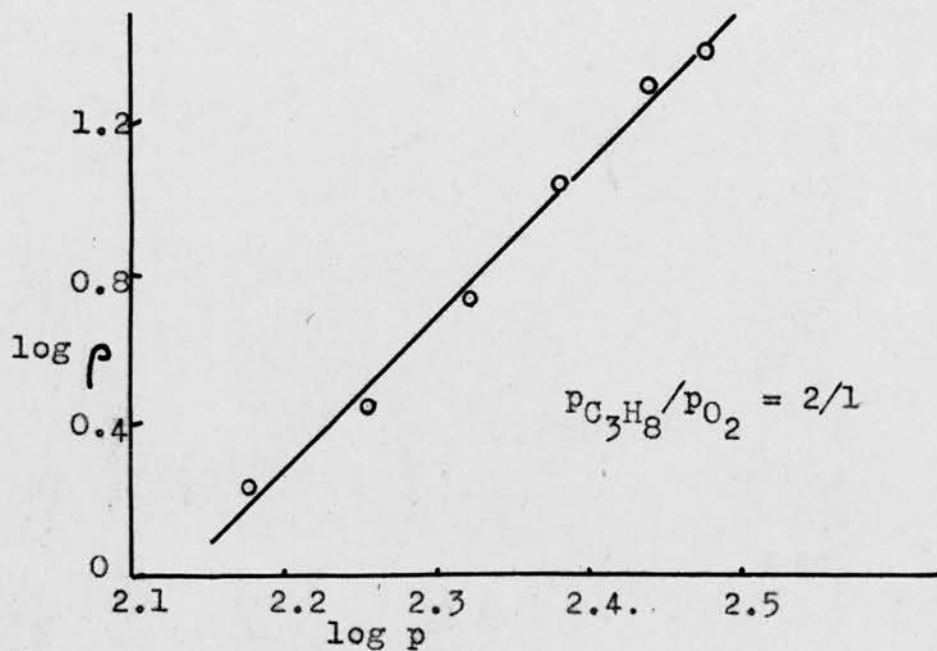


Figure 2.1.1. Plot of $\log \rho$ against $\log p$.

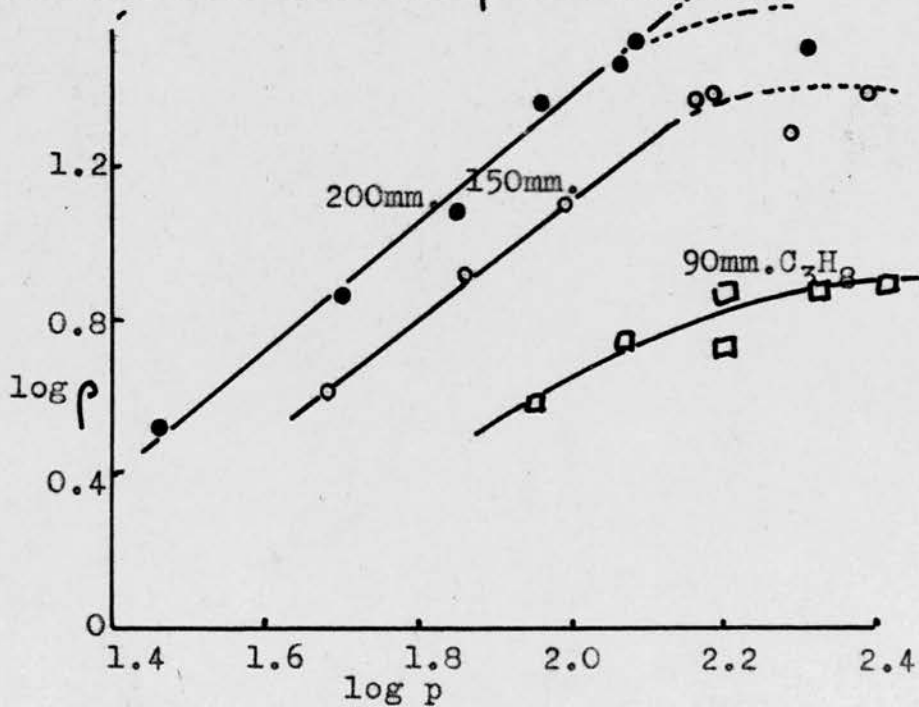


Figure 2.1.2. Plot of $\log \rho$ against $\log p_{O_2}$.

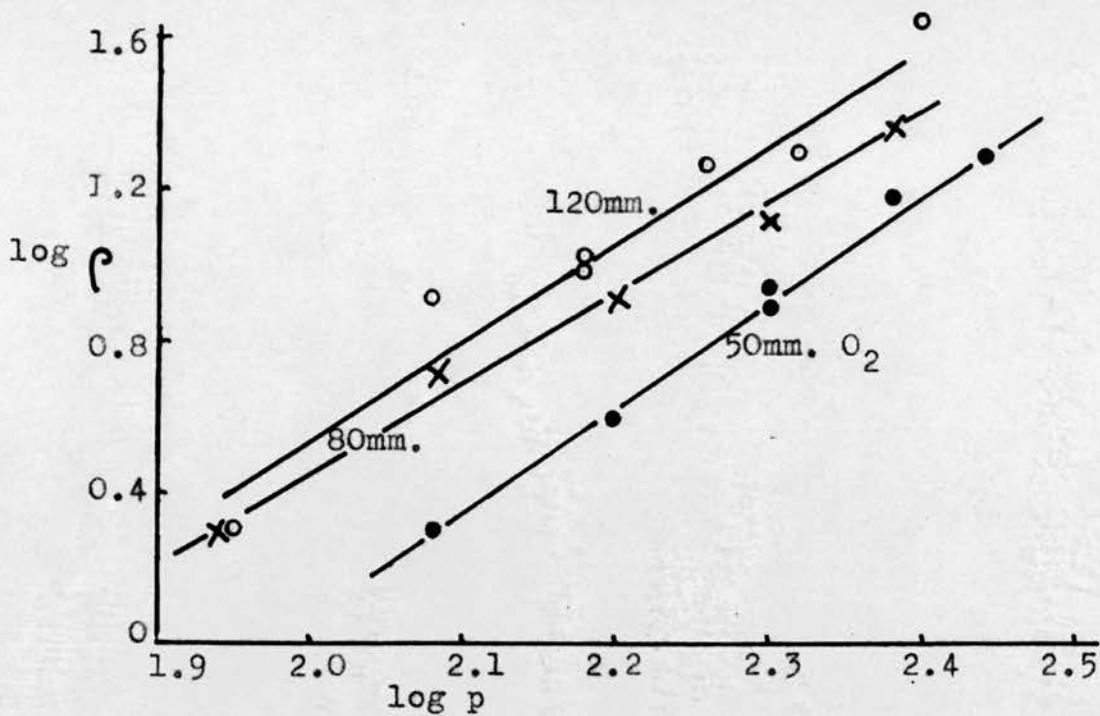


Figure 2.1.3. Plot of $\log \rho$ against $\log p_{C_3H_8}$.

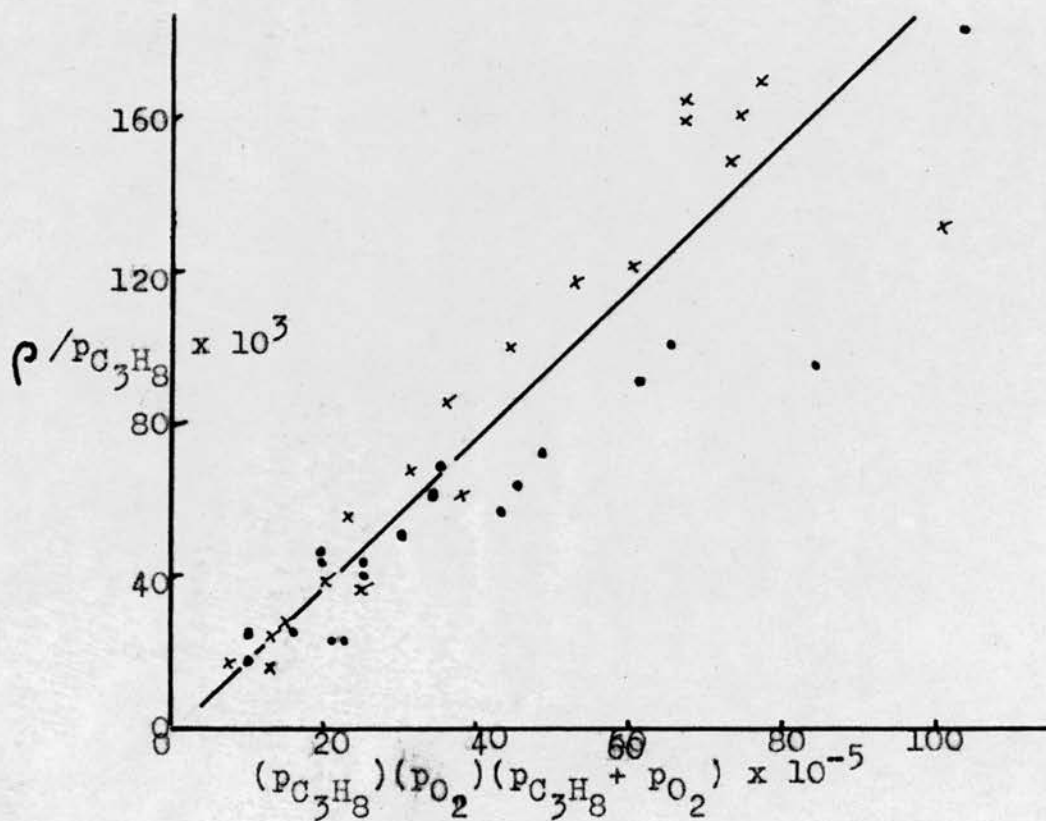


Figure 2.1.4. Plot for $\rho = k (p_{C_3H_8})^2 (p_{O_2}) (p_{C_3H_8} + p_{O_2})$.

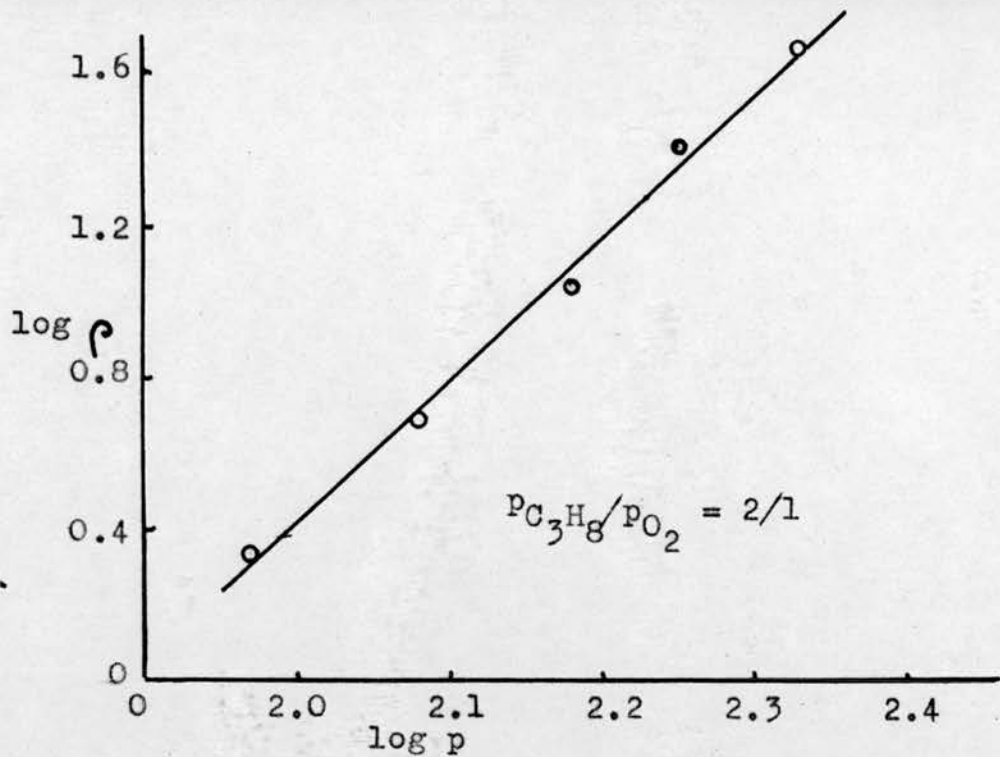


Figure 2.1.5. Plot of $\log p$ against $\log p$ at 460°C .

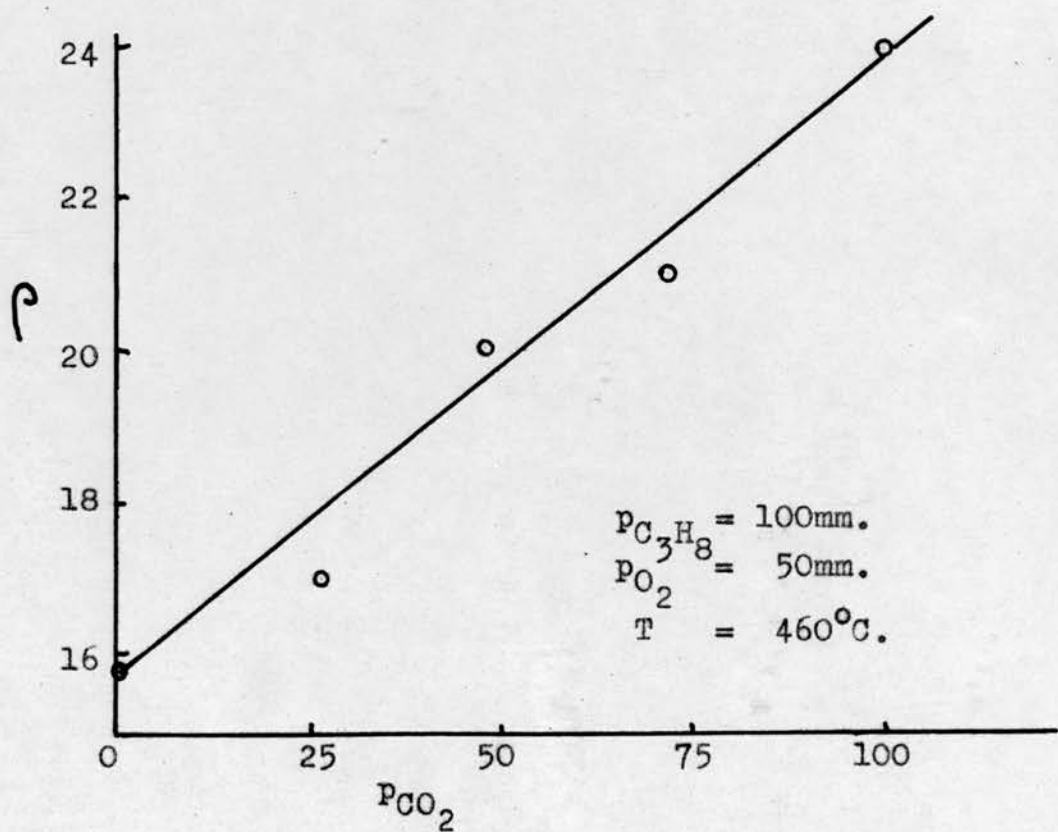


Figure 2.1.8. Dependence of p on pressure of inert gas.

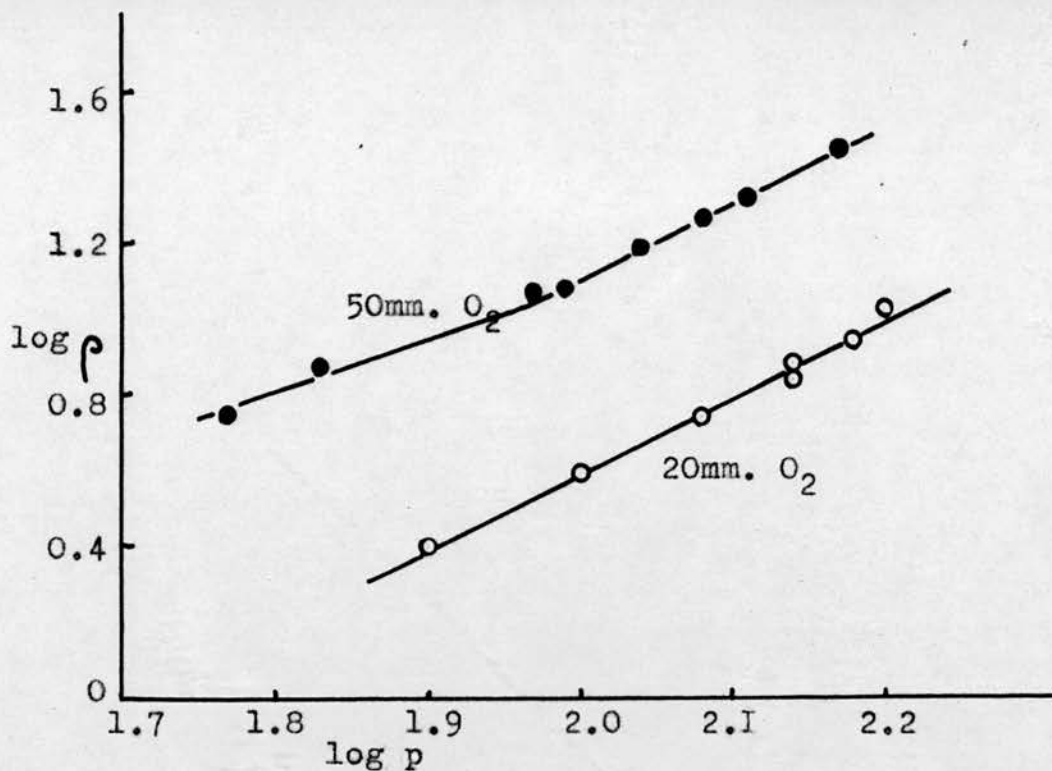


Figure 2.1.6. Plot of $\log \rho$ against $\log p_{C_3H_8}$ at $460^\circ C$.

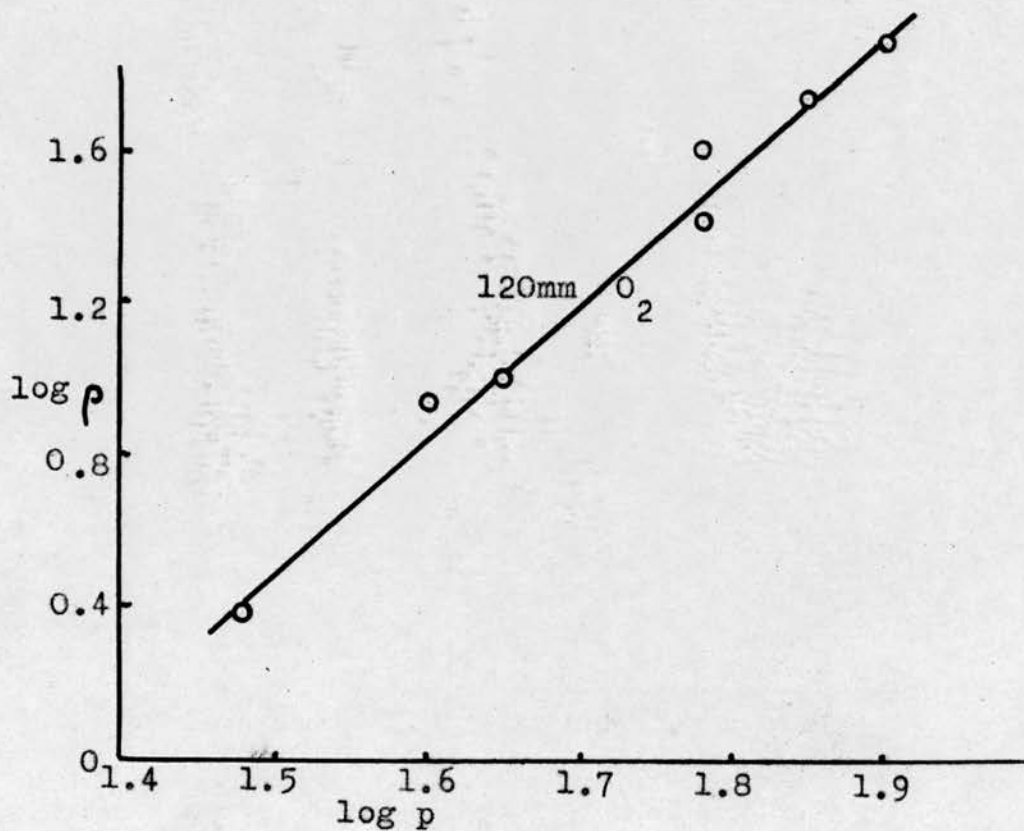


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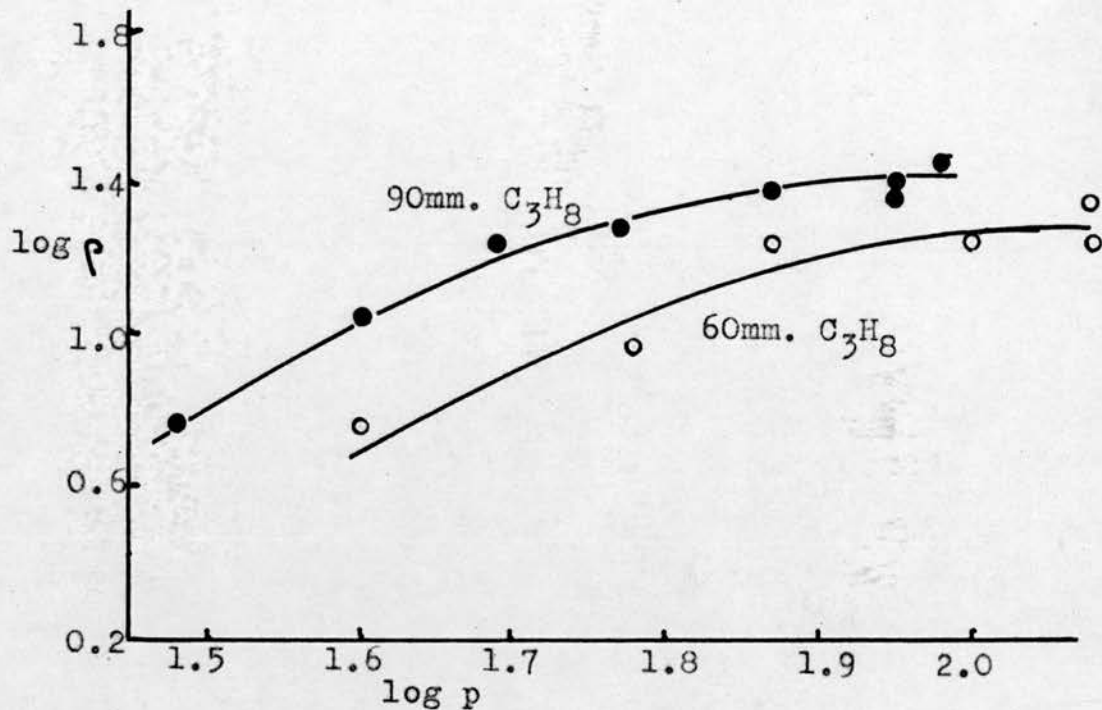


Figure 2.1.7. Plot of $\log p$ against $\log p_{O_2}$ at $460^\circ C$.

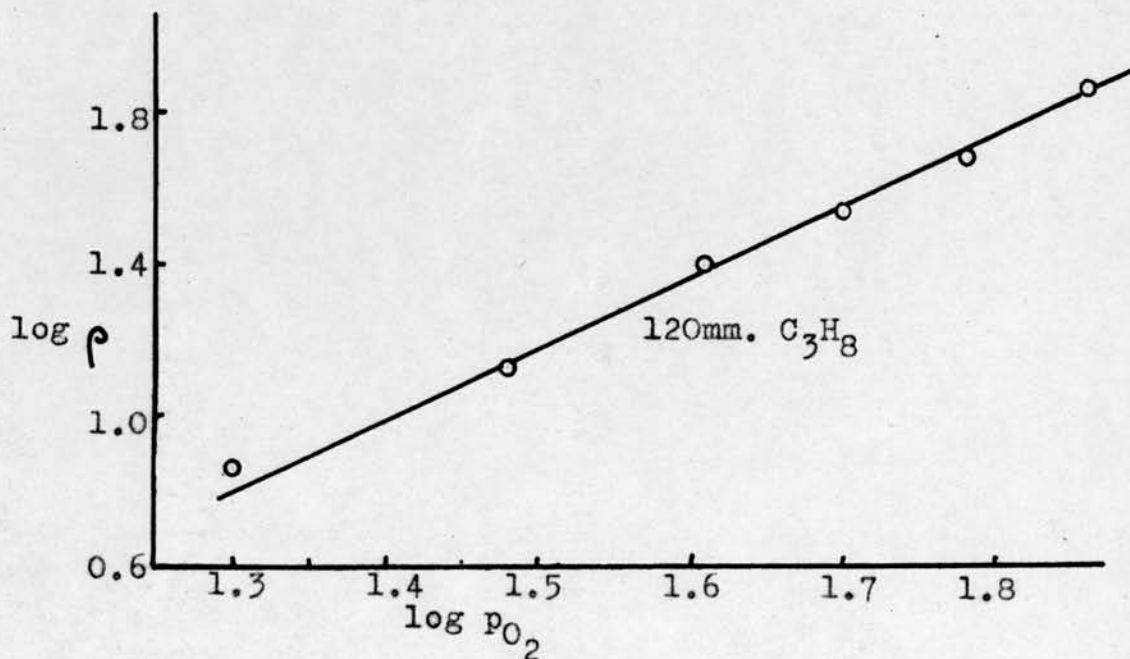


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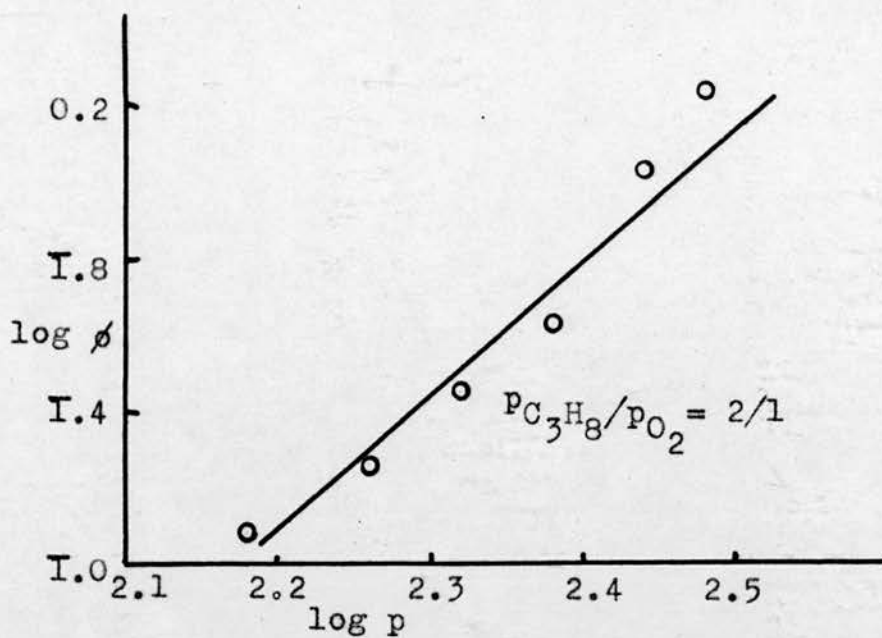


Figure 2.2.1. Plot of $\log \phi$ against $\log p$ at 400°C .

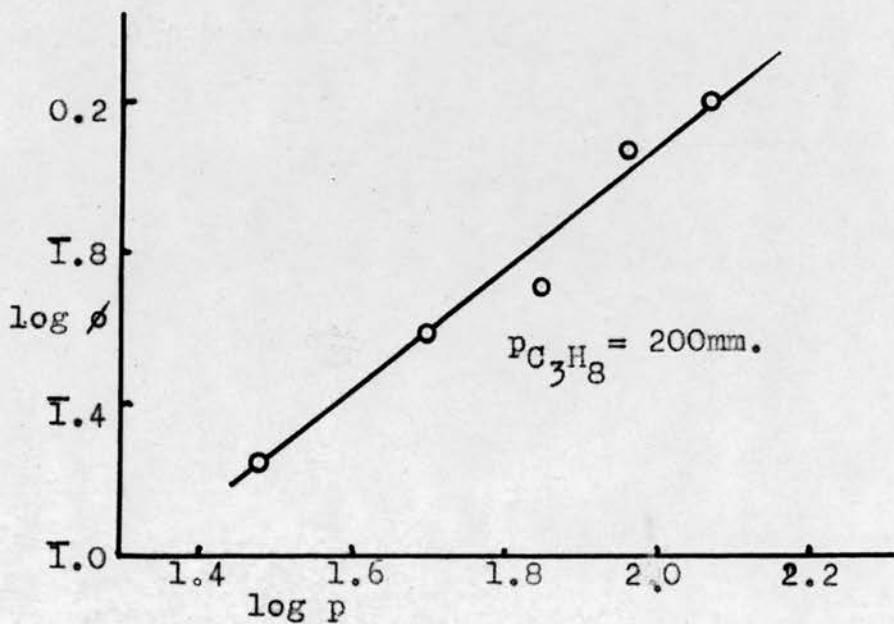


Figure 2.2.2. Plot of $\log \phi$ against $\log p_{\text{O}_2}$ at 400°C .

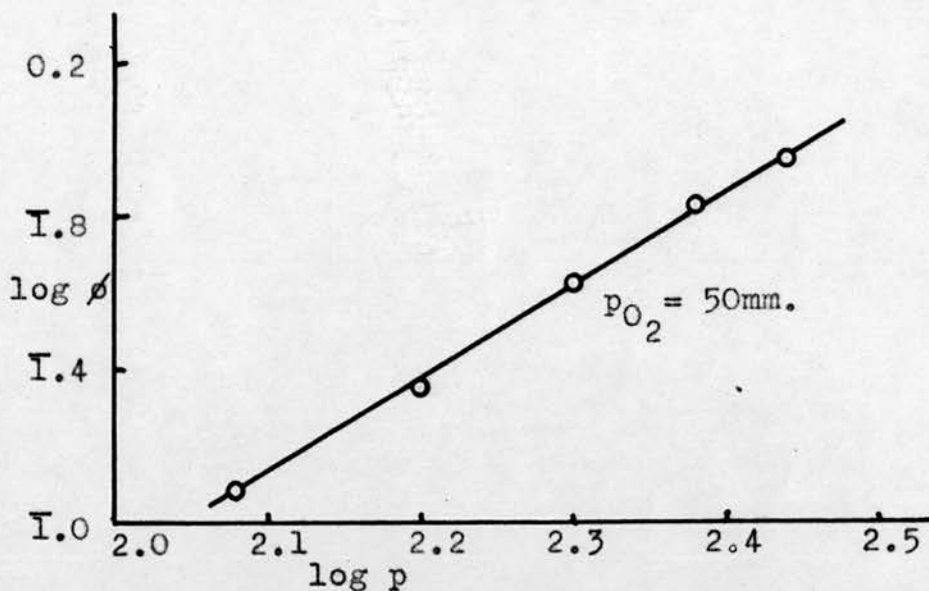


Figure 2.2.3. Plot of $\log \phi$ against $\log p_{C_3H_8}$ at $400^\circ C$.

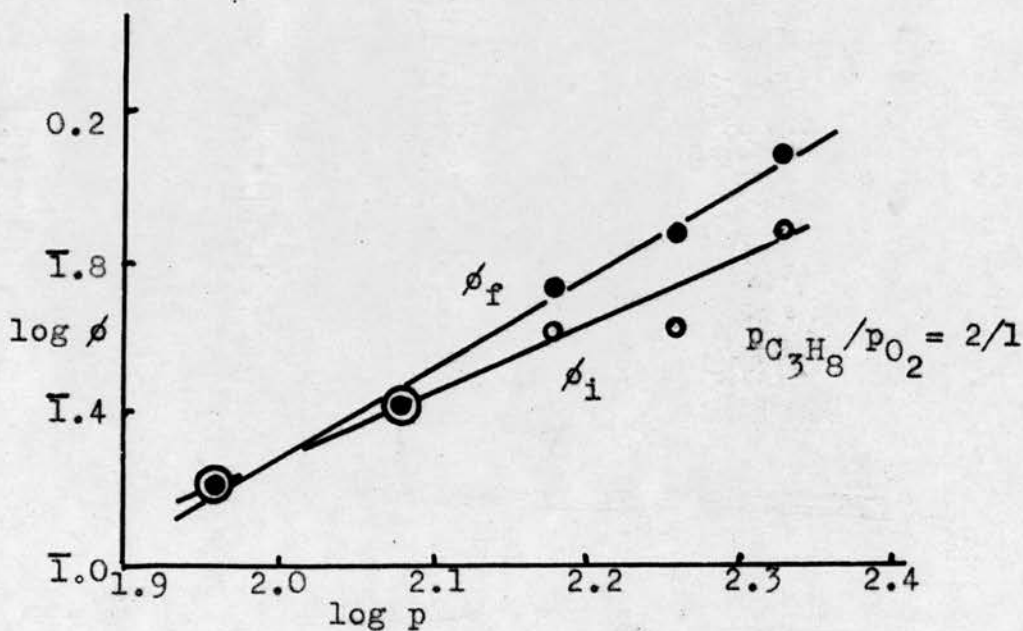


Figure 2.2.4. Plot of $\log \phi$ against $\log p$ at $460^\circ C$.

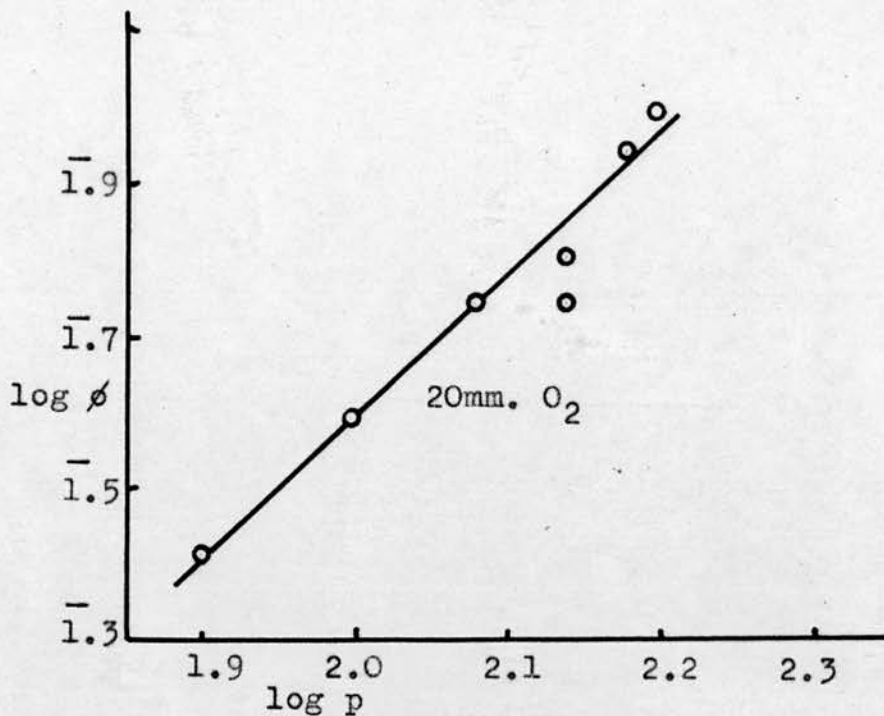


Figure 2.2.5.a. Plot of $\log \phi$ against $\log p_{\text{C}_3\text{H}_8}$ at 460°C .

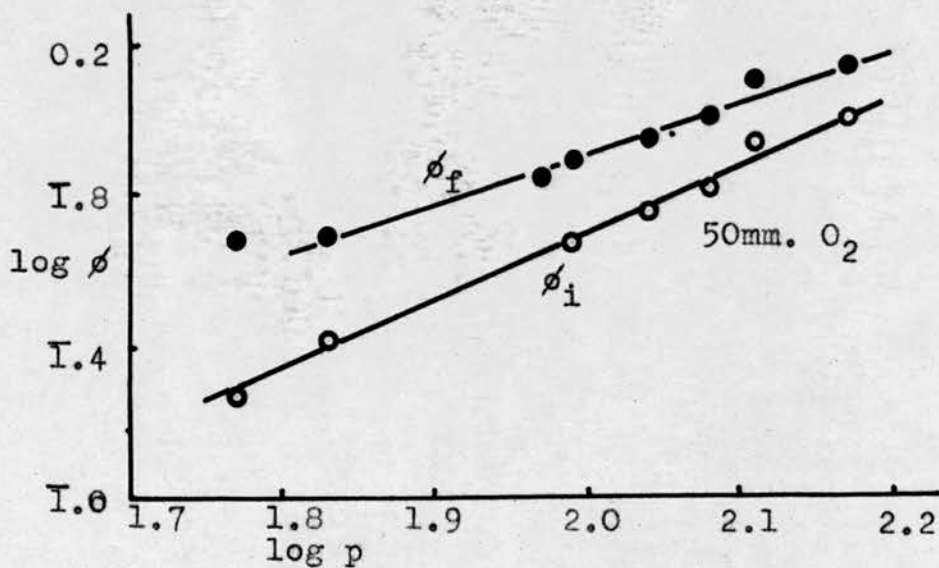


Figure 2.2.5.b. Plot of $\log \phi$ against $\log p_{\text{C}_3\text{H}_8}$ at 460°C .

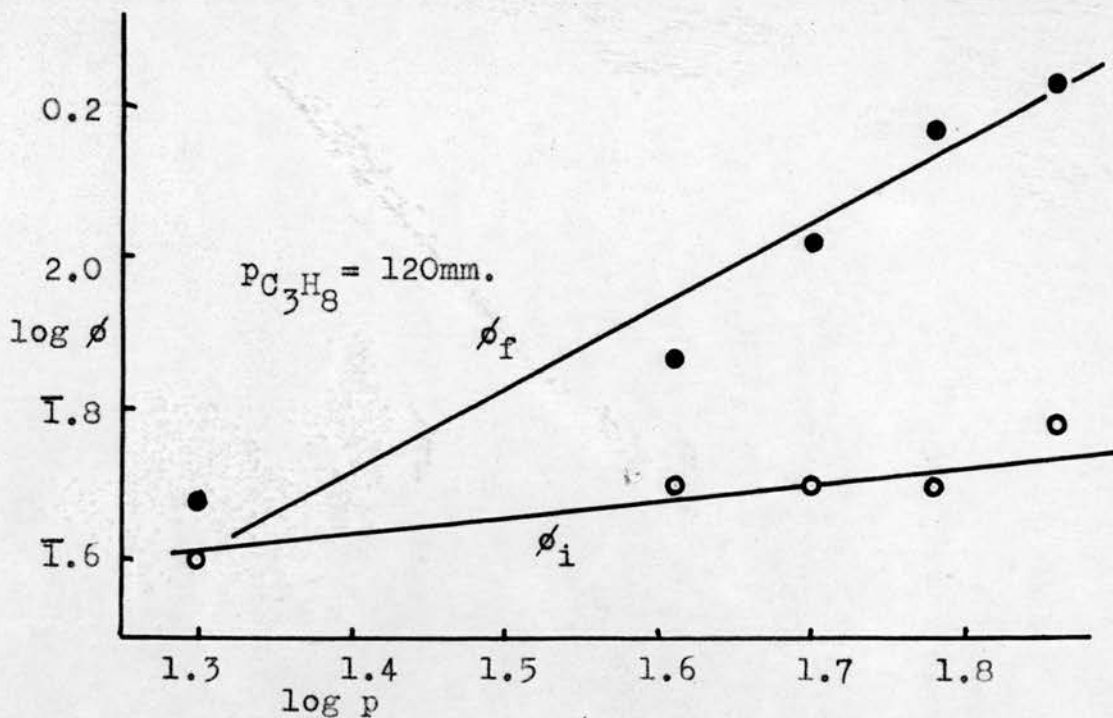


Figure 2.2.6. Plot of $\log \phi$ against $\log p_{O_2}$ at 460°C.

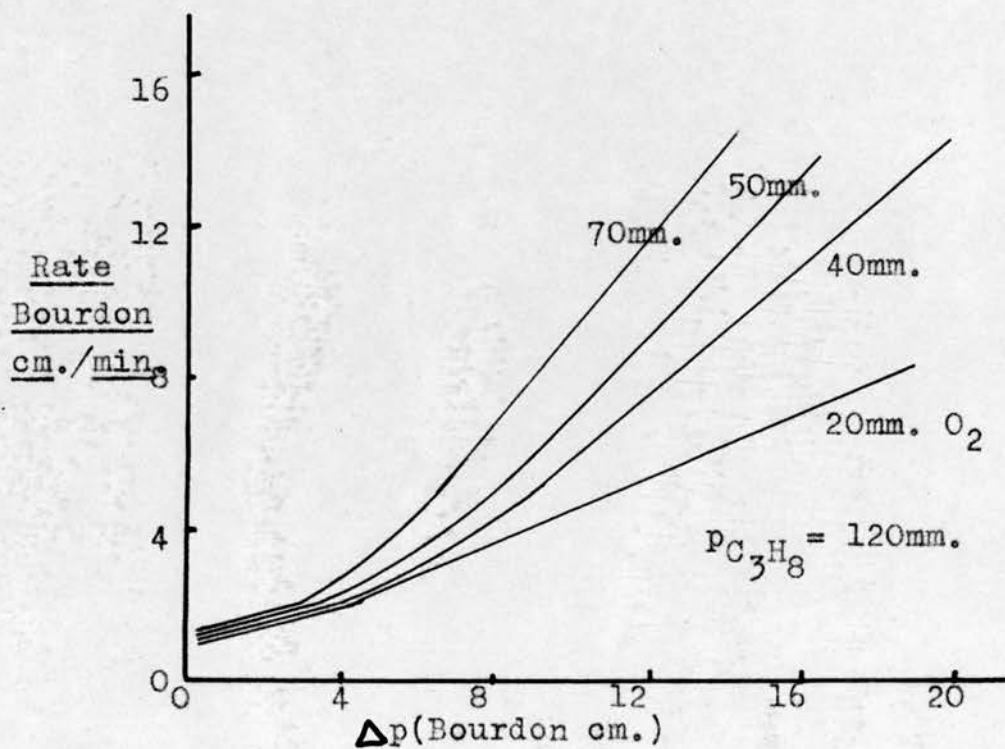


Figure 2.2.6.i. Plots illustrating the two-fold nature of ϕ .

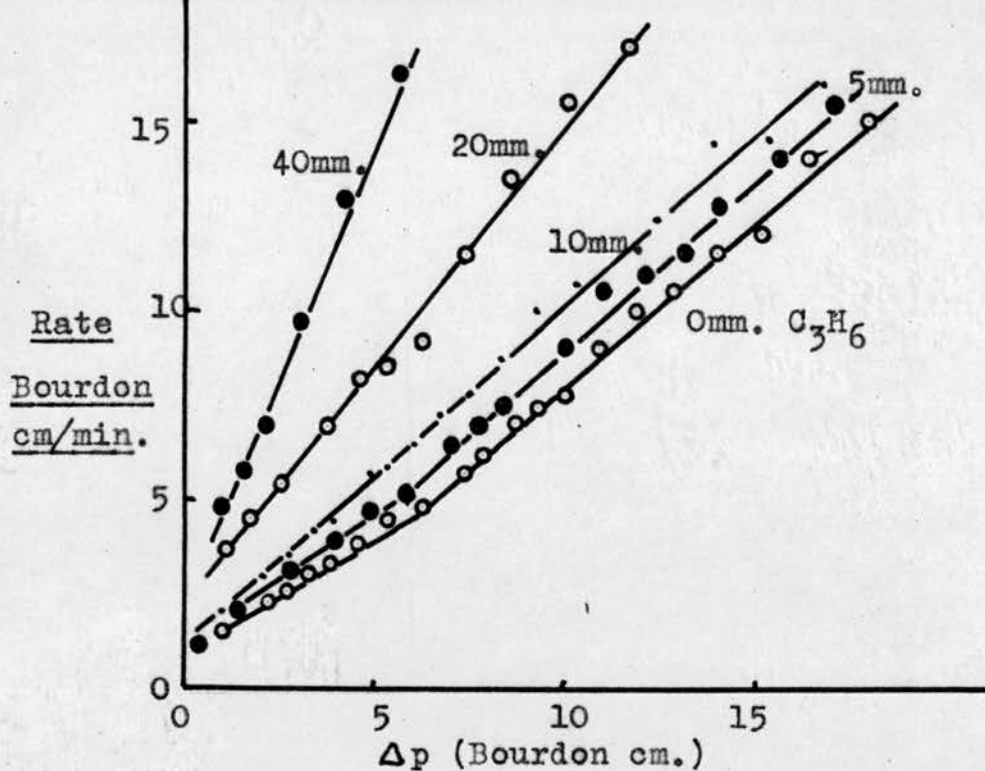


Figure 3.1. Effect of propylene on ϕ for 100 mm. propane and 50 mm. oxygen.

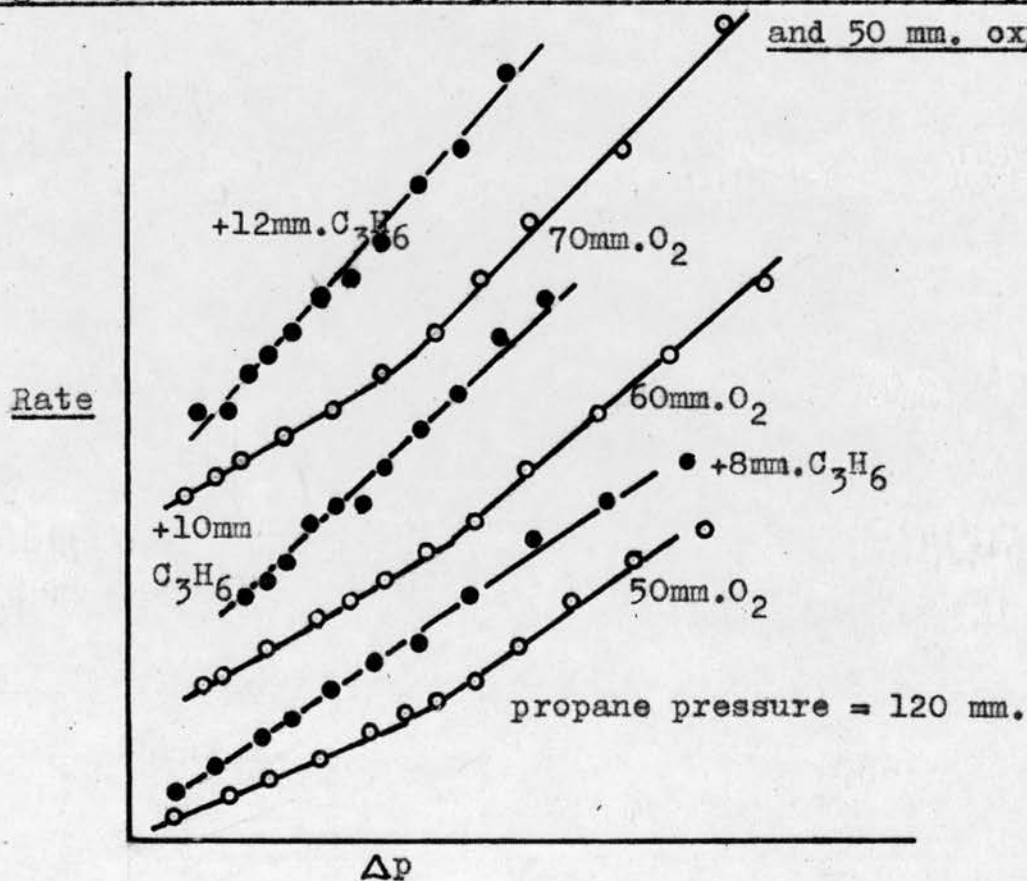


Figure 3.2. Effect of propylene of removing the initial acceleration constants.

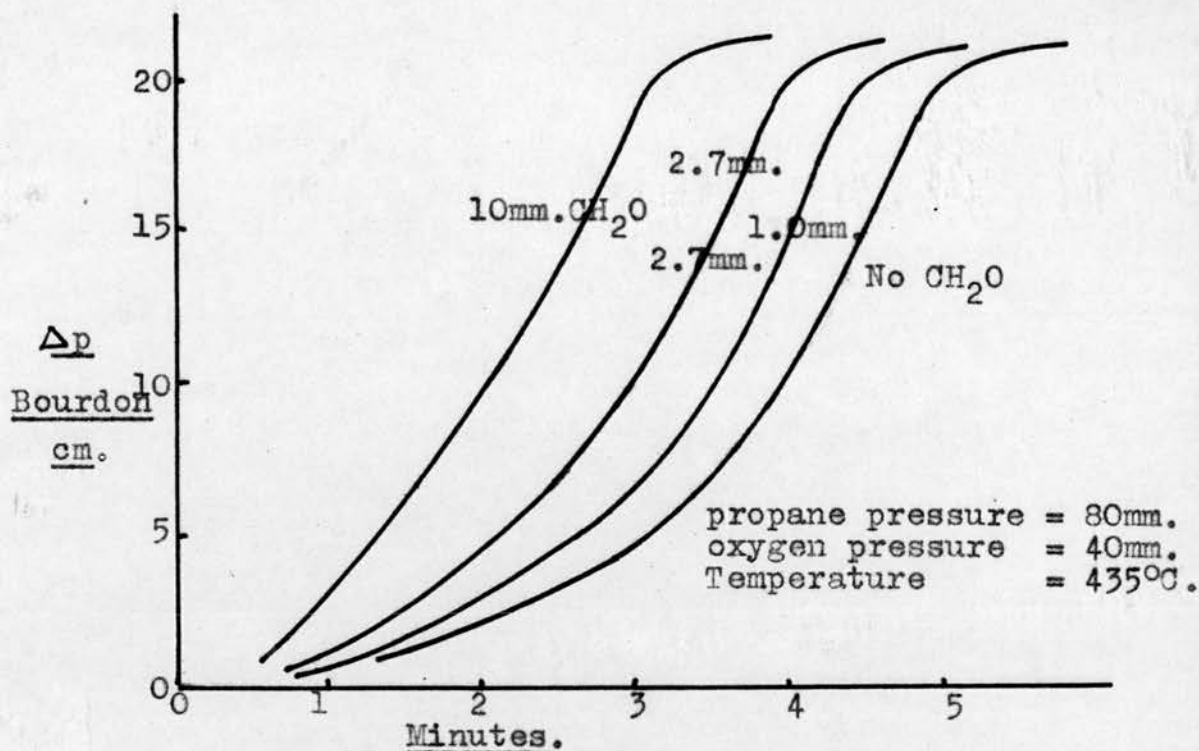


Figure 3.3. Effect of Formaldehyde on reaction rate.

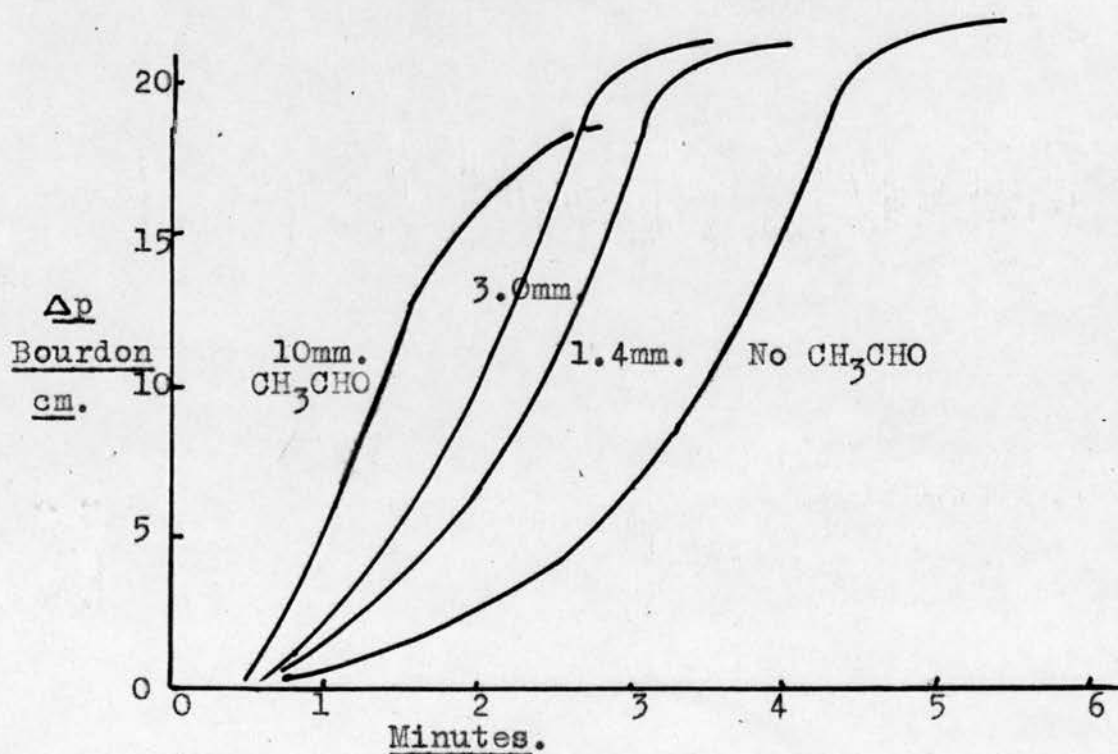


Figure 3.4. Effect of Acetaldehyde on reaction rate.

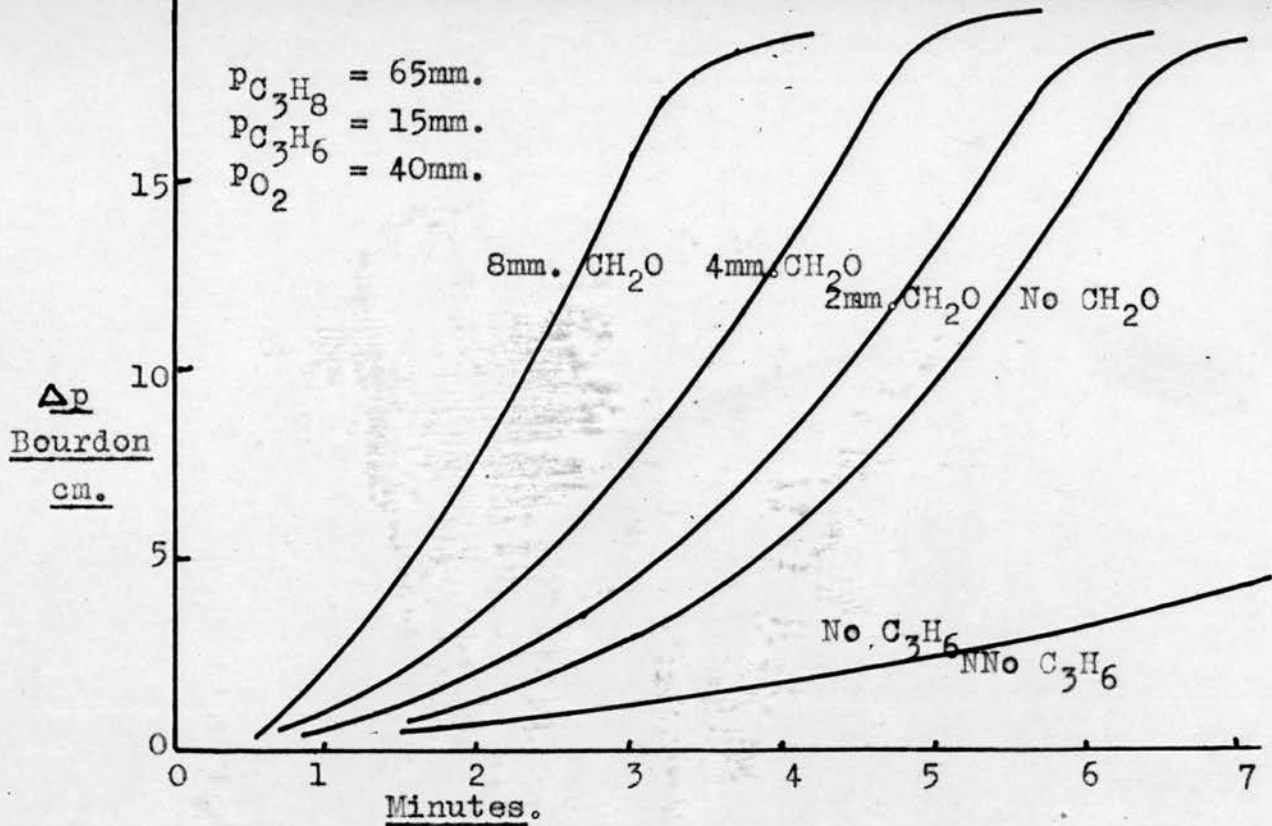


Figure 3.5. Effect of Formaldehyde on the reaction rate.

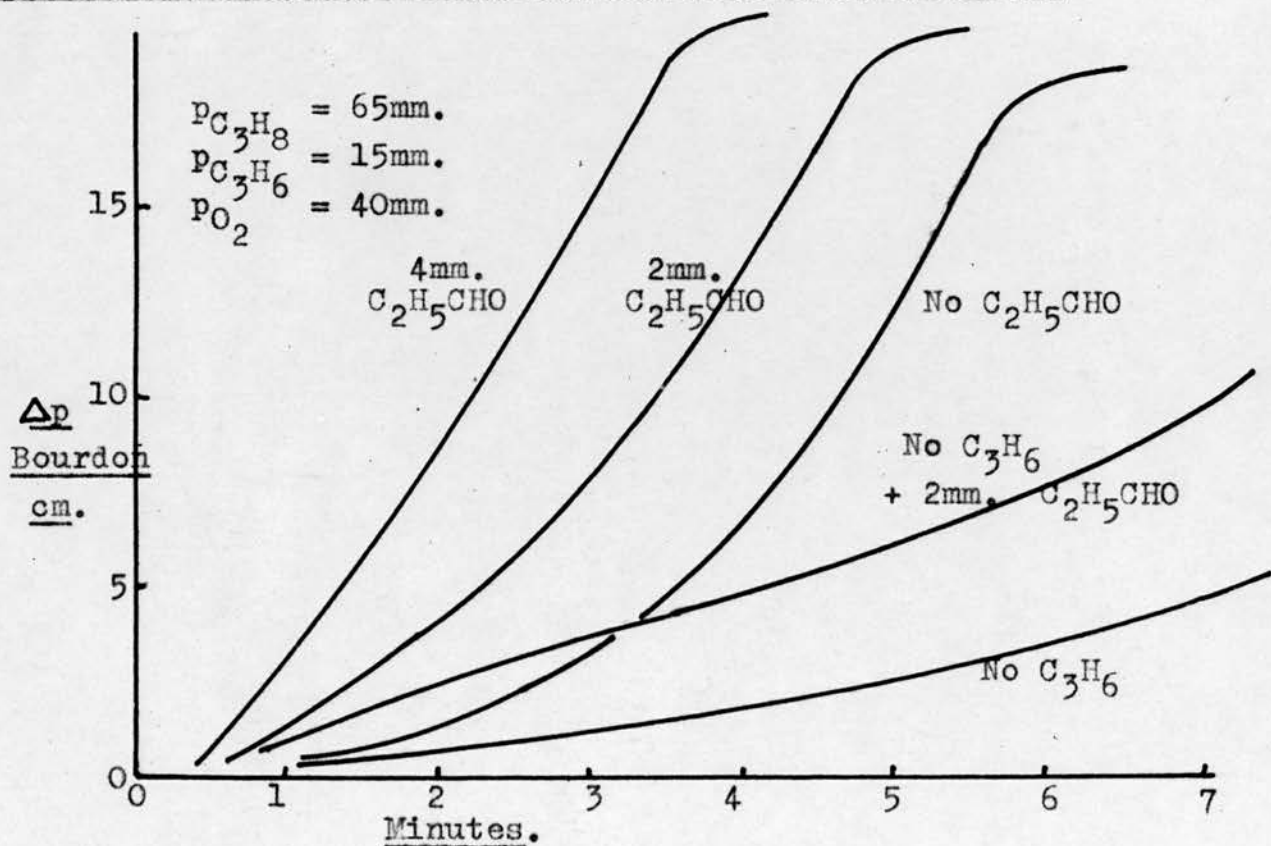


Figure 3.6. Effect of Propionaldehyde on the reaction rate.

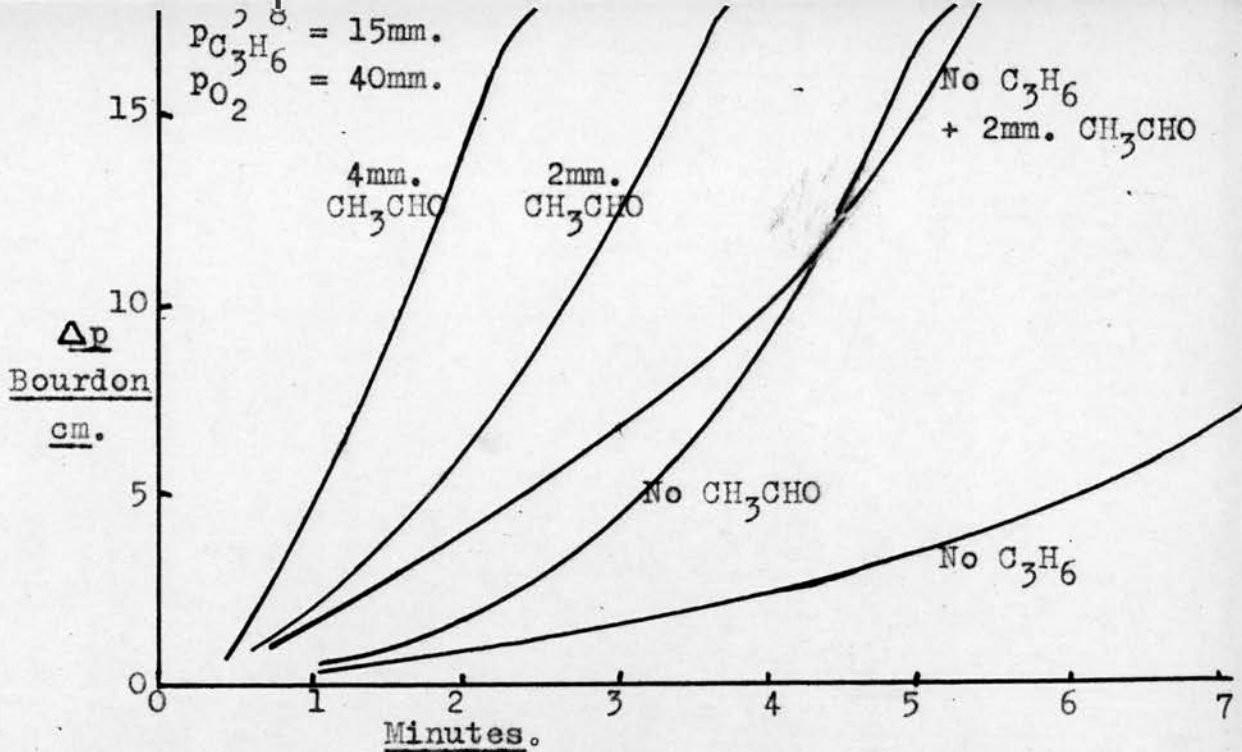


Figure 3.7. Effect of Acetaldehyde on the reaction rate.

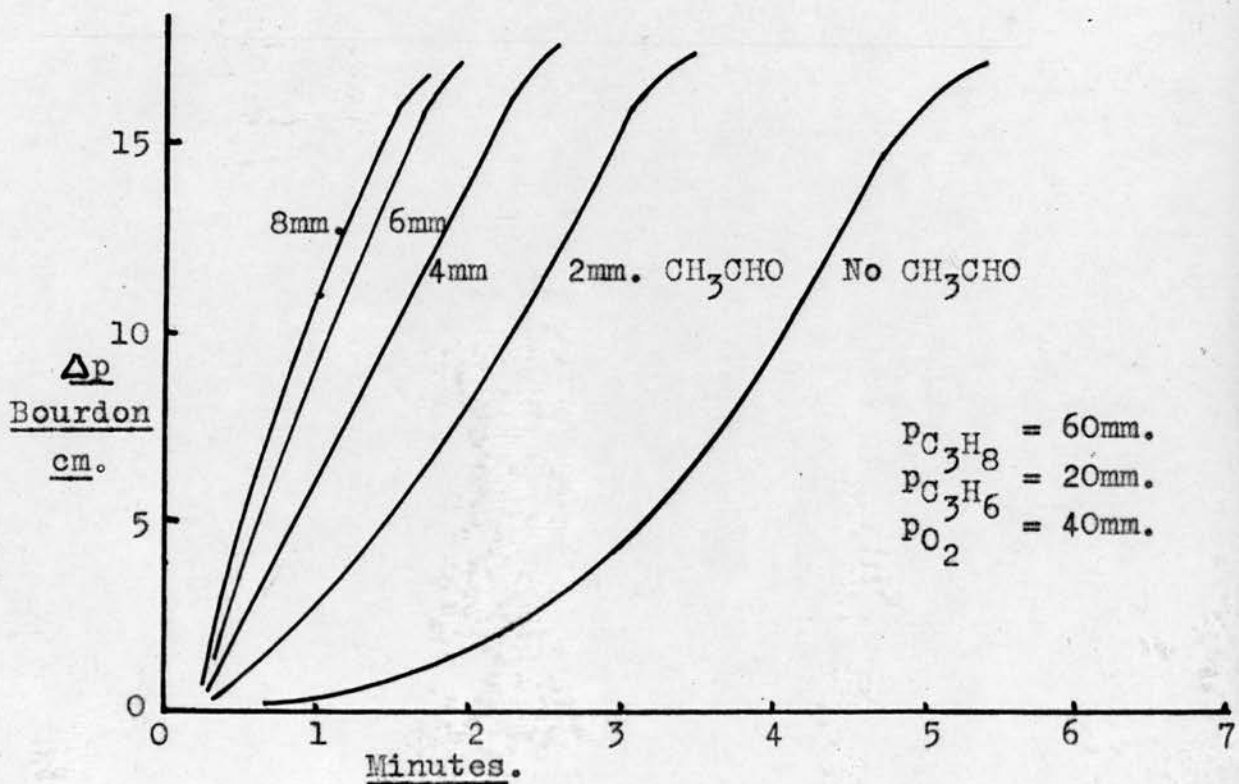


Figure 3.8. Effect of Acetaldehyde on the reaction rate.

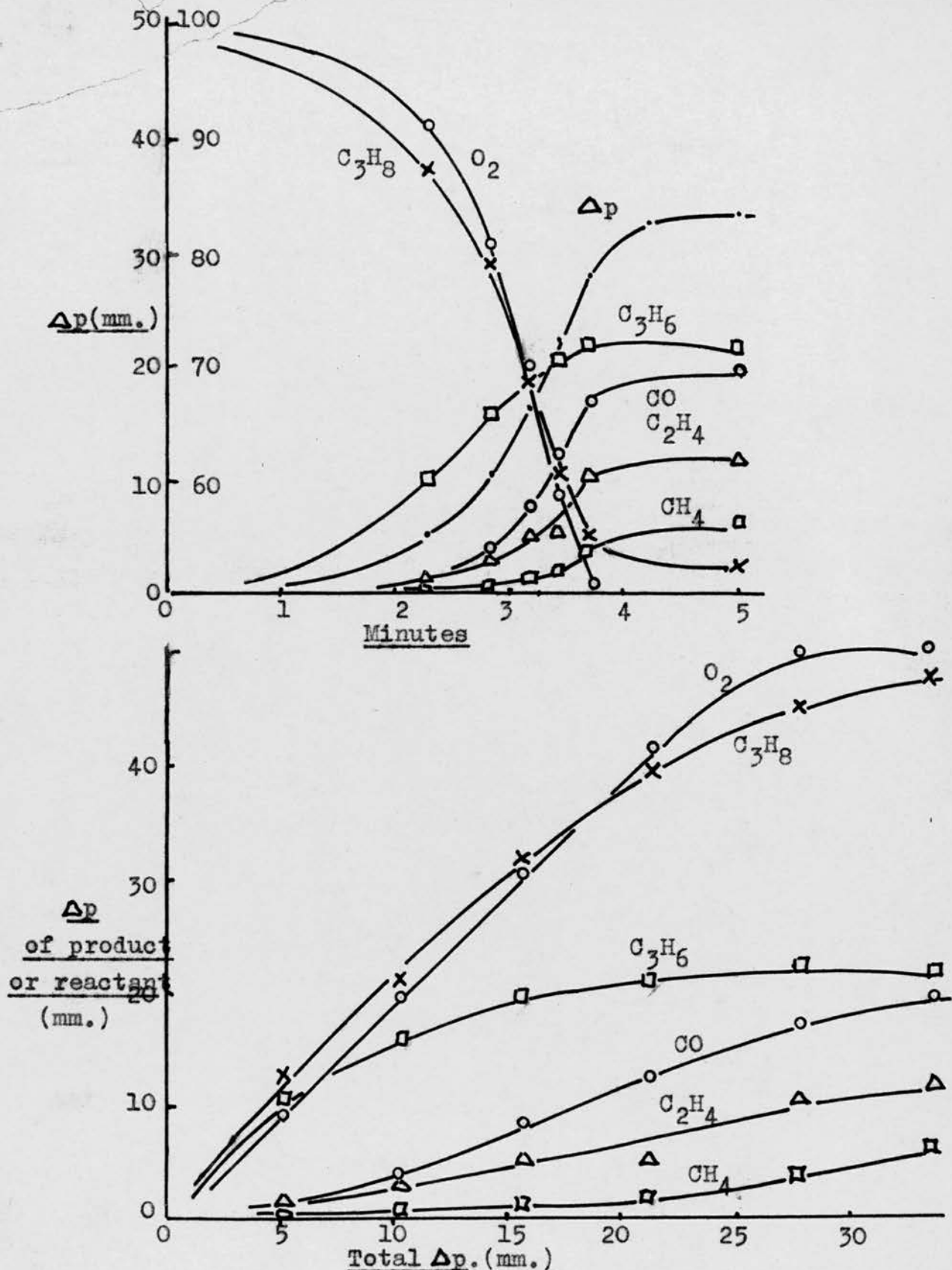


Figure 4.2.1. Products from 100 mm. propane and 50 mm. oxygen at 435°C.

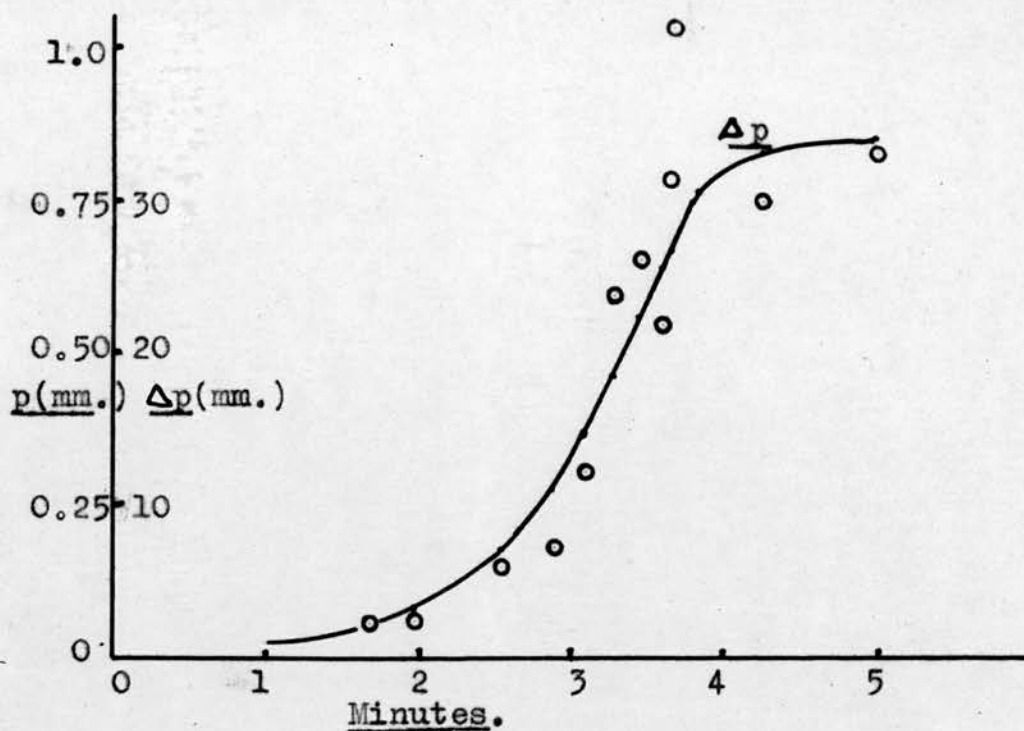


Figure 4.2.1. Development of Formaldehyde from 100 mm. propane and 50 mm. oxygen at 435°C.

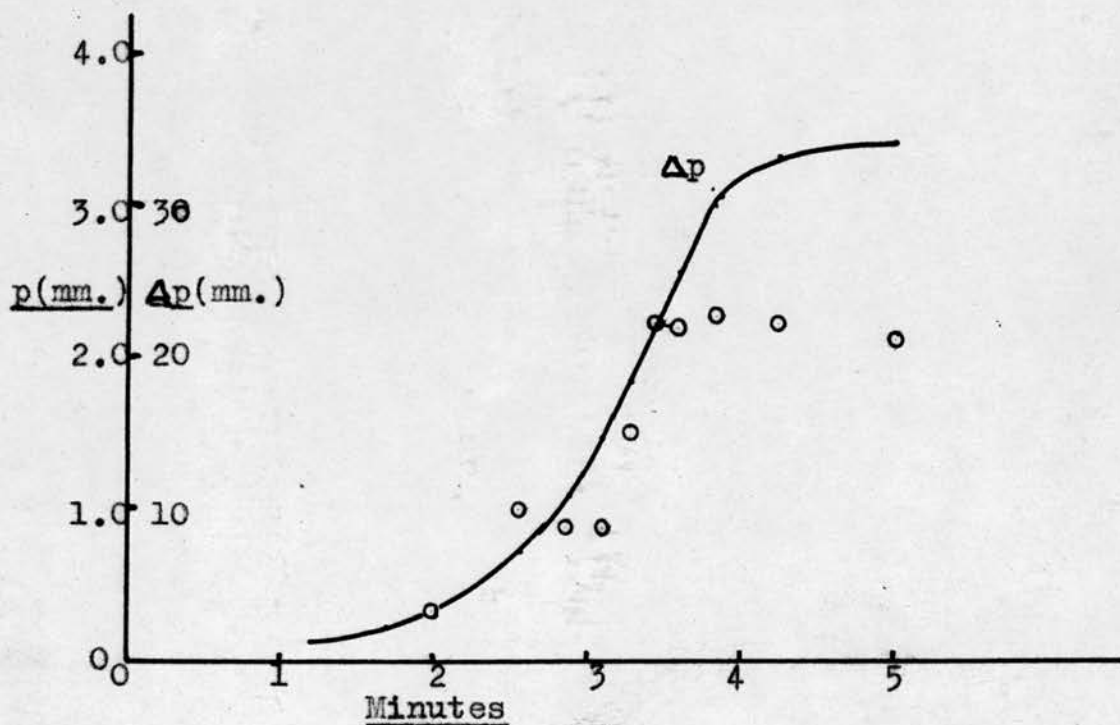


Figure 4.2.1. Development of Methoxyl from 100mm. propane and 50 mm. oxygen at 435°C.

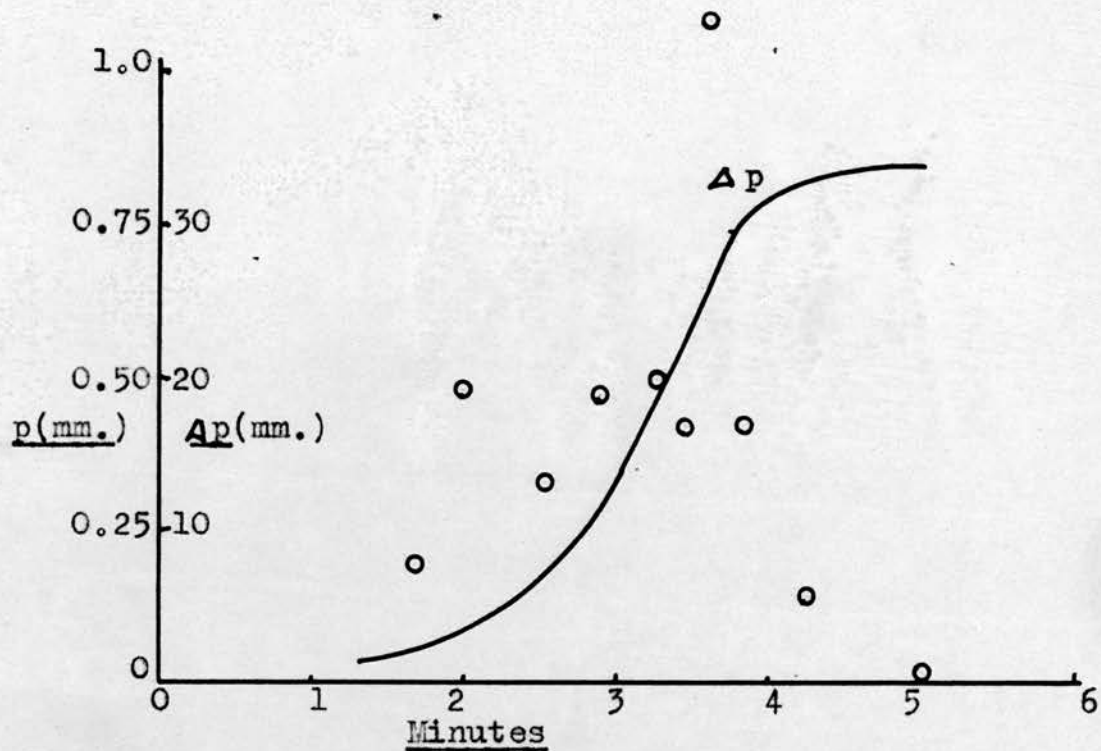


Figure 4.2.1. Development of Peroxide from 100mm. propane and 50 mm. oxygen at 435°C.

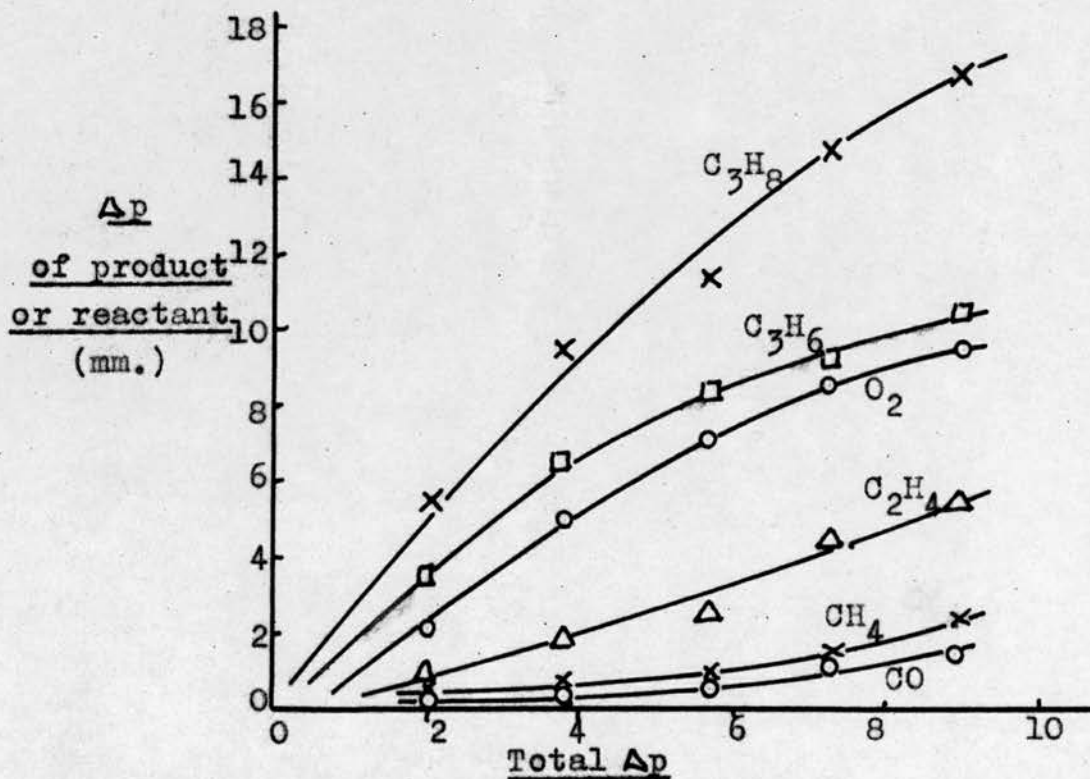
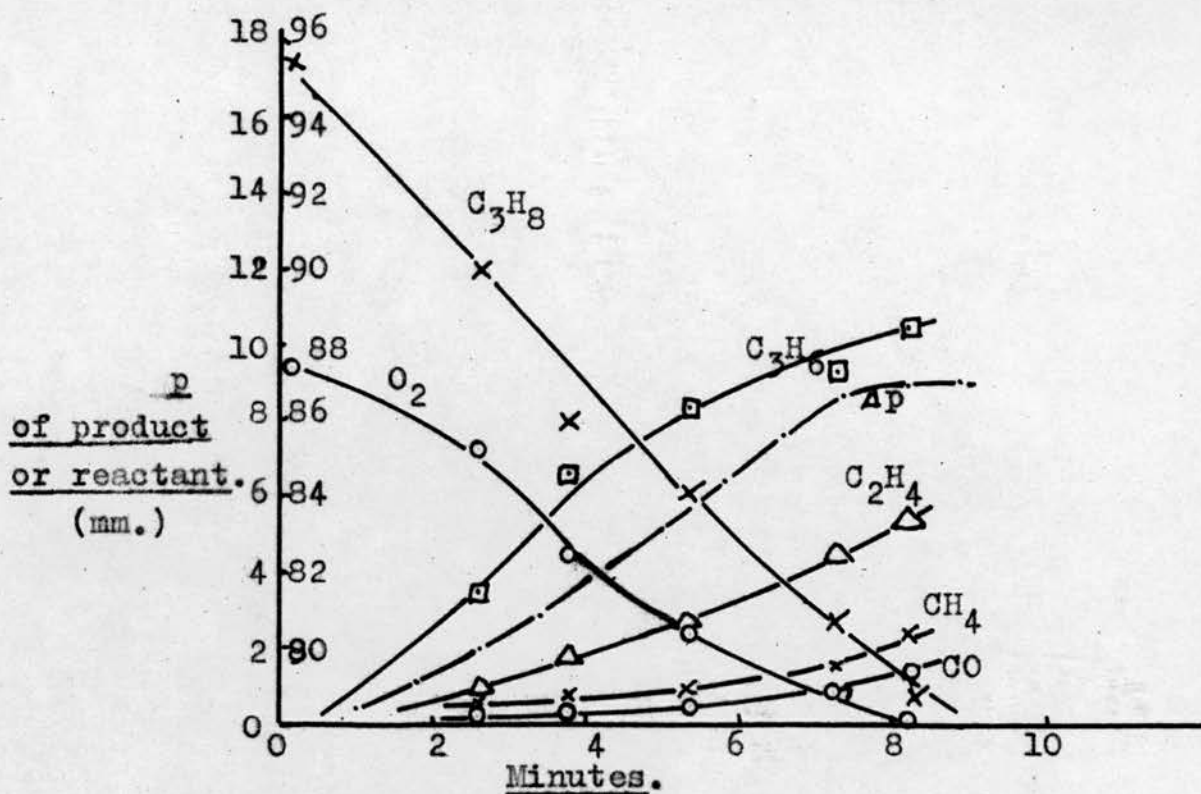


Figure 4.2.2. Products from 95.5 mm. propane and 9.5 mm. oxygen at 435°C.

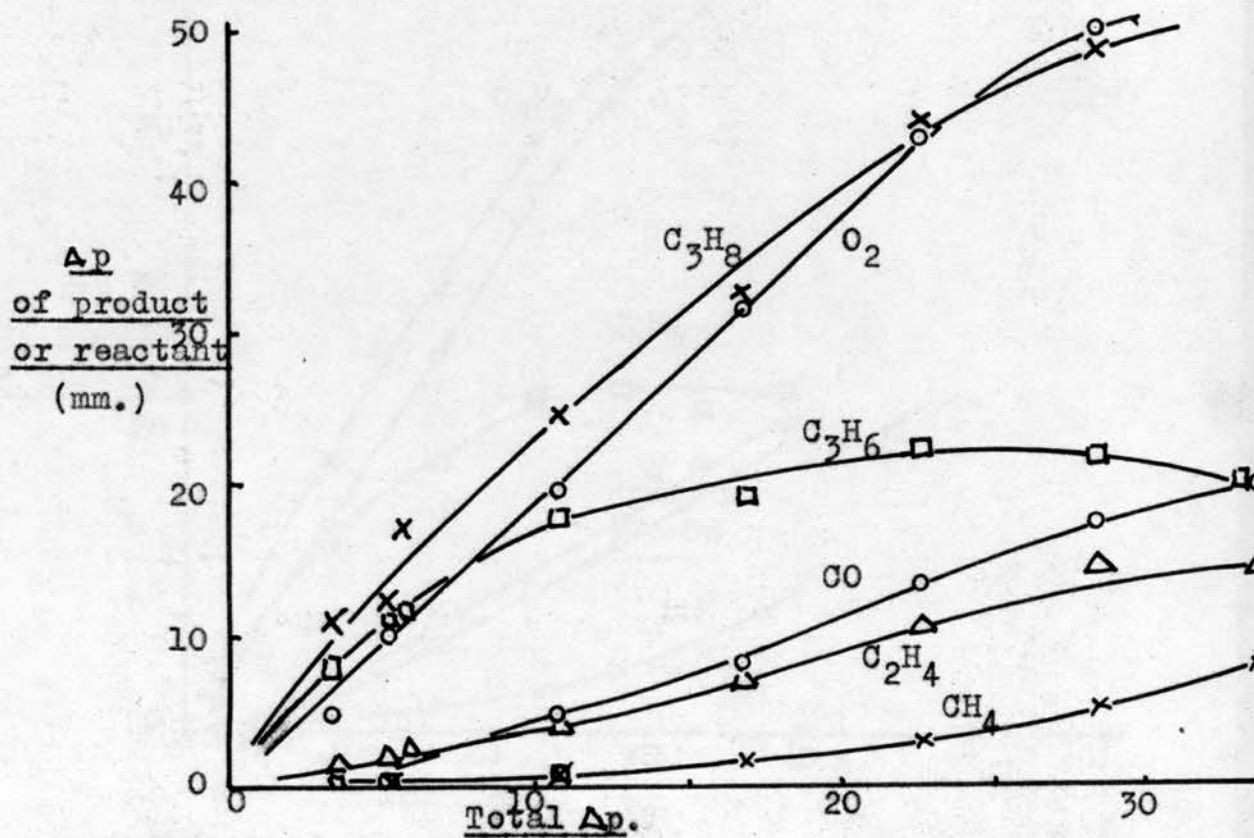
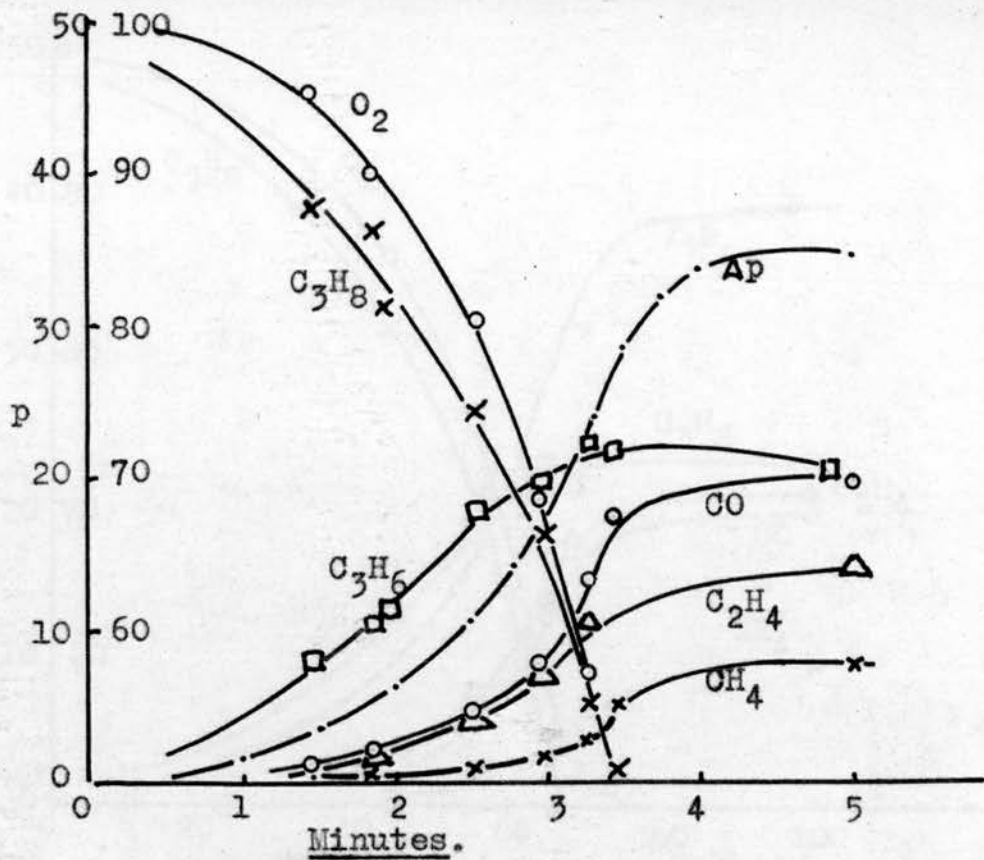


Figure 4.2.4. Products from 100 mm. propane and 50 mm. oxygen at $445^\circ C$.

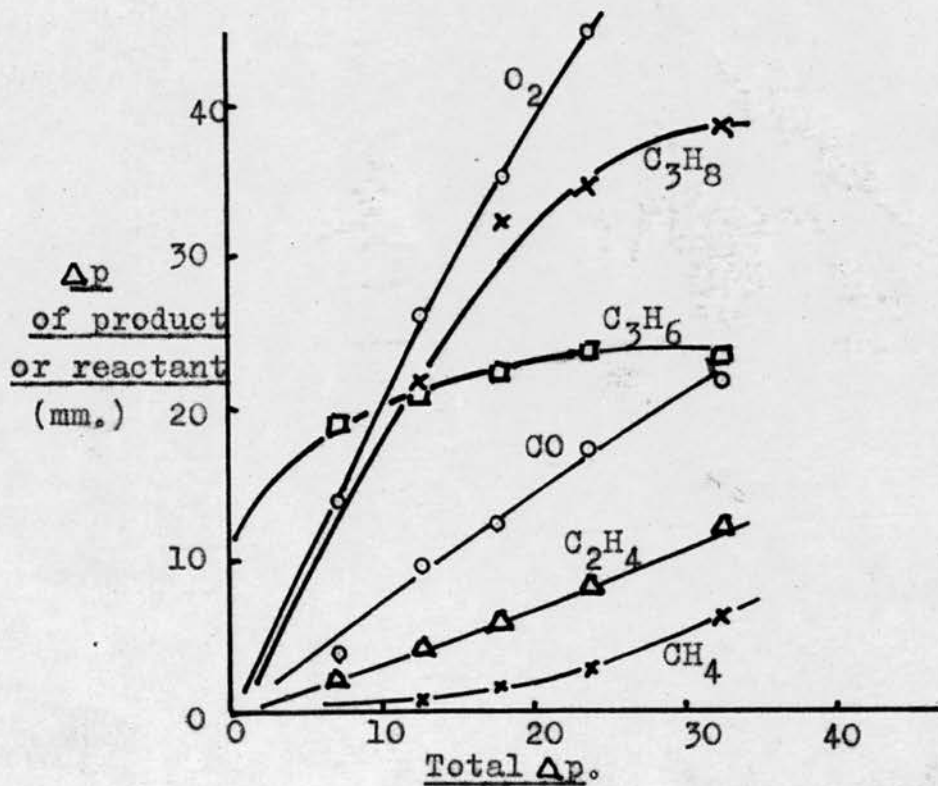
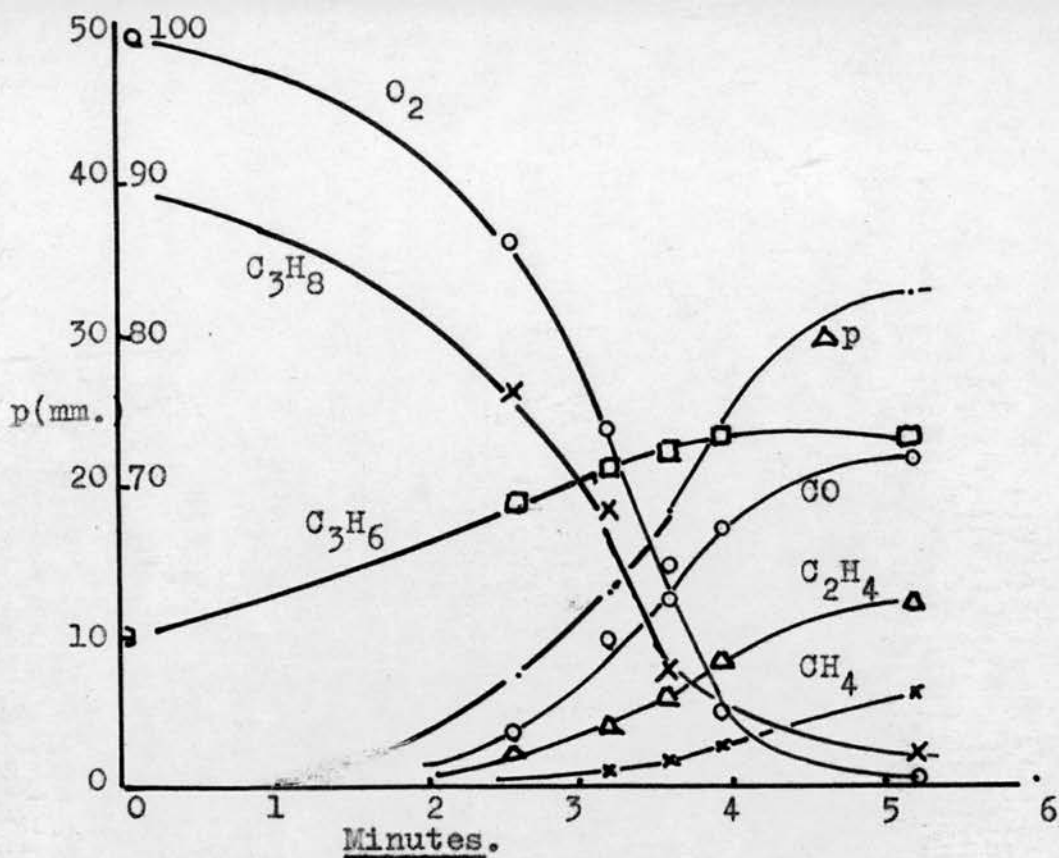


Figure 4.2.6. Products from 90 mm. propane, 10 mm. propylene and 50 mm. oxygen at $435^\circ C$.

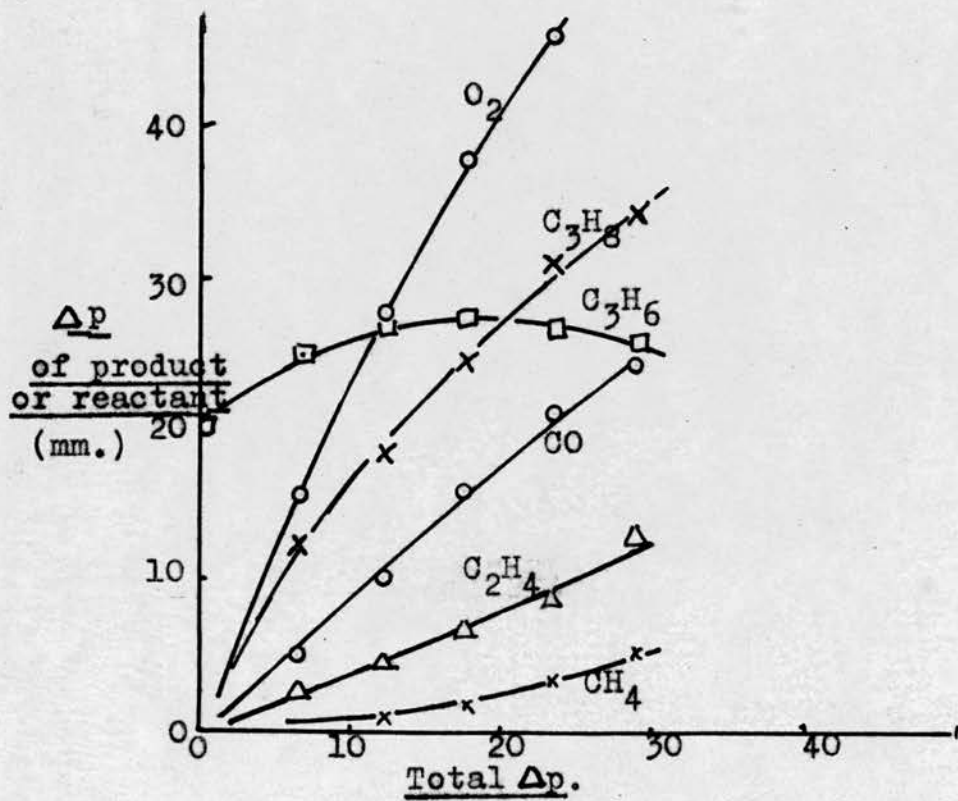
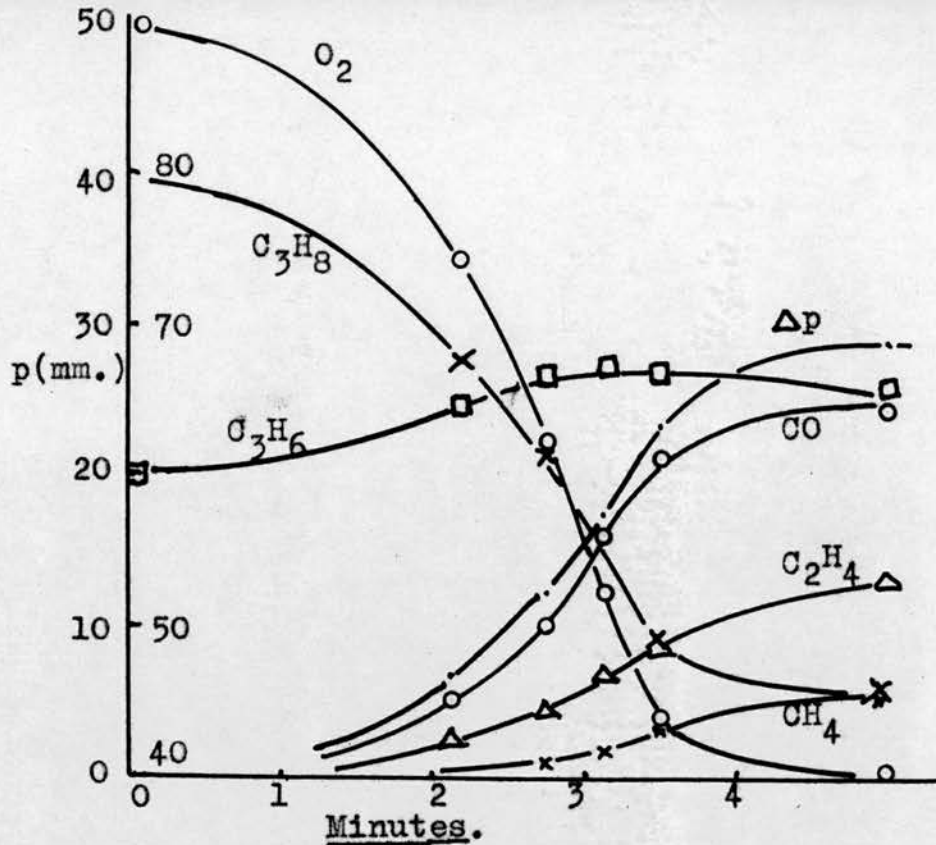


Figure 4.2.7. Products from 80 mm. propane, 20 mm. propylene and 50 mm. oxygen at 435°C .

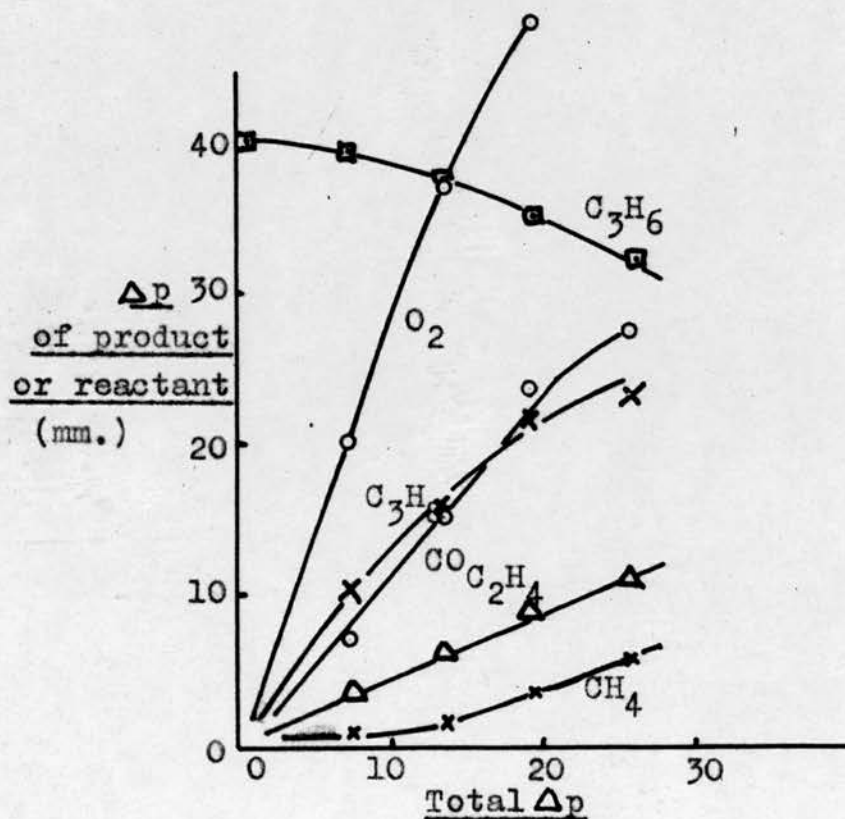
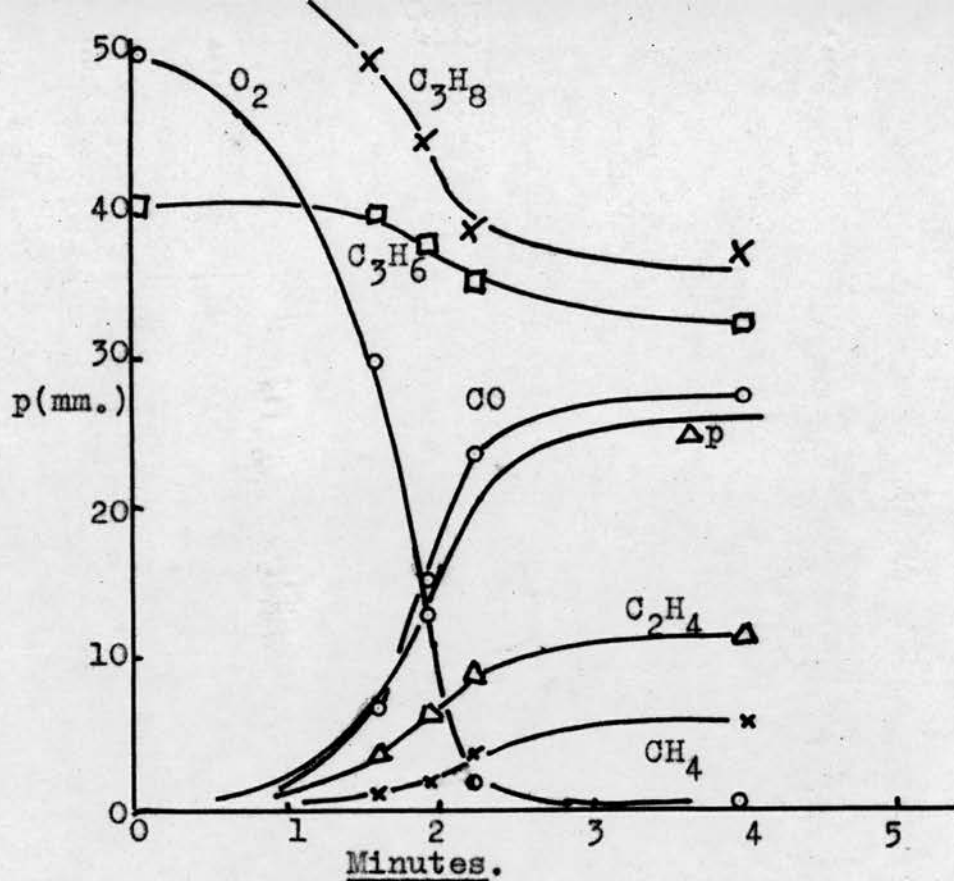


Figure 4.2.8. Products from 60 mm. propane, 40 mm. propylene and 50 mm. oxygen at 435°C .

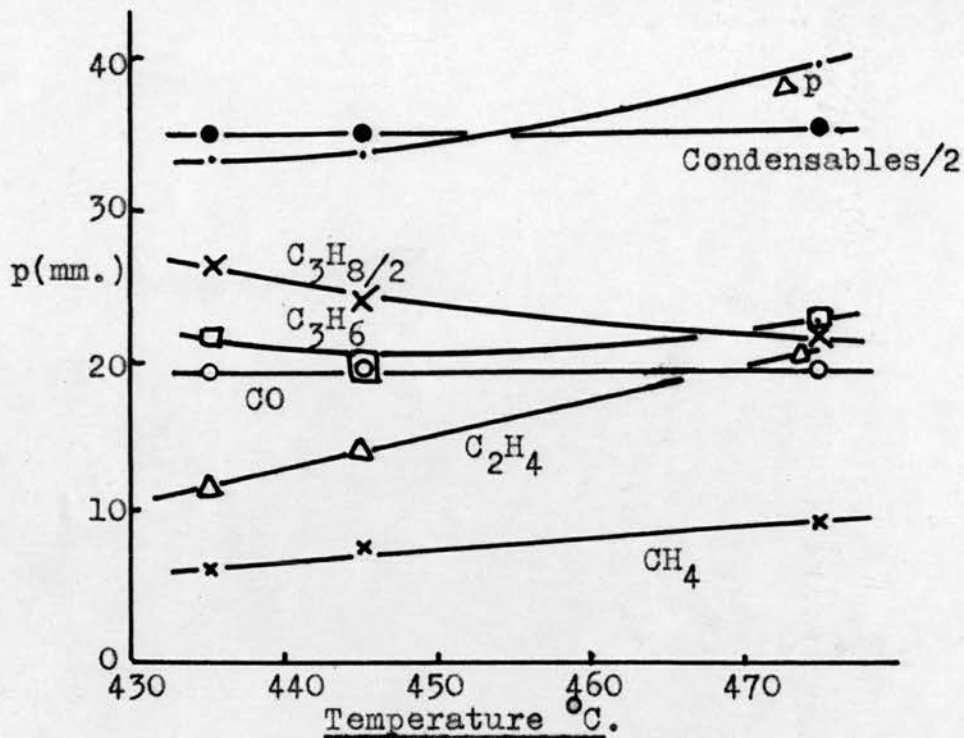


Figure 4.3. Variation in the products with temperature.

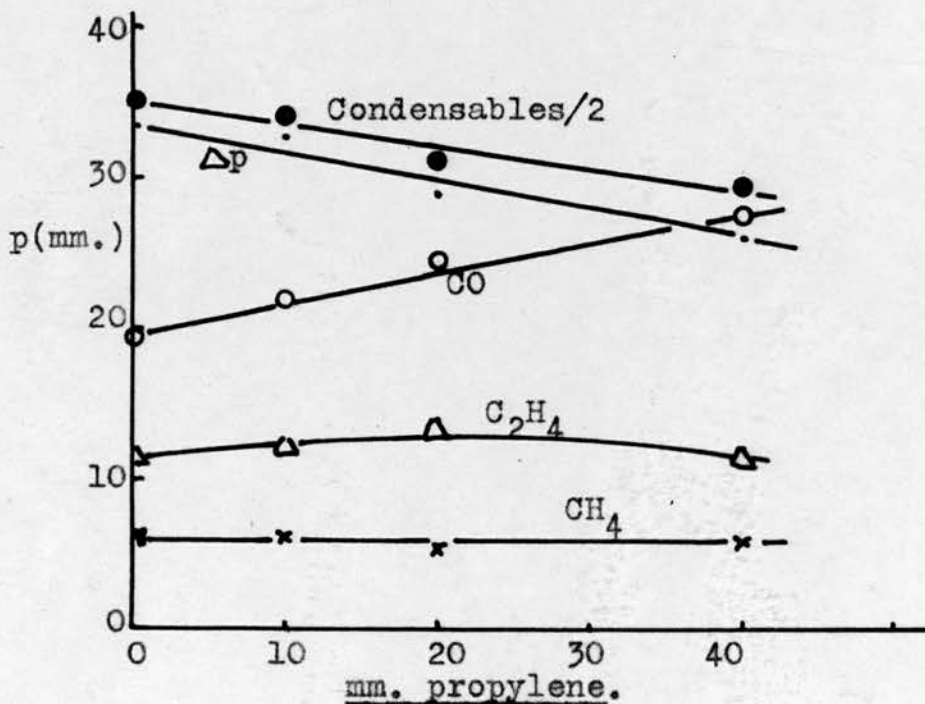


Figure 4.4. Variation in the final products as propane is replaced by propylene.

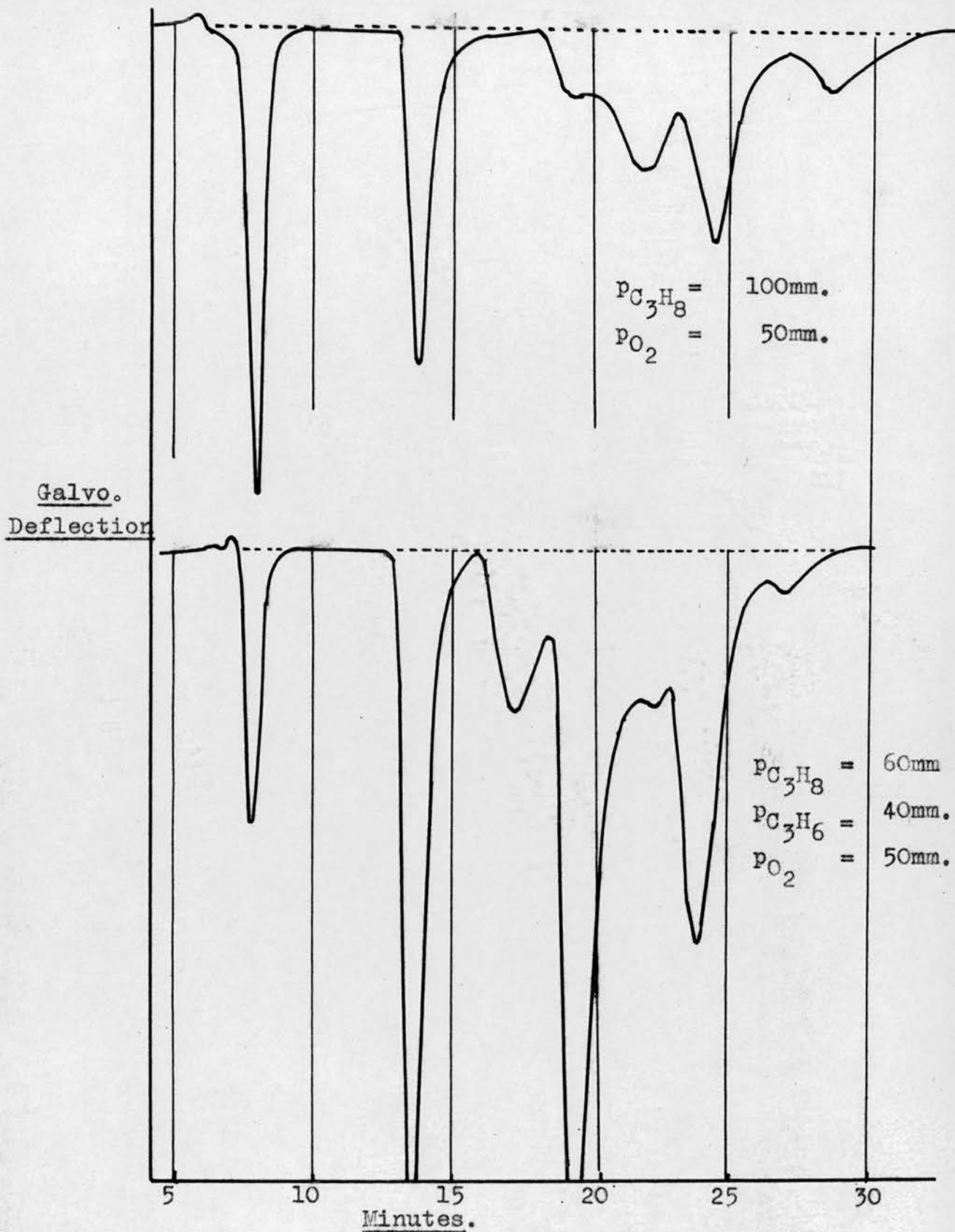


Figure 4.5. . . Chromatogram of Fraction 3 at maximum rate
at 435°C.