THE METATHETICAL REACTIONS OF METHOXYL RADICALS

Thesis

submitted for the degree of

Doctor of Philosophy

by

ROBERT SHAW, B.Sc.

University of Edinburgh.

August, 1959.

To

Isabel

ABSTRACT

The chemistry of methoxyl has been reviewed with emphasis placed on quantitative experiments. The following reactions have been discussed: radical production, combination, disproportionation and hydrogen abstraction. There is very little quantitative information available on the metathetical reactions of methoxyl radicals, and in particular no previous studies of hydrogen abstraction from C_2 to C_5 alkanes has been reported for methoxyl or any other alkoxyl radical.

Three approaches to the study of the metathetical reactions of methoxyl have been described. The first two methods, which depended on measuring the rate of formation of products, had to be abandoned because analysis showed that the systems were more complex than previous work had indicated. The third and apparently successful approach depended on measuring consumption of reactants when methoxyls were generated in mixtures of alkanes between 200°C and 400°C:

$$CH_3O + R_1H = CH_3OH + R_1 \qquad (1)$$

$$CH_3O + R_2H = CH_3OH + R_2 \qquad (2)$$

The alkyl radicals were removed by nitric oxide. The experiments were performed in a cyclic flow system and the residual alkanes were estimated by the Janak technique of gas chromatography.

The relative rate constants were calculated from the equation

$$\frac{k_1}{k_2} = \frac{\log (R_1H) \text{ initial} - \log (R_1H) \text{ final}}{\log (R_2H) \text{ initial} - \log (R_2H) \text{ final}}$$

and did not vary when the ratio of the initial concentrations of

alkanes was varied from 2:1 to 1:2. The relative rate constants were also independent of nitric oxide concentration. Five pairs of alkanes and two radical sources were used. The results obtained using the two sources were in reasonable agreement. Methyl nitrite was not a very efficient source of methoxyl. A large quantity of nitric oxide was produced while a reasonable fraction of the alkanes was consumed. This interfered with the analysis. Dimethyl peroxide proved to be a better source and gave more reproducible results.

The Arrhenius parameters and rate constants at 250°C relative to propane for the hydrogen abstraction by methoxyl are shown below:

Alkane	Runs	Log A	E (cal./mole)	k at 250°C
propane	-	0	0	1.00
ethane	7	+0.24	+1830	0.30
n-butane	7	-0.75	-2300	1.61
i-butane	12	-0.27	-1100	1.56
neopentane	9	+0.55	+2130	0.46
cyclopropane	2	-	-	0.17 at 297°C

The relative activation energies have been compared with similar results obtained for other radicals. The relative rates at which methoxyl attacks primary, secondary and tertiary hydrogen atoms were calculated from the relative rate constants. From a comparison of these results with those calculated for other radicals it was concluded that the reactivity of methoxyl was similar to that of methyl and trifluoromethyl.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the generous assistance that I have received during the past three years of research. I extend my sincere thanks to -

Dr. A.F. Trotman-Dickenson for his enthusiastic guidance. It has been a priviledge to work under his supervision.

Professor J.P. Kendall and Professor E.L. Hirst for the provision of library, technical and laboratory facilities.

Dr. J.H. Knox, Dr. R.F. Smith, Mr. G.C. Fettis, Mr. A.D. Kirk and the other members of the kinetics group for many helpful suggestions and discussions.

Mrs. E. Rutherford and Mr. J.B. Wright for binding and lettering the thesis, and to my parents for their support and encouragement at all times.

I am indebted to the Institute of Petroleum for a grant.

Robert Shaw.

CONTENTS

Page

DISCUSSION

PREFACE

In the 1955 Liversidge Lecture, E.W.R. Steacie[1] has said

> "Considerable progress has been made in the last ten years in building up a chemistry of free radicals in the gas phase. There remains however much to be done.... There is much interest to-day in combustion and other processes involving oxygen containing radicals. This is a very difficult field and as yet not a great deal has been accomplished. It is however a field of very great importance".

It seems reasonable to suppose that, in a difficult field, most progress will be made by studying selected elementary reactions of simple radicals. One of the simplest oxygen containing radicals is methoxyl, and an elementary reaction of particular interest is the metathetical reaction in which a hydrogen atom is abstracted according to the equation

$$CH_3O + RH = CH_3OH + R .$$

The present work describes and discusses some attempts to determine the kinetics of this reaction.

In the Introduction the reactions of methoxyl which have been studied quantatively are reviewed.

In the Experimental section are described three approaches to determine the kinetics of hydrogen abstraction reactions of methoxyl. The results are given in detail, and from them are calculated the relative rates at which methoxyl abstracts primary, secondary and tertiary hydrogen atoms.

These results are compared in the Discussion with those calculated for other radicals and atoms, and conclusions drawn concerning the reactivity of the methoxyl radical.

INTRODUCTION

A. General

Methoxyl, CH_3O, is the first of the series of alkoxyl radicals RO where R is an alkyl group. It is a reactive radical and this has three important consequences. Firstly, methoxyl has not been isolated in sufficient quantity nor for a sufficiently long period of time for its physical properties to be determined. The evidence for the existence of methoxyl is therefore mainly chemical. Secondly, the heat of formation of methoxyl has not been determined directly. Thirdly, most reactions involving methoxyl are complex and it is often difficult to determine the kinetics of the individual elementary reactions.

B. Production of Methoxyl

Methoxyl is best obtained from a molecule of the type CH_3O-X where the O-X bond is weak and X is reasonably stable and unreactive. Secondary reactions are then minimsed.

$$CH_3O-X = CH_3O + X \tag{1}$$

Five compounds which have a conveniently weak O-X bond are among the possible sources listed in Table 1.

Table 1.

Possible Sources of Methoxyl.

Source	CH_3O-X	Bond Strength of CH_3O-X (kcal.)	Reference
Alcohol	CH_3O-H	100	2
Ester	$CH_3O-OCCH_3$	80 - 90	6
Ether	CH_3O-CH_3	77	2
Nitrite	CH_3O-NO	36.4	3
Nitrate	CH_3O-NO_2	39.5	4
Hydroperoxide	CH_3O-OH	35 - 40	6
Symmetrical peroxide	CH_3O-OCH_3	35	5
Unsymmetrical peroxide	$CH_3O-OC(CH_3)_3$	30 - 40	6

Of these five, the nitrate, hydroperoxide and unsymmetrical dialkyl peroxide produce the NO_2, OH and $(CH_3)_3CO$ radicals which are reactive. The most useful sources then are methyl nitrite and dimethyl peroxide. In addition, the kinetics of the decomposition of these last two sources have been investigated and the reaction schemes are reasonably well established.

(i) Methyl Nitrite

Steacie and co-workers[3, 7] pyrolysed methyl nitrite in a static system between 170°C and 230°C. The rate of the reaction was measured by the pressure increase, and was found to be first order. The rate constants were independant of initial pressure of methyl nitrite between 50 mm. and 35 atmospheres, and not significantly affected by increasing the surface to volume ratio by a factor of 9. Analysis of the gaseous products gave, on the average, 85% NO, 10% CO and 5% residue. The involatile products were not analysed but appeared to be methanol and formaldehyde. The total pressure increase during the reaction was never greater than 85% with some evidence of polymerisation of the products.

On the basis of these results, Steacie proposed that the mechanism was

$$CH_3ONO = CH_3O + NO \qquad (2)$$

$$CH_3O = CH_2O + H \qquad (3)$$

$$CH_3O + H = CH_3OH \qquad (4)$$

giving the overall reaction

$$CH_3ONO = NO + \tfrac{1}{2} CH_2O + \tfrac{1}{2} CH_3OH \qquad (5)$$

and the rate constant

$$k = 1.84 \times 10^{13} \exp(-36{,}400/RT)\,\text{sec.}^{-1}$$

The activation energy of 36.4 kcal. is within 2 kcal. of those for the decomposition of ethyl, n-propyl, i-propyl, and n-butyl nitrites[8].

Carter and Travers[9] have studied the pyrolysis of methyl nitrite in a static system at 200°C. They measured the rate of production of NO (the main product), CO and N_2O, and concluded that the decomposition of methyl nitrite is not unimolecular.

However, assuming that the rate determining step is

$$CH_3ONO = CH_3O + NO \qquad (2)$$

and that the rate of the reaction can be determined from the rate of production of NO, we have calculated a reasonable first order plot from Carter and Travers' results (Table 2 and Figure 1). Further, the rate constant is in good agreement with that calculated from the work of Steacie and Shaw.

At 200°C, $k = 2.75 \times 10^{-4}$ sec.$^{-1}$ (calculated from Carter and Travers)

$k = 2.6 \times 10^{-4}$ sec.$^{-1}$ (Steacie and Shaw)

Table 2.

The Pyrolysis of Methyl Nitrite

A first order plot calculated by the present author from the results of Carter and Travers[9].

Initial concentration of methyl nitrite 0.02 g.moles/l. Temperature = 200°C.

Time (mins.)	N as NO (x) (g.moles/l)	a-x	log (a-x)
0	0	0.02000	1.3010
10	0.00084	0.01916	1.2923
15	0.00298	0.01702	1.2309
20	0.00362	0.01638	1.2143
25	0.00465	0.01535	1.1861
30	0.00791	0.01209	1.0823
40	0.00891	0.01109	1.0448
45	0.00952	0.01048	1.0161
50	0.01090	0.00910	0.9590
60	0.01203	0.00797	0.9015
80	0.01496	0.00604	0.7810

Although it is debatable whether formaldehyde and methanol are produced by reactions 3 and 4, it seems likely that the rate determining step in the pyrolysis of methyl nitrite is

$$CH_3ONO = CH_3O + NO . \qquad (2)$$

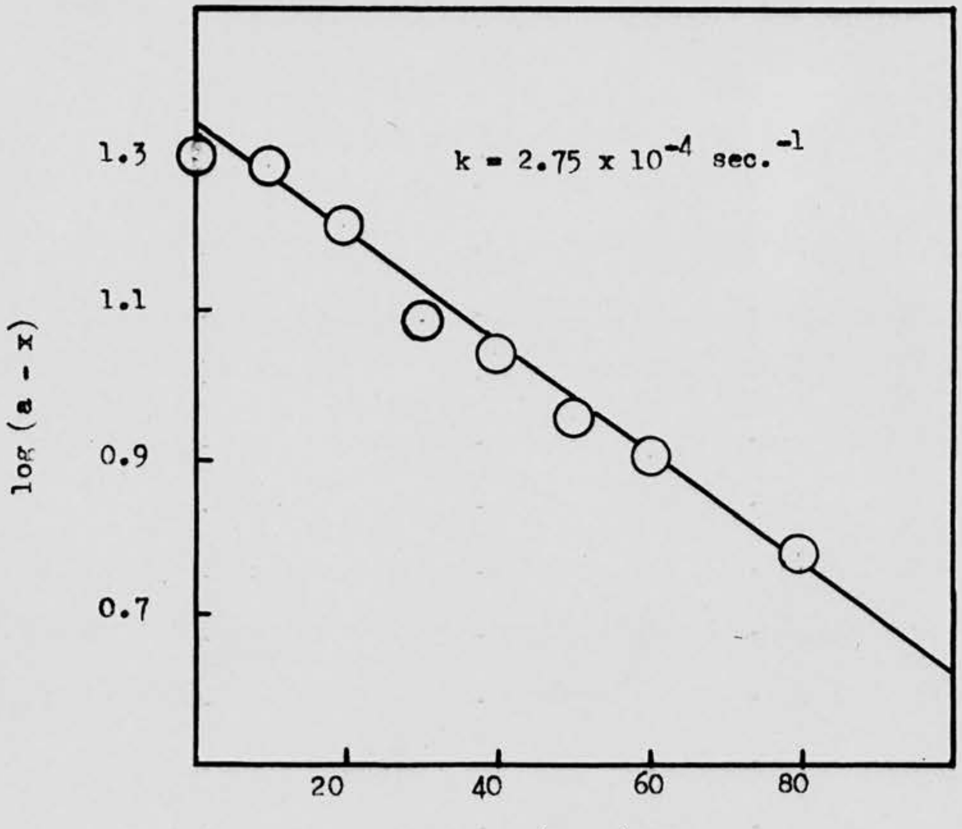


Figure 1. Pyrolysis of Methyl Nitrite at 200°C.
(calculated from Carter and Travers' results).

(ii) Dimethyl Peroxide

Calvert and Hanst[5] have pyrolysed dimethyl peroxide in a static system between 110°C and 150°C. The progress of the reaction was followed by infra-red spectroscopy. The only major products were methanol and carbon monoxide, obtained in the ratio of 3 to 1. The following reaction scheme was postulated.

$$CH_3OOCH_3 = CH_3O + OCH_3 \qquad (7)$$

$$CH_3O + CH_3O = CH_3OH + CH_2O \qquad (8)$$

$$CH_3O + CH_2O = CH_3OH + CHO \qquad (9)$$

$$CH_3O + CHO = CH_3OH + CO \qquad (10)$$

Formaldehyde does not build up as a product so reactions 11 and 12 are not important.

$$CH_3O + CH_3OOCH_3 = CH_3OH + CH_2OOCH_3 \qquad (11)$$

$$CH_2OOCH_3 = CH_2O + OCH_3 \qquad (12)$$

The kinetics were first order and most of the rate constants were calculated by measuring the rate of formation of methanol and carbon monoxide and assuming the stoichiometry

$$2\,CH_3OOCH_3 = 3\,CH_3OH + CO\,, \qquad (13)$$

However good agreement was obtained by measuring directly the rate of removal of dimethyl peroxide.

When the peroxide was pyrolysed in nitric oxide the sole major product was methyl nitrite. A rate constant in good agreement with those obtained by the previous two methods was obtained by measuring the rate of formation of methyl nitrite and assuming that

$$CH_3OOCH_3 = 2\ CH_3O \qquad (7)$$

$$2\ CH_3O + 2\ NO = 2\ CH_3ONO\ . \qquad (-2)$$

Rate constants obtained by the first two methods were used to give an Arrhenius plot from which was obtained

$$k = 1.6 \times 10^{15} \exp(-35.3/RT)\text{sec.}^{-1}$$

These results are good evidence that methoxyls are produced in the pyrolysis of dimethyl peroxide.

C. The Heat of Formation of Methoxyl

In common with many other radicals, methoxyl is so reactive that its heat of formation must be determined indirectly. Gray[10] has recently calculated it to be -0.5 kcal. (in the gaseous state at 25°C). He has used this value to determine the strengths of (a) the O-H bond in methanol, (b) the C-O bond in methoxyl and (c) the C-O bond in dimethyl and methyl ethyl ethers.

The basis of the method[10] is to consider a molecule of the type RO-X.

$$RO{-}X \underset{E_{-14}}{\overset{E_{14}}{\rightleftharpoons}} RO + X, \qquad \Delta H \qquad (14)$$

where ΔH is the heat of the reaction,

E_{14} is the activation energy of the forward reaction,

E_{-14} is the activation energy of the back reaction.

Now $\Delta H = \Delta H_f^o(RO) + \Delta H_f^o(X) - \Delta H_f^o(ROX)$

where $\Delta H_f^o(A)$ is the heat of formation of A.

Furhter, $\Delta H = E_{14} - E_{-14}$.

The back reaction, which is the recommendation of two radicals, is assumed to have negligible activation energy, i.e. $\Delta H = E_{14}$.

$$\therefore \Delta H_f^o(RO) = E_{14} - \Delta H_f^o(X) + \Delta H_f^o(ROX).$$

It appears that Gray has made an arithmetical mistake in his calculation of the heat of formation of methoxyl. Using the same values as Gray for E, $\Delta H_f^o(X)$ and $\Delta H_f^o(ROX)$, we have recalculated the heat of formation of methoxyl:-

For methyl nitrite,

$$E = 36.4 \text{ kcal.}; \Delta H_f^o(NO) = 21.6 \text{ kcal.}, \Delta H_f^o(CH_3ONO) = -14.9 \text{ kcal.}$$

$$\therefore \quad \Delta H_f^o(CH_3O) = 36.4 - 21.6 - 14.9 \text{ kcal.}$$

$$= -0.1 \text{ kcal.}$$

For methyl nitrate, ($CH_3ONO_2 = CH_3O + NO_2$), the experimentally derived activation energy[4] is 39.5 kcal. Gray, however, uses E = 38.4 kcal. but does not explain why this value is preferred.

$$\Delta H_f^o(NO_2) = 8.0 \text{ kcal.}, \Delta H_f^o(CH_3ONO_2) = -29.0 \text{ kcal.}$$

$$\therefore \Delta H_f^o(CH_3O) = 38.4 - 8.0 - 29.0 \text{ kcal.}$$

$$= +1.4 \text{ kcal.}$$

These two values for the heat of formation of methoxyl are in reasonable agreement and the average is +0.7 kcal. This is 1.2 kcal. higher than the value obtained by Gray. If the experimentally obtained value for the activation energy for the decomposition of methyl nitrate is used in the calculation, the discrepancy is even greater.

It would be very interesting if the heat of formation of dimethyl peroxide were known, for then a third value of the heat of formation could be calculated.

$$\Delta H_f^o(CH\ O) = \tfrac{1}{2}E + \tfrac{1}{2}\Delta H_f^o(CH_3OOCH_3)$$

as $E = 35.3$ kcal.[5]

D. The Elementary Reactions of Methoxyl

Although many reactions have been postulated, those for which there is evidence are (i) Decomposition, (ii) Combination and Disproportionation and (iii) Hydrogen abstraction.

(i) Decomposition

Methoxyl may decompose by reaction 15.

$$CH_3O = CH_2O + H \qquad (15)$$

A large yield of hydrogen (33%) was obtained in the pyrolysis of dimethyl ether at 500°C by Hinshelwood and Askey[11]. From this work Rice and Herzfeld[12] calculated $E_{15} = 20\text{-}45$ kcal. As this activation energy is high compared with most other reactions of methoxyl, the decomposition will be important only at high temperatures. Most of the investigations of methoxyl reactions are at low temperatures so there is very little other evidence for the decomposition. For example in the pyrolysis of methyl nitrite[3, 9] and dimethyl peroxide[5] and in the photolysis of methyl acetate[13] between 100°C and 250°C, no hydrogen was detected among the products. It was postulated to occur in the photolysis of methyl nitrite[14] between 30°C - 160°C, but the lack of hydrogen was attributed to the combination of the hydrogen atom with nitric oxide.

$$H + NO = HNO \qquad (16)$$

(ii) Combination and Disproportionation

It is convenient to discuss combination and disproportionation in the same section because the two reactions are similar and in the literature their rates are often expressed as a ratio.

Methoxyl combines with itself (autocombination) and disproportionates with itself (autodisproportionation) by reactions 17 and 18 respectively.

$$CH_3O + CH_3O = CH_3OOCH_3 \quad (17)$$

$$CH_3O + CH_3O = CH_3OH + CH_2O \quad (18)$$

Reaction 17 has not so far been isolated, but there is no reason to doubt that it does take place. Reaction 18 occurs in the pyrolysis of dimethyl peroxide[5], and in the photolysis of methyl acetate[13]. In the latter system, methyl radicals were also present so reaction 19 (cross-combination) and reaction 20 also occurred.

$$CH_3O + CH_3 = CH_3OCH_3 \quad (19)$$

$$CH_3 + CH_3 = C_2H_6 \quad (20)$$

It has recently been shown[18] that for many pairs of radicals, the rate of cross-combination equals twice the geometric mean of rates of autocombination. Hence it might be expected that

$$k_{19} = 2\sqrt{k_{20}k_{17}} \quad \text{(approximately)}$$

i.e. $$\frac{k_{19}^{2}}{k_{20}k_{17}} = 4.$$

From experiment[13], Wijnen found that

$$\frac{k_{18}k_{20}}{k_{19}^{2}} \leqslant 20$$

$$\therefore \frac{k_{18}}{k_{17}} = \frac{k\ \text{disp.}}{k\ \text{comb.}} \leqslant 80 .$$

Trideuteromethoxyl reacts in a manner similar to methoxyl[15].

$$CD_3O + CD_3O = CD_3OOCD_3 \quad (21)$$

$$CD_3O + CD_3O = CD_3OD + CD_2O \quad (22)$$

Again there is no evidence for reaction 21, but reaction 22 occurs in the photolysis of methyl d_3-acetate[15]. Also, as methyl radicals are present

$$CH_3 + CH_3 = C_2H_6 \quad (20)$$

and

$$CH_3 + CD_3O = CH_3OCD_3 . \quad (23)$$

From experiment, Wijnen found that

$$\frac{k_{20}k_{22}}{k_{23}^2} \leqslant 11 .$$

Again it is a reasonable assumption that

$$k_{23} = 2\sqrt{k_{20}k_{21}}$$

i.e.

$$\frac{k_{23}^2}{k_{20}k_{21}} = 4$$

hence

$$\frac{k\text{ disp.}}{k\text{ comb.}} = \frac{k_{22}}{k_{21}} \leqslant 44.$$

It is unfortunate that the experimental value of $\frac{k_{18}k_{20}}{k_{19}^2}$ and $\frac{k_{20}k_{22}}{k_{23}^2}$ are so indeterminate that little comment can be be made on these values of $\frac{k\text{ disp.}}{k\text{ comb.}}$ except that they appear to be high (see Table 3).

Table 3.

Disproportionation and Combination

	$\frac{k\ disp.}{k\ comb.}$	Edisp.-Ecomb. (in kcal.)	Temp. °C	Reference
$\frac{CH_3O}{CH_3O}$	$\leqslant 80$	-	-	a
$\frac{CD_3O}{CD_3O}$	$\leqslant 44$	-	-	b
$\frac{CH_3}{CH_3O}$	1.2 to 2.6	+ 1.5	29 - 142	13
$\frac{CH_3}{CD_3O}$	1.4	0	30 - 200	15
$\frac{CD_3}{CD_3O}$	1.8	0	30 - 200	15
$\frac{CH_3}{CH_3CO}$	0.06	-	29	13
$\frac{CH_3}{C_2H_5}$	0.06	-	90	16
$\frac{C_2H_5}{C_2H_5}$	0.15	0	50 - 315	17

a is calculated from 13.

b is calculated from 15.

The cross-disproportionation of methoxyl and methyl radicals has also been studied by Wijnen[13],

$$CH_3 + CH_3O = CH_4 + CH_2O . \qquad (24)$$

He found that the ratio

$$\frac{k\ disp.}{k\ comb.} = \frac{k_{24}}{k_{19}}$$

varied from 1.2 at 29°C to 2.6 at 142°C. The Arrhenius plot gave $E_{24} - E_{19} = 1.5$ kcal.

Similarly, in the photolysis of methyl d_3-acetate[15],

$$CH_3 + CD_3O = CH_3OCD_3 \qquad (23)$$

$$CH_3 + CD_3O = CH_3D + CD_2O \qquad (25)$$

$$\frac{k\ disp.}{k\ comb.} = \frac{k_{25}}{k_{23}} = 1.4$$

also $$CD_3 + CD_3O = CD_3OCD_3 \qquad (26)$$

and $$CD_3 + CD_3O = CD_4 + CD_2O \qquad (27)$$

$$\frac{k\ disp.}{k\ comb.} = \frac{k_{27}}{k_{26}} = 1.8$$

Further, $\frac{k_{25}}{k_{23}}$ and $\frac{k_{27}}{k_{26}}$ were temperature independant.

$\therefore E_{25} - E_{23} = 0$, and $E_{27} - E_{26} = 0$.

It is reasonable to assume that $E_{23} - E_{26} = 0$ and that $k_{23} = k_{26}$.

$$\therefore \frac{k_{25}}{k_{27}} = \frac{k(CH_3 + D-CD_2O)}{k(CD_3 + D-CD_2O)}$$

$$= \frac{1.4}{1.8}$$

$$= 0.8$$

A deuterium atom in trideuteromethoxyl is therefore abstracted faster by trideuteromethyl than by methyl.

Two interesting reactions occurred when Calvert and Hanst pyrolysed dimethyl peroxide in the presence of added gases[5]. With oxygen in the system, large quantities of formaldehyde were produced. This was accounted for by reaction 28,

$$CH_3O + O_2 = CH_2O + HO_2 \qquad (28)$$

This reaction might be expected to play a part in the production of aldehydes in the low temperature oxidation of hydrocarbons.

With nitric oxide in the system the only major product was methyl nitrite.

$$CH_3O + NO = CH_3ONO \qquad (-2)$$

It is interesting that no evidence was obtained for the alternative disproportionation reaction which might have been expected to occur.

$$CH_3O + NO = CH_2O + HNO \qquad (29)$$

$$2HNO = N_2O + H_2O \qquad (30)$$

(iii) Hydrogen Abstraction

When methanol is detected in the products of a reaction involving methoxyl, reaction 1 is usually postulated.

$$CH_3O + RH = CH_3OH + R \qquad (1)$$

The particular case where RH is itself a radical has already been discussed as disproportionation. The remaining examples will be considered in this section.

Vaughan and co-workers[19] pyrolysed methyl t-butyl peroxide in the gas phase at 195°C in an excess of cyclohexene. For every 100 moles of peroxide decomposed, 76 moles of methanol were obtained.

$$CH_3O\text{-}OC(CH_3)_3 = CH_3O + OC(CH_3)_3 \tag{31}$$

$$CH_3O + C_6H_{10} = CH_3OH + C_6H_9 \tag{32}$$

As only 8 moles of formaldehyde and 5 moles of carbon monoxide were produced most of the methoxyls must react via 32.

Similar work has been done in solution by McBay and Tucker[20]. They pyrolysed dimethyl peroxydicarbonate in several solvents between 110°C and 160°C. The following scheme was postulated:-

$$CH_3OCOO\text{-}OOCOCH_3 = CH_3OCOO + CO_2 + CH_3O \tag{33}$$

$$CH_3OCOO = CH_3O + CO_2 \tag{34}$$

$$CH_3O + RH(\text{solvent}) = CH_3OH + R \tag{35}$$

$$2R = R_2 \tag{36}$$

$$CH_3OCOO + R = CH_3OCOOR\ (\text{ester}) \tag{37}$$

$$R + CH_3OCOO\text{-}OOCOCH_3 = CH_3OCOOR(\text{ester}) + CH_3OCOO \tag{38}$$

$$CH_3O + CH_3OCOO\text{-}OOCOCH_3 = CH_3OH + CH_2OCOO\text{-}OOCOCH_3 \tag{39}$$

$$CH_2OCOO\text{-}OOCOCH_3 = CH_2O + 2CO_2 + CH_3O \tag{40}$$

From this scheme McBay and Tucker derived the following equations.

(a) The percentage of all methoxyls which abstract hydrogen from the solvent RH $= \dfrac{(2 \text{ x moles of dimer} + \text{moles of ester}) \text{ x } 100}{\text{Total moles of } CH_3OH + \text{moles of } CH_2O}$.

(b) The percentage of all methoxyls which abstract hydrogen from the parent peroxide $= \dfrac{(2 \times \text{moles of } CH_2O) \times 100}{\text{Total moles of } CH_3OH + \text{moles of } CH_2O}$.

According to the reaction scheme proposed by McBay and Tucker, the only way in which methoxyls can react is to abstract a hydrogen atom to produce methanol. The total number of molecules of methoxyls will then be given by the total number of molecules of methanol produced. It seems then that equation (a) is in error and should be:- The percentage of all methoxyls which abstract hydrogen from the solvent RH $= \dfrac{(2 \times \text{moles of dimer} + \text{moles of ester}) \times 100}{\text{Total moles of } CH_3OH}$.

Further, for each methoxyl which abstracts a hydrogen atom from the parent peroxide, one molecule of formaldehyde will be produced. Equation (b) is therefore also in error and should be:- The percentage of all methoxyls which abstract hydrogen from the parent peroxide $= \dfrac{(\text{Moles of } CH_2O) \times 100}{\text{Total moles of } CH_3OH}$.

The results recalculated by us using the modified equations are given in Table 4. However, as the yield of formaldehyde is usually small the overall picture given by McBay and Tucker is not altered.

Table 4.

Hydrogen Abstraction in Solution by Methoxyls

Solvent	Temp. ^{o}C	% H abstraction from solvent	% H abstraction from parent peroxide
p-methyl *i*-propyl benzene	110	73.0	0
	155	68.4	0
trimethyl acetic acid	130	42.0	44.0
toluene	110	100	0
i-propyl benzene	110	61	0

The conclusion to be drawn from the work of McBay and Tucker and from that of Vaughan and co-workers is that when methoxyl is generated in the presence of molecules containing weakly bonded hydrogen atoms, large yields of methanol are obtained.

Results of a more quantitative nature have been obtained by Wijnen[13, 15] in the gas phase photolysis of methyl acetate and methyl d_3-acetate. In the first experiment methyl and methoxyl were produced giving the following reactions:-

$$CH_3O + CH_3O = CH_3OH + CH_2O \qquad (18)$$

$$CH_3 + CH_3O = CH_3OCH_3 \qquad (19)$$

$$CH_3 + CH_3 = C_2H_6 \qquad (20)$$

$$CH_3O + CH_3COOCH_3 = CH_3OH + CH_2COOCH_3 . \qquad (41)$$

It follows that

$$\frac{R_{CH_3OH}R_{C_2H_6}}{R^2_{CH_3OCH_3}} = \frac{k_{18}k_{20}}{k^2_{19}} + \frac{k_{41}k^{\frac{1}{2}}_{20}}{k_{19}} \times \frac{R^{\frac{1}{2}}_{C_2H_6}\,(MeAc)}{R_{CH_3OCH_3}},$$

Hence by plotting

$$\frac{R_{CH_3OH}R_{C_2H_6}}{R^2_{CH_3OCH_3}} \quad \text{against} \quad \frac{R^{\frac{1}{2}}_{C_2H_6}\,(MeAc)}{R_{CH_3OCH_3}}$$

a straight line graph was obtained, the slope of which gave

$$\frac{k_{41}k^{\frac{1}{2}}_{20}}{k_{19}}.$$

From the Arrhenius plot $E_{41} + E^{\frac{1}{2}}_{20} - E_{19} = 4.5$ kcal.

and assuming $E_{20} - E_{19} = 0$, $E_{41} = 4.5$ kcal.

However, from the published results and graphs, one may deduce that this represents the lower limit of E_{41} which may lie between 4.5 and 9 kcal.

For the corresponding methyl radical abstraction in the same system,

$$CH_3 + CH_3COOCH_3 = CH_4 + CH_2COOCH_3 . \qquad (42)$$

Wijnen obtains $E_{42} = 10 \pm 0.5$ kcal. Taking log A_{20} to be 13.6 log $mole^{-1}cc.sec.^{-1}$ as determined by Gomer and Kistakowsky[21] we have calculated from Wijnen's results that

$$\log A_{42} = 11.2 \log mole^{-1}cc.sec.^{-1}$$

Making the reasonable approximations that $A_{42} = A_{41}$, and taking E_{41} to be between 4.5 and 9 kcal. we have calculated from Wijnen's results that log A_{19} lies between 14.8 and 12.6 log mole^{-1}cc. sec.$^{-1}$. Reaction 19 is the combination of a methoxyl and a methyl radical and its A factor might be expected to be similar to that of reaction 20, which is the combination of two methyl radicals. Log A_{20} is 13.6 log mole^{-1}cc. sec.$^{-1}$, which is in the middle of the range 14.8 to 12.6 calculated by us for log A_{19}. This in turn is therefore a useful indication that E_{41} is between 4.5 and 9 kcal.

Good correlation with E_{41} and E_{42} was obtained by Wijnen in photolysis of methyl d_3-acetate. Although the system was complicated by the presence of trideuteromethyl in addition to methyl, Wijnen isolated

$$CD_3O + CH_3COOCD_3 = CD_3OH + CH_2COOCD_3 \qquad (43)$$

$$E_{43} = 5 \text{ kcal.}$$

and

$$CH_3 + CH_3COOCD_3 = CH_4 + CH_2COOCH_3 \qquad (44)$$

$$E_{44} = 10 \pm 0.5 \text{ kcal.}$$

In a similar manner to that described previously, we have calculated from Wijnen's results that log A_{44} = 11.0 log mole^{-1}cc. sec.$^{-1}$, and that log A_{24} = 14.4 log mole^{-1}cc. sec.$^{-1}$. The value of log A_{24} is higher than might be expected when it is compared with log A_{20} which is 13.6 log mole^{-1}cc. sec.$^{-1}$. This indicates that E_{43} may be a few kcal. higher than the value of 5 kcal. proposed by Wijnen.

In passing, it may be noted that the Arrhenius parameters for reactions 42 and 43 are similar to those for the abstraction of a hydrogen atom from acetone by methyl[22]. (see Table 6).

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3 \qquad (45)$$

$E_{45} = 9.7$ kcal., and log A = 11.6 log mole^{-1}cc. sec.$^{-1}$.

Table 6.

Hydrogen Abstraction by Methyl

Reactant	E	Log A	Reference
Methyl acetate	10	11.2	13 and this work
Methyl d_3-acetate	10	11.0	15 and this work
Acetone	9.7	11.6	22

Units: E is in kcal., and log A is in log mole^{-1}cc. sec.$^{-1}$.

Conclusion

It may be concluded from this survey that the general pattern of methoxyl chemistry is fairly well established. However, compared with the vast amount of information available for the hydrogen abstraction reactions of methyl, very little is known about the similar reactions of methoxyl. In particular, no kinetic studies have been reported for the variation of the rates of hydrogen abstraction by methoxyl from a series of alkanes, RH.

EXPERIMENTAL AND RESULTS

A. Preparation and Purification of Materials

(i) Radical Sources

These preparations were carried out behind a Triplex glass screen.

(a) Methyl nitrite[3] (b.pt. -12°C)

$$CH_3OH + HONO = CH_3ONO + H_2O \qquad (1)$$

57 ml. of dilute sulphuric acid (33% V/V) was added dropwise, with stirring, to a mixture of 36 g. sodium nitrite, was condensed at -80°C as a yellow green liquid. This liquid was distilled in a low temperature still and the middle third fraction retained and transferred to a black painted storage bulb. There was no appreciable decomposition over periods as long as one month.

(b) Methyl <u>t</u>-butyl peroxide, (b.pt. not quoted in Literature. Explosive).

$$(CH_3)_3\ COOH + KOH = (CH_3)_3\ COOK \qquad (2)$$

$$(CH_3)_3\ COOK + (CH_3)_2\ SO_4 = (CH_3)_3\ COOCH_3 \qquad (3)$$

Crystalline potassium t-butyl peroxide was prepared by the method of Kornblum and de la Mare[23]. From this intermediate, small quantities (2-3 g.) of methyl t-butyl peroxide were prepared by the method of Rust, Seubald and Vaughan[19].

(c) Dimethyl peroxide (b.pt. 13.5°C. Explosive.)

$$HOOH + KOH + (CH_3)_2\ SO_4 = CH_3OOCH_3 \qquad (4)$$

This peroxide was prepared by the method of Hanst and Calvert[5]. Ten cc. (about 0.1 mole) of dimethyl sulphate and 15 cc. (about 0.14 mole) of 30% aqueous hydrogen peroxide were placed in a 250 cc. three necked flask fitted with a stirrer through a mercury seal, a 250 cc. dropping funnel and an outlet tube. The outlet tube was connected to a trap. The flask was immersed in an ice/water mixture in a bath fitted with an immersion heater. From the dropping funnel, 20 cc. (about 0.15 mole) of 40% aqueous potassium hydroxide was added slowly, with stirring. A nitrogen cylinder was connected by a tube to the top of the dropping funnel. A weak flow of nitrogen was started and the trap was immersed in liquid oxygen. The water bath heater was switched on and the flask warmed up, until at between 50°C and 60°C, the contents began to bubble smoothly, and the reaction then maintained itself. The volatile dimethyl peroxide was carried in the nitrogen stream to the cold trap. When bubbling ceased, the trap containing the product in about 50% yield was removed to the vacuum line. The dimethyl peroxide was degassed and separated from the possible impurities, water (b.pt. 100°C), hydrogen peroxide (b.pt. 152°C) and methyl hydroperoxide (b.pt. 38-40°C at 65 mm.) by repeated bulb to bulb distillation from -10°C to -80°C. It was stored as a gas in a black painted storage bulb and showed no appreciable decomposition in a month.

(ii) Hydrocarbons

Hydrocarbon	Source	G.C. Analysis
ethane	B.O.G. cylinder	1.2% ethylene
propane	I.C.I. cylinder (a gift)	0.5% i-butane
n-butane	B.P. cylinder (a gift)	no impurity detected
i-butane	B.P. cylinder (a gift)	no impurity detected
neo-pentane	D.S.I.R. ampoule	no impurity detected
cyclo-propane	B.O.G. cylinder	less than 0.1% propane

(iii) Inhibitor. Nitric Oxide[24]

$$2NO_2^- + 4H^+ + 2I^- = 2NO + I_2 + H_2O \quad (5)$$

17 g. sodium nitrite and 40 g. potassium iodide were dissolved in 100 ml. water in a 3 necked 1 litre flask. This flask, the delivery tube and trap were flushed out with nitrogen. 100 ml. of hydrochloric acid (50%) was added dropwise with stirring. Nitric oxide was evolved and condensed as a green liquid at -183°C. It was purified by distillation from -183°C to -200°C.

(iv) Carrier gases

(a) Hydrogen (B.O.G. cylinder) was dried by passage through phosphorus pentoxide.

(b) Nitrogen (B.O.G. cylinder) was dried by passage through phosphorus pentoxide.

(c) Carbon Dioxide (I.C.I. Drikold) was dried by passage through indicator silica gel.

(v) Column Packing

(a) Partition Chromatography

The solid support used for partition columns was celite (John Mansville). It was graded and purified as described by Phillips[25]. After seiving to a convenient mesh size, the same author's instructions were followed in the addition of the fixed phase and the filling of the 4 mm. i.d. pyrex columns.

(b) Adsorption Chromatography

Active carbon (Sutcliffe and Speakman) was seived and then heated at 100°C under vacuum for two hours to remove adsorbed water. Thus activated, the carbon was poured into 6 mm. i.d. pyrex columns.

Active alumina (Spence) was seived and then roasted in a porcelain basin over a meker burner for 3 hours. It was packed in 6 mm. i.d. columns. There is a tendency for alumina to give asymmetric peaks especially with the higher alkanes so its activity was usually reduced by poisoning it with 1% squalane.

B. Requirements for the Study of Hydrogen Transfer Reactions of Methoxyl

Compared with the large number of rate constants and rate factors which have been determined for the hydrogen transfer reactions of methyl[26], very little is known about the corresponding reactions of methoxyl.

$$CH_3O + RH = CH_3OH + R \qquad (6)$$

$$R_{CH_3OH} = R_R = -R_{RH} = k_6(CH_3O)\,(RH)$$

In the kinetic study of this reaction, three problems must be faced. First, a good clean source of methoxyl is required. As stated in the Introduction, two of the best sources are methyl nitrite and dimethyl peroxide. Second, a means of measuring the concentration of the reactants must be found. The hydrogen donor, RH, is usually kept in large excess so its concentration is effectively constant. In methyl radical work, the concentration of methyl is usually expressed in terms of the rate of production of the dimer, ethane. When methyl nitrite is used as a source, the temperature required to break the CH_3O-NO bond is so high that little of the dimer would be detected in the products. If dimethyl peroxide itself is used as a source, the dimer is indistinguishable from the parent. Accordingly, alternative means of measuring the concentration of methoxyl must be found. The third problem is to measure the rate of production of the products methanol and alkyl radical R. The former can be determined by analysis, and if iodine is present in the system, the rate of formation of the corresponding iodides will be equal to the rate of formation of the alkyl radical R.

C. Preliminary Experiments. Measurement of Rate of Formation of Products

The first approach to the study of the hydrogen transfer reactions of methoxyl depended on the following reaction scheme.

$$CH_3ONO = CH_3O + NO \tag{7}$$

$$CH_3O + CH_3O = CH_3OH + CH_2O \tag{8}$$

If RH is present in large excess,

$$CH_3O + RH = CH_3OH + R \tag{6}$$

The alkyl radical is assumed to be removed by the nitric oxide.

$$\text{Now } R_{CH_2O} = k_8(CH_3O)^2 \; ; \; \therefore (CH_3O) = \frac{R_{CH_2O}^{\frac{1}{2}}}{k_8^{\frac{1}{2}}}$$

$$R_{CH_3OH} = R_{CH_2O} + \frac{k_6}{k_8^{\frac{1}{2}}} (RH) R_{CH_2O}^{\frac{1}{2}}$$

$$\text{i.e. } \frac{k_6}{k_8^{\frac{1}{2}}} = \frac{R_{CH_3OH} - R_{CH_2O}}{(RH) R_{CH_2O}^{\frac{1}{2}}}$$

(RH) is effectively constant and R_{CH_3O} and R_{CH_2O} may be measured by analysis. Hence $k_6/k_8^{\frac{1}{2}}$ may be determined for a series of alkanes.

A conventional high vacuum static system was constructed of pyrex glass. The 350 cc. reaction vessel was heated electrically. Assuming first order kinetics, the progress of the reaction was followed by the increase in pressure. Linear first order plots were obtained (Figure 1). The rate constants are compared with those of Steacie and Shaw[3] in Table 1.

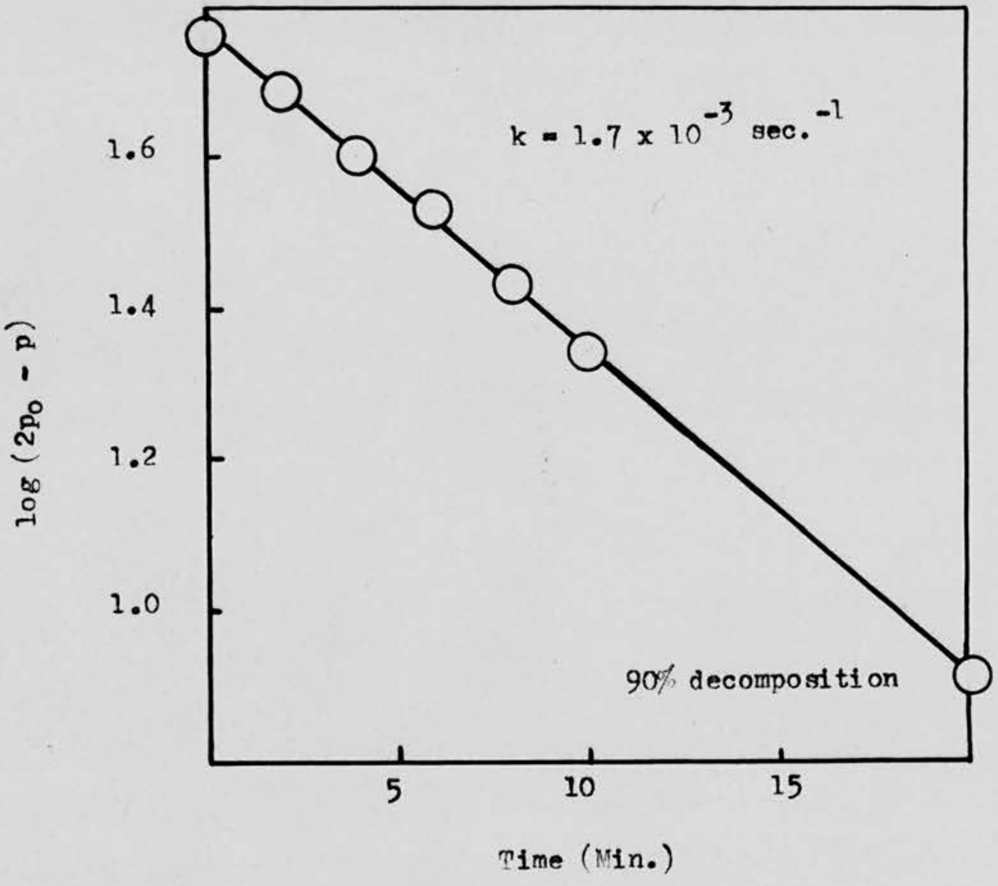


Figure 1. Pyrolysis of Methyl Nitrite at 233°C.

Table 1.

Initial Press (mm.)	Temp. (^{o}C)	k (sec.$^{-1}$) this work	k (sec.$^{-1}$) calculated from Steacie and Shaw
75	212	3.7×10^{-4}	7.1×10^{-4}
78	212	3.3×10^{-4}	7.1×10^{-4}
58	233	1.7×10^{-3}	3.5×10^{-3}

The products were analysed by gas chromatography using nitrogen as carrier gas and a thermal conductivity guage detector. After a large number of trials the column which gave the best resolution was found to be celite/diethyl phthalate/glycerol in a weight ratio of 40: 10:1. Linear calibration curves of pressure against peak height or peak area were obtained for nitric oxide, methyl nitrite and methanol. Figure 2 is a typical chromatogram of the products of the pyrolysis of methyl nitrite. The observed products were more diverse than was suggested by the simple reaction scheme. The relative sizes of the peaks were not altered by raising the temperature from 210^{o}C to 230^{o}C. However, the amount of methanol produced was greatly increased when isobutane was present (see Table 2), indicating that hydrogen abstraction from the alkane does take place although the system was too complex for quantitative study.

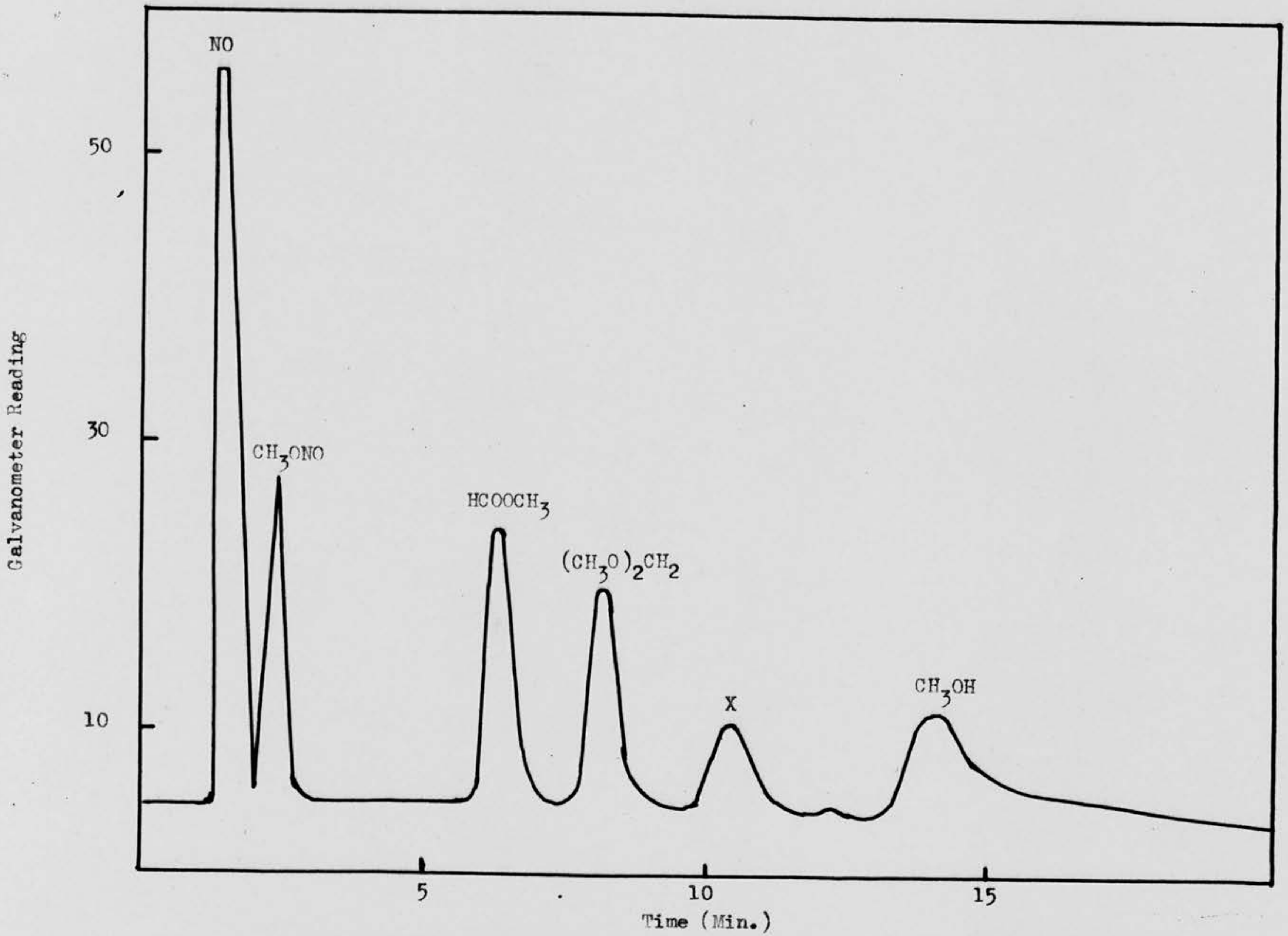


Figure 2. Gas chromatogram of products of the pyrolysis of methyl nitrite at 210°C.

Table 2.

Reactants	Temp.°C	Peak heights of products relative to $HCOOCH_3$			
		$HCOOCH_3$	$(CH_3O)_2\ CH_2$	Unidentified Product	CH_3OH
CH_3ONO	210	1	0.8	0.4	0.4
CH_3ONO	230	1	0.9	0.4	0.5
CH_3ONO/iC_4H_{10}	210	1	0.9	0.5	1.5

A second approach to the problem was made by adding iodine to the system

$$CH_3O + RH = CH_3OH + R \qquad (6)$$

$$R + I_2 = RI + I \qquad (9)$$

Thus if RH is propane, the products will be

$$CH_3 - CHI - CH_3 \text{ and } CH_3 - CH_2 - CH_2I$$

Analysis of the relative amounts of each isomer then gives the relative rates of attack on the appropriate hydrogen atoms of the original alkane.

The reactants were sealed into pyrex tubes which were immersed in a glycerol bath at 250°C for an hour. Although iodides were detected in the products, the yields were unexpectedly low. In a control experiment 10 mm. of n-propyl iodide and 0.5 g. iodine were heated for 2 hours at 260°C. Analysis gave 0.3 mm. n-propyl iodide and 1.7 mm. i-propyl iodide. That is, under the conditions of the experiment the iodides isomerised and decomposed.

In an attempt to reduce the isomerisation and decomposition the temperature was lowered and methoxyls were produced by photolysing the methyl nitrite with an unfiltered mercury vapour lamp. However when 10 mm. of i-propyl iodide and 5 g. iodine were heated at 177°C for 45 minutes, analysis gave 3 mm. i-propyl iodide and a large peak with the retention time of propylene. This system was therefore abandoned.

D. Successful Reaction Scheme. Measurement of Consumption of Reactants

The third and apparently successful method of determining the kinetics of the reaction depends on measuring the rate of consumption of reactants. If methoxyls are generated in a mixture of alkanes $R^{i}H$ and $R^{ii}H$ in the presence of nitric oxide,

$$CH_3O + R^{i}H = CH_3OH + R^{i} \qquad (i)$$

and

$$CH_3O + R^{ii}H = CH_3OH + R^{ii} \qquad (ii)$$

R^{i} and R^{ii} are removed by nitric oxide.

Now

$$\frac{-d\,R^{i}H}{dt} = k^{i}\,(CH_3O)\,(R^{i}H)$$

and

$$\frac{-d\,R^{ii}H}{dt} = k^{ii}\,(CH_3O)\,(R^{ii}H)$$

i.e. these reactions are first order with respect to RH and

$$\frac{k^{i}}{k^{ii}} = \frac{\log (R^{i}H)\text{ initial} - \log (R^{ii}H)\text{ final}}{\log (R^{ii}H)\text{ initial} - \log (R^{ii}H)\text{ final}}$$

If the initial concentrations of each alkane are measured before the experiment, and if the residual concentrations are measured by analysis then the ratio of rate constants, k^{i}/k^{ii}, is obtained.

E. The Apparatus

The apparatus was constructed from pyrex glass. Although it was essentially a unit, it is convenient to consider it as three parts: (i) the pumping and storage system, (ii) the cyclic flow system and (iii) the gas chromatographic analysis system. Each part will be described generally. The particular conditions required for each source and each pair of alkanes will be given with the results. Finally, (iv), a typical run will be described with details of the calculations involved.

(i) The pumping system consisted of a two-stage mercury diffusion pump backed by a rotary oil pump. The pressure, which was read on a McLeod guage, could be reduced to 10^{-5} mm. after 30 minutes pumping. The alkanes were stored in a two two-litre bulbs. Nitric oxide was stored in a five-litre bulb fitted with a pump-down trap. The radical source was stored in a two-litre black painted bulb, and was connected through a tap to a 10 cc. storage vessel. This was connected in turn through a capillary tap to the cyclic flow system. The two and five litre bulbs were each fitted with a manometer and trap for degassing.

(ii) The cyclic flow system (Figure 3).

(a) Summary

Suitable quantities (about 10 cc.) of each alkane were accurately measured in the gas burette and were circulated in an anticlockwise direction by an automatic Toepler pump.

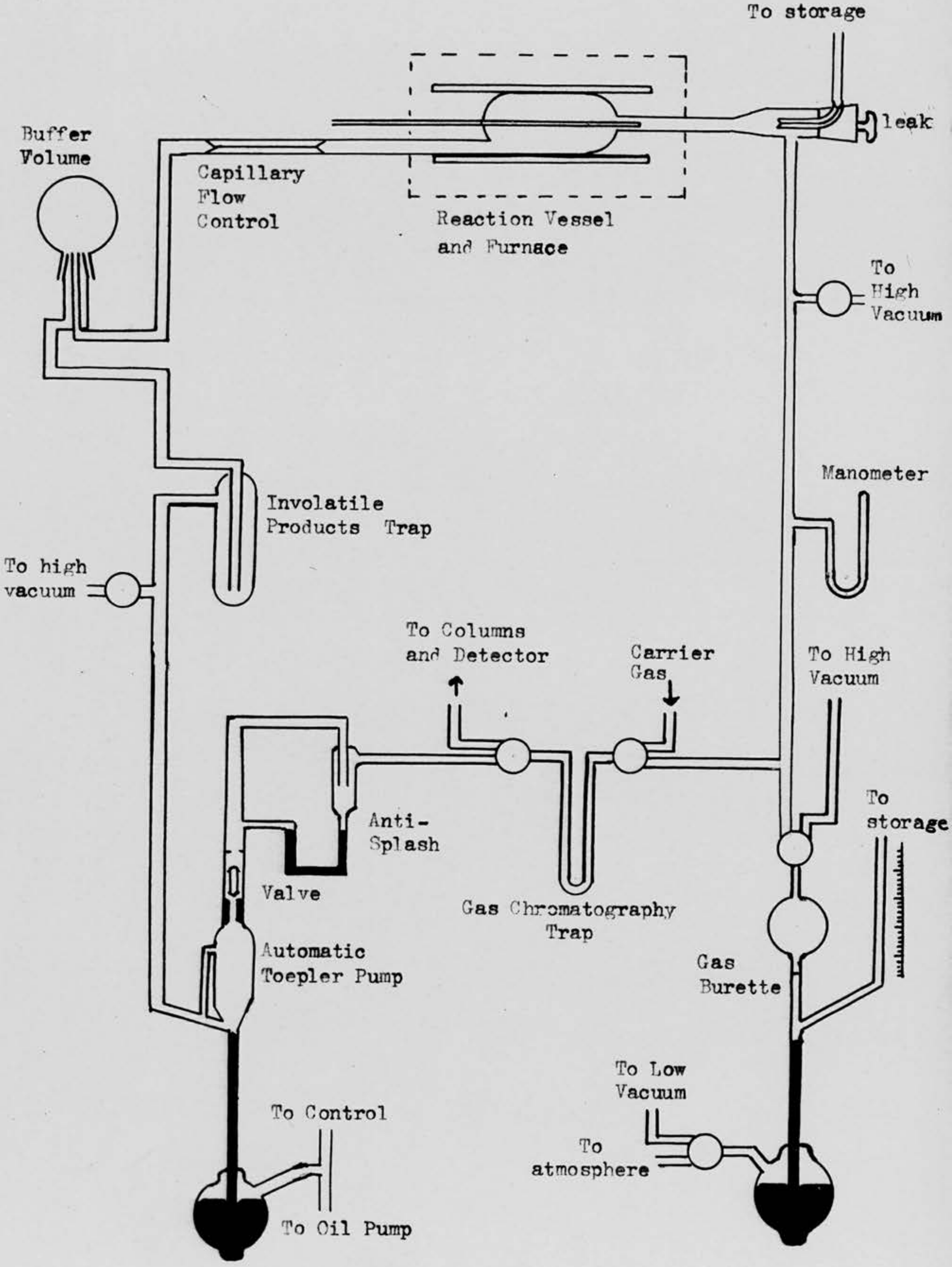


Figure 3. The Cyclic Flow System.

The radical source was bled into the stream just ahead of the reaction vessel. Between 200°C and 400°C the radical source rapidly decomposed, a proportion of the molecules forming methoxyls. Some of these methoxyls abstracted hydrogen from an alkane, yielding methanol and an alkyl radical which reacted with nitric oxide previously added. A cold trap placed after the reaction vessel reduced the concentration of the less volatile products. At the end of the run the products were condensed in a trap at -183°C. The residual hydrocarbons were then analysed by gas chromatography.

(b) The volume of the gas burette.

The gas burette was calibrated with distilled mercury. The mean of two determinations which differed by less than 0.1% was 66.04 cc. The calibration mark was level with 2.51 cm. on the scale. All volumes of gas were corrected to N.T.P.

(c) The automatic Toepler pump.

The design of this pump is shown in Figure 3 where the mercury level is at the bottom of the downstroke. The volume of the pump barrel was 45 cc. A bypass was fitted to it to prevent surging of the mercury at the end of the downstroke, when a fresh charge of gas entered the barrel. The length and period of the stroke depend on the dimensions of the control and the speed of the large capacity oil pump. In these experiments the conditions were arranged to give a length of 25 cm. and a period of 7 seconds.

(d) The reaction vessel

The volume of the reaction vessel was approximately 150 cc. The dead space necessitated by the flow system was less than 10%.

(e) The furnace

The furnace was of conventional design. An iron former, in which the reaction vessel was a close fit, was wrapped in several layers of asbestos paper and then wound with nichrome heating tape. The resistance of this heating element was 140 ohms. Electrical power was supplied by a variable transformer and 35 watts were required to heat the furnace to 250°C.

(f) The measurement of temperature

The temperature was measured by a thermocouple in conjunction with a Doran D.C. potentiometer. The thermocouple was constructed from commercial thermocouple wire which was provided with a calibration scale. The tolerance quoted was ±3°C up to 400°C. The cold junction was contained in a Dewar flask filled with water, and the hot junction in the axial well of the reaction vessel. The temperature of the latter was calculated from

$$\text{Temperature} = T - (20 - t)^{\circ}\text{C},$$

where T is the temperature corresponding to the observed e.m.f. (obtained from the calibration graph),

and t is the temperature of the cold junction.

Despite careful insulation of the furnace the temperature varied by 3°C along the reaction vessel. The hot junction was positioned to record the "average" temperature, which did not vary by more than 1°C during a run.

(iii) The gas chromatographic analysis system:

Janak method. (Figure 4).

(a) Summary

This method depends on the use of carbon dioxide as the carrier gas. When the separate components of the mixture are eluted at the end of the column, the carbon dioxide is absorbed in concentrated potassium hydroxide solution and the volume of each component estimated in a nitrometer. The Janak detector has the advantage over the thermal conductivity guage that an integrated chromatogram is obtained and no calibration is required. This technique is therefore extremely useful for rapid and accurate analysis of $C_1 - C_5$ alkanes.

(b) Carrier gas supply

Powdered Drikold was contained in a 120 cc. tube partly immersed in a mixture of Drikold/methylated spirits at -70°C. Carbon dioxide gas was evolved at a convenient rate and was dried by passage through indicator silica gel. The gas stream was then divided, part going to the injection system and part going to a series of water bubblers, where a constant head of water ensured a constant carbon dioxide pressure. This pressure was measured by a mercury manometer.

(c) The injection system

The injection system consisted of a U-tube trap containing the substance to be analysed and two-way taps which

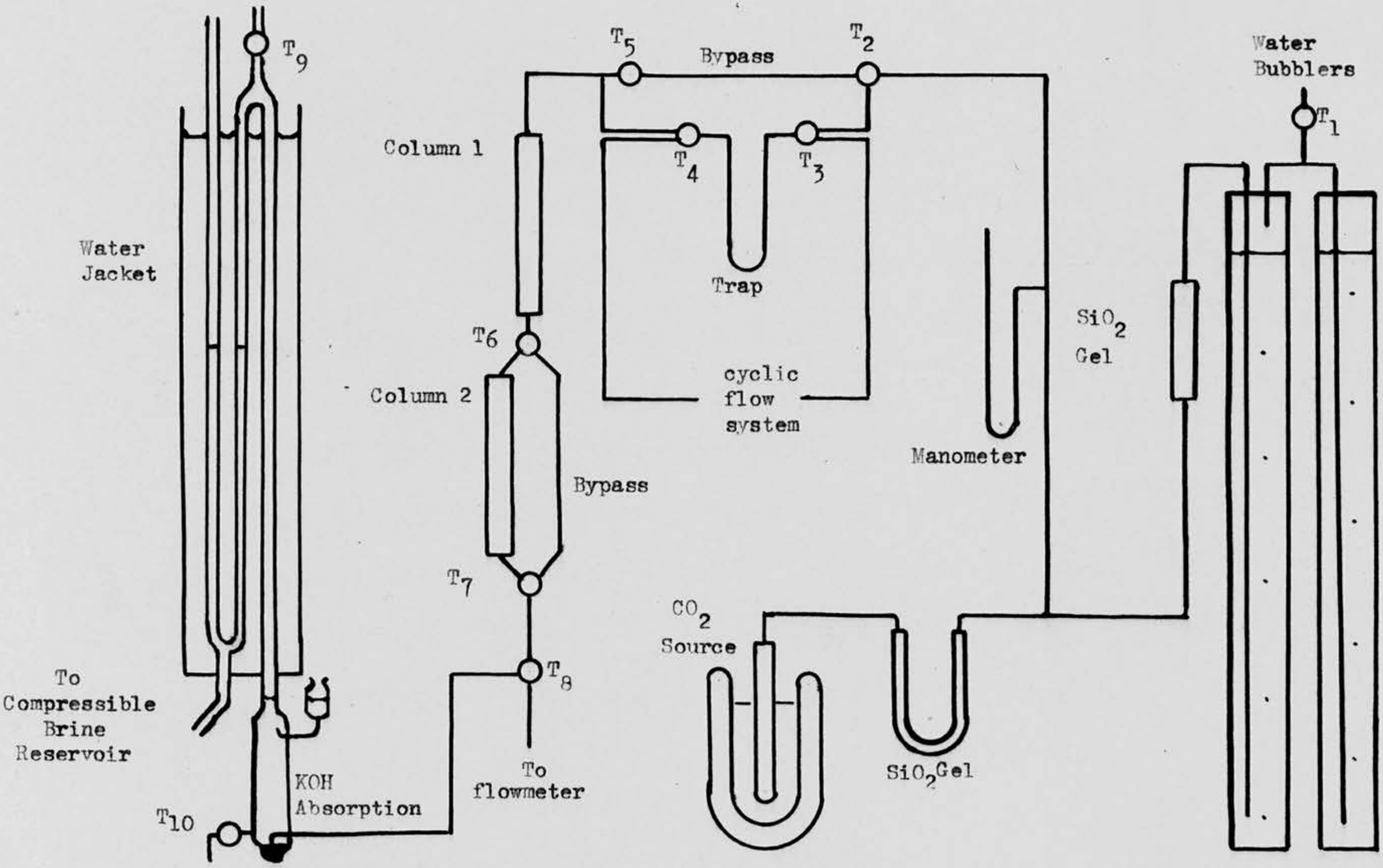


Figure 4. The Analysis System.

allowed the carrier gas either to flow through the U-tube, picking up the sample, or to bypass it completely.

(d) The columns

Two sections of column were connected in series. Each could be heated or cooled. The second section was fitted with a bypass. This was extremely useful when it was required to separate two substances which had widely different retention times. For example, consider a mixture of A and B, where A has a short retention time and B a long retention time. The mixture is injected into the gas stream with the columns connected in series. A travels quicker and is on column 2 while B is still on column 1. Column 2 is now bypassed and B is eluted from column 1. After the analysis of B is complete, carrier gas is once more admitted to column 2, and A is eluted and determined. The time for the complete analysis is thus greatly reduced.

(e) The detector

The detector consisted of an absorption vessel connected to a 10 cc. gas burette. The absorption vessel contained 50% potassium hydroxide to fill the wide portion and a few millimetres of the narrow neck of the absorption vessel. Most of the subsequent expansion of this solution then occurred in the wide bore filler tube. The liquid in the gas burette was saturated brine with a few drops of fluorescein solution to give a sharp meniscus. The level of the liquid in the gas burette was controlled by a compressible rubber reservoir.

As the separated components were eluted from the column the carbon dioxide gas was absorbed by the potassium hydroxide and each component collected and estimated in the gas burette. In practice a small but constant increase in volume was observed when carbon dioxide was being absorbed. This was attributed to the expansion of the absorbing solution due to the formation of potassium carbonate. An allowance was always made for this drift. The quantities of each component were recorded as volumes corrected to N.T.P.

(iv) A typical run; No. 183, Propane/Neopentane/Dimethyl peroxide

The alkanes, nitric oxide and dimethyl peroxide were degassed. Carbon dioxide was allowed to flow through the analysis system. Atmospheric pressure was noted. A trap containing a salt/ice mixture at about -10°C was placed round the involatile products trap. A quantity of dimethyl peroxide corresponding to 3 cm. pressure in the two-litre bulb was condensed in the 10 cc. storage vessel and maintained at 0°C. The cyclic flow system (figure 3) was evacuated and then closed off from the vacuum line. Using the mercury in the gas burette as a manometer, approximately 10 cm. of propane was admitted to the gas burette. The mercury was then raised to the calibration mark, and, with the graduated limb evacuated, the pressure and temperature were noted. The two-way tap was opened and the propane was condensed in the U-shaped gas chromatography trap. The same procedure was repeated for neopentane and nitric oxide, noting the pressure and temperature readings in each case.

The automatic Toepler pump was started and the condensed alkanes and nitric oxide warmed up. The gases were circulated for several minutes to ensure complete mixing. The total pressure of the system, the time and the thermocouple readings were noted. The capillary tap was opened for half an hour, then closed. After a further half hour's circulation to remove most of the remaining peroxide, the gas chromatography trap was immersed in a Dewar of liquid oxygen at -183°C. After ten minutes the pressure on the manometer was constant indicating that the residual alkanes had condensed. As a precaution, pumping was continued for an additional half hour then the Toepler pump was stopped. The two-way taps (T_1 and T_2 in figure 4) of the gas chromatography trap were closed and the contents of the trap allowed to warm up. The column and gas burette temperatures were noted. Tap 1 was opened so that one bubbler was in use. The flow rate was noted. Tap 5 was closed and taps 2, 3, 4 and 8 arranged so that carbon dioxide flowed through the trap on to the column and out to the atmosphere via the flowmeter. The stop watch was started. In this analysis columns 1 and 2 were both activated alumina poisoned with 1% squalane.

After seven minutes, all the nitric oxide had been eluted and tap 8 was turned so that the gas flow entered the Janak detector. In the gas burette (nitrometer), the level of the liquid was between 0 and 0.1 cc. Tap 9 was closed and burette readings taken at convenient time intervals. After all the propane had been eluted (17 minutes), tap 1was closed so that the pressure head, and therefore the flow rate, increased. At 29 minutes tap 9 was opened, the level brought up to between 0 and 0.1 cc., tap 9 closed again and readings taken. After 52 minutes, all the neopentane had been eluted and taps 1, 2, 3, 4, 5, 8 and 9 were returned to the position they occupied before the run. The cyclic flow system was evacuated ready for the next experiment. The liquid levels in the nitrometer were returned to their upper limit to keep the glass wetted.

The readings and calculations are shown below.

Run 183

	C_3H_8	C_5H_{12}	NO
Temperature ($^{\circ}$C)	23	23	23
Pressure reading (cm.)	12.55	13.40	1.7
Zero (cm.)	2.51	2.51	2.5
	10.04	10.89	14.5
Volume at N.T.P. (cc.)	$\frac{10.04 \times 237.2}{296}$	$\frac{10.89 \times 237.2}{296}$	$\frac{14.5 \times 237.2}{296}$
	= 8.044	= 8.728	= 12

(Volume of gas burette = 66.04 cc. $\therefore \frac{66.04 \times 273}{76} = 237.2$)

Thermocouple Reading = 9.23 mv. = 245°C

Cold junction temperature = 19°C

$\therefore$ Furnace temperature = 245 - (20-19)$^{\circ}$C

= 244°C

Manometer Reading (cm.)	Time (mins.)	Operation
5.7	0	Capillary tap opened
6.9	35	Capillary tap closed
6.5	65	G.C. trap cooled to -183°C
3.5	100	Pump stopped. Analysis

Analysis 281. Column Temperature 23°C. Burette Temperature 23°C.

Atmospheric Pressure 74 cm. Flow rate (i) 30 cc./min.
(ii) 42 cc./min.

Time (mins.)	Burette Reading (cc.)	T	B.R.	T	B.R.	T	B.R.
5		10	2.78	20	3.18	40	4.5
.30		11	2.83	22	3.30	42	5.6
6		12	2.85	24	3.36	44	6.26
.30		13	2.86	26	3.44	46	6.52
7	0.04	14	2.87	28	3.48	48	6.60
.30	0.05	15		30	0.51	50	6.66
8	0.055	16		32	0.53	52	6.68
.30	0.15	17≠		34	0.57	54	
9	1.4	18		36	0.61	56	
.30	2.4	19		38	2.6	58	

≠ Flow rate increased.

Component	Elution time (mins.)
NO	2 - 5
C_3H_8	7 - 12
C_5H_{12}	30 - 50

The "drift rate" was 0.01 cc./min.

	C_3H_8	C_5H_{12}
Found (cc.)	$2.85-0.04-(5 \times 0.01)$ $= 2.76$	$6.66-0.51-(20 \times 0.01)$ $= 5.95$
Volume at N.T.P. (cc.)	$\frac{2.76 \times 74 \times 3.592}{296}$ $= 2.478$	$\frac{5.95 \times 74 \times 3.592}{296}$ $= 5.343$

$$3.592 = \frac{273}{76}$$

i.e.

Alkane	Volume at N.T.P. (cc.)
C_3H_8 initial	8.044
C_5H_{12} initial	8.728
C_3H_8 final	2.478
C_5H_{12} final	5.343

Now $$\frac{k_1}{k_2} = \frac{\log(R_1H \text{ initial}) - \log(R_1H \text{ final})}{\log(R_2H \text{ initial}) - \log(R_2H \text{ final})}$$

$$\therefore \quad \frac{k_{\text{propane}}}{k_{\text{neopentane}}} = \frac{0.9055 - 0.3942}{0.9409 - 0.7278}$$

$$= \frac{0.5113}{0.2131}$$

$$= 2.408; \text{ at } 244^{\circ}\text{C.}$$

From time to time, blank runs were performed to ensure that the quantities of alkanes measured out initially were equal to the amounts recovered by analysis. Within the limits of experimental error this was found to be so. For example for ethane and propane.

Alkane	Initial Volume (cc.)	Final Volume (cc.)	% Recovery
C_2H_6	7.381	7.355	99.65
C_3H_8	7.157	7.173	100.2

F. Results and Experimental Details

(i) Summary

The relative rate constants were calculated from

$$\frac{k_1}{k_2} = \frac{\log (R_1H) \text{ initial} - \log (R_1H) \text{ final}}{\log (R_2H) \text{ initial} - \log (R_2H) \text{ final}} .$$

for five pairs of alkanes, propane/ethane, propane/n-butane, propane/i-butane, propane/neopentane, propane/cyclopropane, and two radical sources, methyl nitrite and dimethyl peroxide. The results obtained using the two sources are in reasonable agreement. Some exploratory experiments were performed with methyl t-butyl peroxide, but this source had to be abandoned due to the formation of products which interfered with the alkane analysis. Values of k_1/k_2 were independant of nitric oxide concentration and did not alter when the ratio of the initial alkane concentrations was varied between 1:2 and 2:1.

The logarithms of the relative rate constants were plotted against the reciprocal of the corresponding absolute temperatures. The difference in activation energies and difference in the logarithms of the A factors were obtained from the slope and intercept of the line respectively.

$$k = A \exp(-E/RT)$$

$$\log k = \log A - E/2.303\ RT$$

$$\therefore \log k_1/k_2 = (\log A_1 - \log A_2) - (E_1 - E_2)/2.303\ RT.$$

The best straight line was found by the method of Least Squares. In the work with methyl nitrite, large quantities of nitric oxide were produced. This interfered with the analysis and impaired the reproducibility of the relative rate constants. The 50% probability limits were therefore calculated for the methyl nitrite results.

The results are summarised in Tables 3 and 4 in terms of the Arrhenius parameters and rate constant for propane. Units:- Log A is in log $mole^{-1} cc. sec.^{-1}$ and E is in cal/mole.

Table 3.

Arrhenius Parameters and Rate Constants Relative to Propane, Using Methyl Nitrite as source of methoxyls between 300°C and 400°C.

Hydrocarbon	Runs	Log A	E	k at 350°C
Propane	-	0		1.00
Ethane	18	+0.08±0.23	+1200±700	0.46
n-butane	5	-0.96±0.61	-3000±1700	1.21
i-butane	18	-0.38±0.17	-1300±500	1.24
neo-pentane	9	-1.77±0.15	-4700±400	0.77
cyclo-propane	7	-0.63±0.25	-1100±700	0.59

Table 4.

Arrhenius Parameters and Rate Constants Relative to Propane, Using Dimethyl Peroxide as Source of Methoxyls Between 200°C and 300°C.

Hydrocarbon	Runs	Log A	E	k at 250°C
Propane	-	0	0	1.00
Ethane	7	+0.24	+1830	0.30
n-butane	7	-0.75	-2300	1.61
i-butane	12	-0.27	-1110	1.56
neo-pentane	9	+0.55	+2130	0.46
cyclo-pentane	2	-	-	0.17 at 297°C

(ii) Experiments using methyl nitrite as source of methoxyl

(a) Ethane/propane

Methoxyls were generated in mixtures of ethane and propane in the cyclic flow system for 1 to 3 hours. Large quantities of nitric oxide were produced. This made the analysis very difficult. Ethane and propane were separated from nitric oxide and other products using a very long column of activated alumina (mesh, 25-52; weight, 80 g. ; length, 300 cm.). The temperature was maintained at $+13^\circ$C by a cold water bath. The initial flow rate was 35 cc./min. (One bubbler). Nitric oxide was vented to the atmosphere for 9 minutes. The retention time of ethane was 11 minutes. After all the ethane had been eluted (20 minutes), the flow rate was increased to 50 cc./min. (two bubblers). Consequently, the propane was speeded up, and its retention time was reduced to 33 minutes. The analysis was completed in 40 minutes.

The results are shown in Table 5, and from the Arrhenius plot (Figure 5),

$$\log A_{\text{ethane}} - \log A_{\text{propane}} = 0.08 \pm 0.23 \text{ log mole}^{-1}\text{cc. sec.}^{-1}$$

$$E_{\text{ethane}} - E_{\text{propane}} = 1200 \pm 700 \text{ cal./mole}$$

and $$k_{\text{ethane}}/k_{\text{propane}} = 0.46 \text{ at } 350^\circ\text{C} .$$

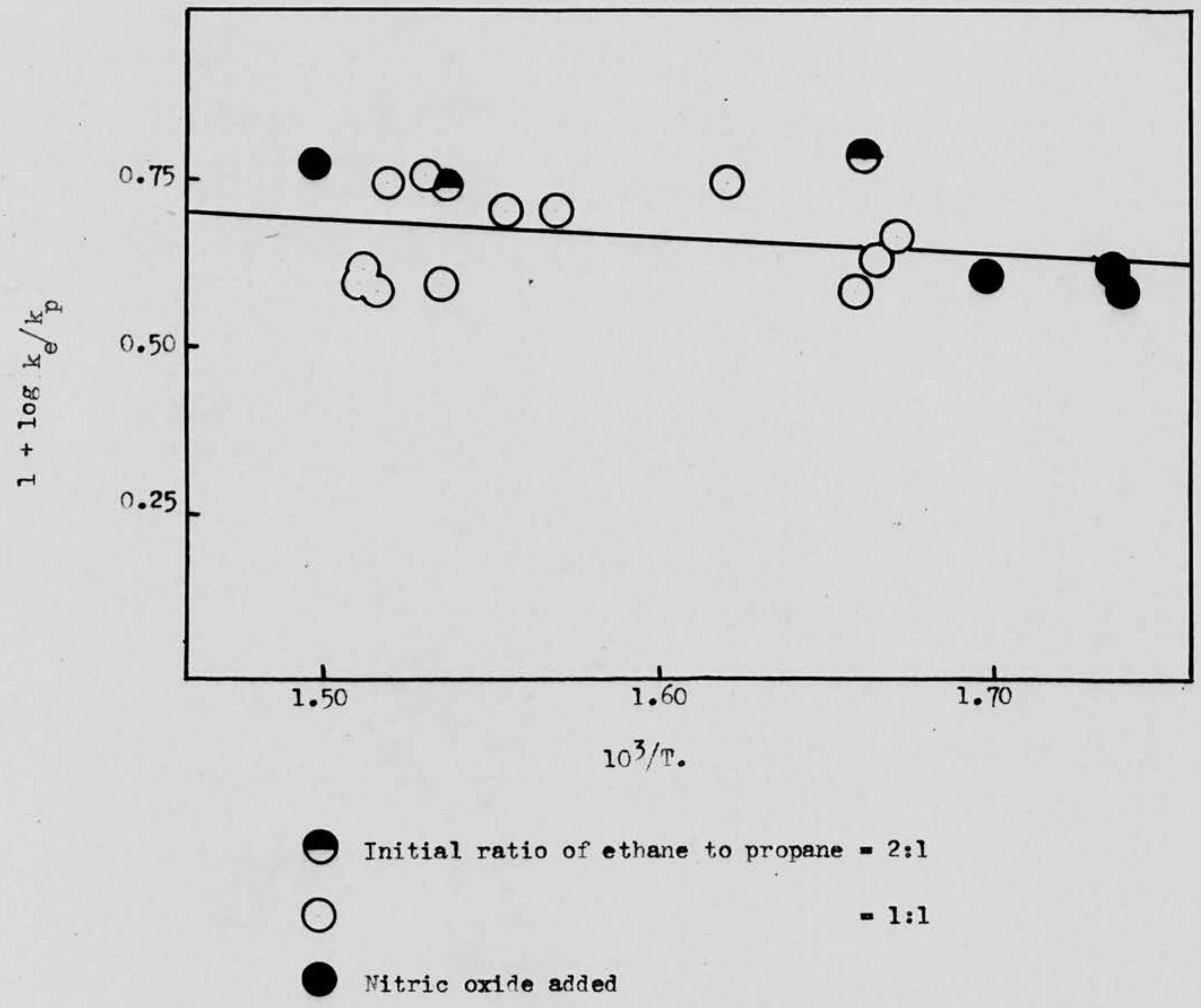


Figure 5. ETHANE/PROPANE.

Table 5.

Ethane/Propane

Run	Temp. °A	C_3H_8(cc.) initial	C_2H_6(cc.) initial	C_3H_8(cc.) final	C_2H_6(cc.) final	NO (cc.) initial	k_e/k_p
5	575	4.617	4.520	4.353	4.419	12	0.384
3	576	4.644	4.722	4.077	4.463	12.5	0.429
1	589	4.883	4.949	4.020	4.594	9	0.382
34	598	8.048	8.385	6.101	7.375	0	0.463
28	600	8.307	8.604	6.949	7.977	0	0.425
29	602	8.853	8.401	7.398	7.820	0	0.380
30	603	3.397	8.132	3.091	7.683	0	0.604
37	616	7.311	8.424	5.484	7.190	0	0.552
36	637	8.226	9.294	6.440	8.230	0	0.496
35	643	8.275	8.459	5.883	7.125	0	0.503
26	650	3.234	7.916	2.588	6.995	0	0.554
24	651	8.477	8.347	6.970	7.732	0	0.390
15	653	8.044	8.470	5.082	6.563	0	0.555
22	658	7.690	8.429	4.596	6.965	0	0.550
25	659	8.299	8.461	6.504	7.794	0	0.377
19	661	8.476	8.428	6.392	7.515	0	0.406
16	662	8.496	8.224	6.042	7.193	0	0.393
20	667	8.489	8.521	6.995	7.498	3	0.585

(b) Propane/n-butane

Methoxyls were generated in mixtures of propane and n-butane for about an hour. In the subsequent analysis, the alkanes were separated from each other and from the products of the reaction by using split columns. This technique has been described generally in the previous section. In this particular case, columns 1 and 2 were both activated alumina (Mesh, 25-52; weight 20 g. ; length, 75 cm.). The columns were maintained at room temperature and the flow rate was initially 35 cc./min. The nitric oxide was vented to the atmosphere for 10 minutes, then column 2 was bypassed. The flow rate increased to 60 cc./min., and in a further 20 minutes all the n-butane was eluted. Column 2 was reconnected and the propane was eluted in 8 minutes. The analysis was completed in 40 minutes.

The results are shown in Table 6, and from the Arrhenius plot (Figure 6),

$$\log A_{\text{propane}} - \log A_{\underline{n}\text{-butane}} = 0.96 \pm 61 \text{ log mole}^{-1}\text{cc. sec.}^{-1}$$

$$E_{\text{propane}} - E_{\underline{n}\text{-butane}} = 3000 \pm 1700 \text{ cal./mole}$$

and $k_{\text{propane}}/k_{\underline{n}\text{-butane}} = 0.83$ at 350°C.

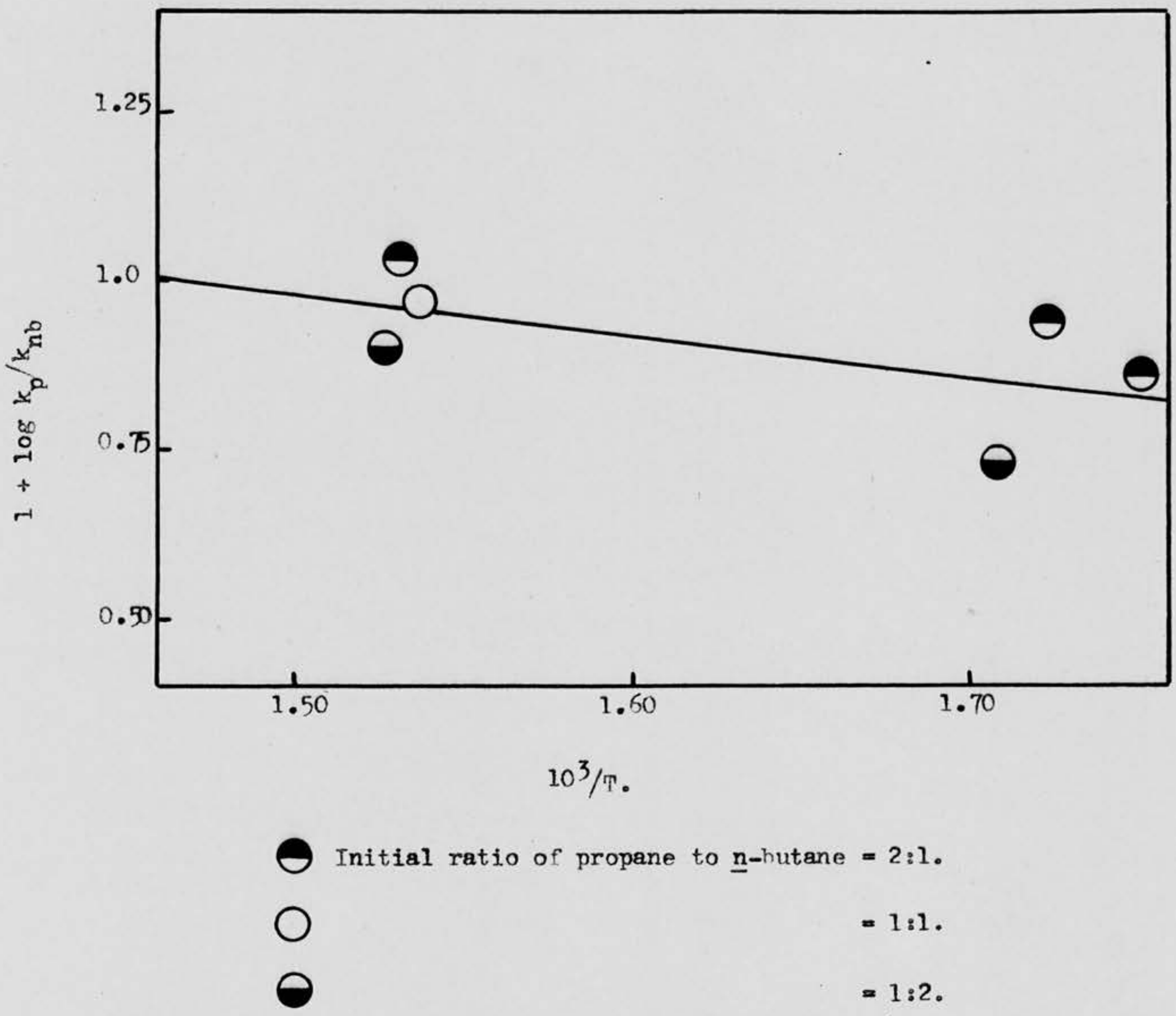


Figure 6. PROPANE/n-BUTANE.

Table 6.

Propane/n-butane

Run	Temp. °A	C_3H_8(cc.) initial	C_4H_{10}(cc.) initial	C_3H_8(cc.) final	C_4H_{10}(cc.) final	k_p/k_{nb}
92	571	7.982	3.970	6.972	3.297	0.725
94	580	8.299	4.066	6.834	3.263	0.882
95	585	4.488	7.485	3.878	5.705	0.537
89	650	7.969	8.549	5.663	5.947	0.940
90	653	8.266	4.732	6.569	3.870	1.148
91	655	4.685	7.188	3.715	5.370	0.796

(c) Propane/i-butane

Methoxyls were generated in mixtures of propane and i-butane for between 2 and 3 hours. In the subsequent analysis, the alkanes were separated from each other and from the products of the reaction by a single column of poisoned alumina (mesh, 25-52; weight, 80 g. ; length, 300 cm.). The columns were maintained at room temperature, and the flow rate was 60 cc./min. Nitric oxide was vented to atmosphere for 10 minutes. The retention time of propane and i-butane were 13 and 30 minutes respectively. The analysis was completed in 40 minutes. Runs in the absence of i-butane showed that a minor unidentified product was eluted with the same retention time as i-butane. A small correction, amounting to 0.12 cc. per 100 cc. of pyrolysed methyl nitrite, was made to the estimation of i-butane.

The results are shown in Table 7, and from the Arrhenius plot (figure 7),

$$\log A_{\text{propane}} - \log A_{\underline{\text{i}}\text{-butane}} = 0.38 \pm 0.17 \text{ log mole}^{-1}\text{cc. sec.}^{-1}$$

$$E_{\text{propane}} - E_{\underline{\text{i}}\text{-butane}} = 1300 \pm 500 \text{ cal./mole}$$

and $$k_{\text{propane}}/k_{\underline{\text{i}}\text{-butane}} = 0.81 \text{ at } 350^{\circ}\text{C}.$$

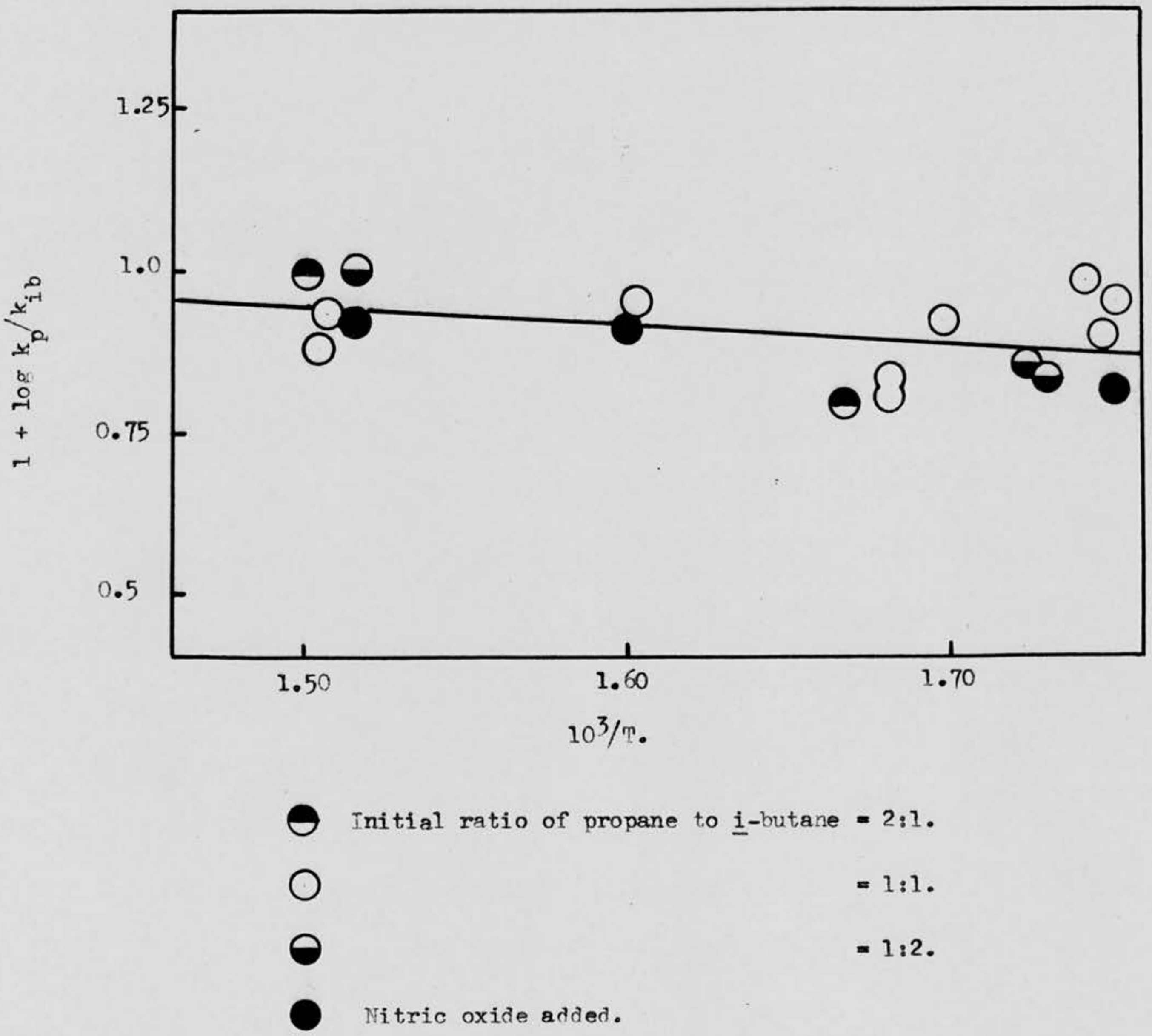


Figure 7. PROPANE/i-BUTANE.

Table 7.

Propane/i-butane

Run	Temp. °A	C_3H_8(cc.) initial	C_4H_{10}(cc.) initial	C_3H_8(cc.) final	C_4H_{10}(cc.) final	NO (cc.) initial	k_pk_{ib}
64	571	7.345	7.168	6.325	6.060	0	0.890
70	571	4.850	8.245	4.235	6.662	7	0.636
63	572	7.330	7.743	6.331	6.340	7	0.791
65	574	7.474	7.532	6.279	6.256	0	0.955
66	578	4.746	7.532	4.106	6.095	0	0.684
67	580	4.448	7.785	3.915	6.498	0	0.705
72	589	8.786	8.584	7.769	7.403	0	0.831
46	595	7.224	8.106	6.661	7.147	0	0.631
47	595	8.933	8.366	8.215	7.379	0	0.668
52	599	7.369	4.737	6.805	4.164	0	0.618
62	624	7.330	7.743	6.117	6.340	0	0.904
38	625	8.254	7.807	7.129	6.518	0	0.815
39	625	7.899	8.206	6.885	6.937	8	0.811
41	659	4.407	6.797	3.939	6.087	0	1.010
44	661	8.672	8.060	7.521	6.797	8	0.835
43	663	7.925	7.949	6.719	6.554	0	0.851
40	664	8.119	8.002	7.055	6.630	0	0.747
42	666	8.012	4.403	6.673	3.741	0	0.968

(d) Propane/neopentane

Methoxyls were generated in mixtures of propane and neopentane for about 2 hours. In the subsequent analysis, the alkanes were separated from each other and from the products of the reaction by using split columns. Columns 1 and 2 were both poisoned alumina (mesh, 25-52; weight 20 g. ; length, 75 cm.). The columns were maintained at room temperature and the flow rate was initially 35 cc./min. Nitric oxide was vented to atmosphere for 9 minutes then column 2 was bypassed. The flow rate increased to 60 cc./min. and in a further 10 minutes all the neopentane was eluted. Column 2 was reconnected and the propane was eluted in 8 minutes. The analysis was completed in 25 minutes.

The results are shown in Table 8, and from the Arrhenius plot (Figure 8).

$$\text{Log } A_{\text{propane}} - \log A_{\text{neopentane}} = 1.77 \pm 0.15 \text{ log mole}^{-1}\text{cc. sec.}^{-1}$$

$$E_{\text{propane}} - E_{\text{neopentane}} = 4700 \pm 400 \text{ cal./mole}$$

$$\text{and } k_{\text{propane}} - k_{\text{neopentane}} = 1.30 \text{ at } 350^{\circ}\text{C.}$$

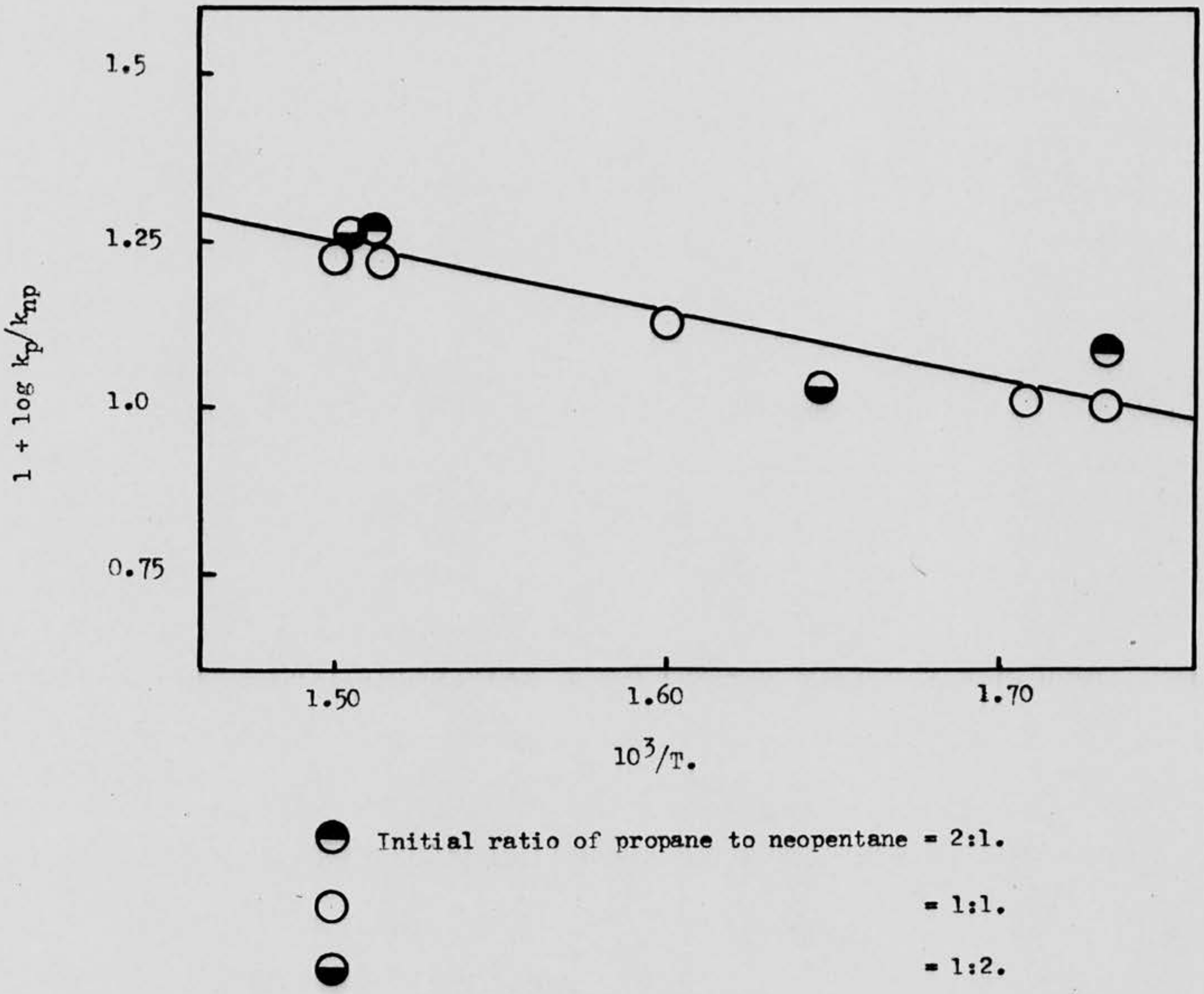


Figure 8. PROPANE/NEOPENTANE.

Table 8.

Propane/Neopentane

Run	Temp. °A	C_3H_8(cc.) initial	C_5H_{12}(cc.) initial	C_3H_8(cc.) final	C_5H_{12}(cc.) final	k_p/k_{np}
101	577	8.622	8.712	7.584	7.676	1.014
102	577	8.256	4.468	6.984	3.871	1.167
100	585	8.486	8.923	7.196	7.602	1.029
104	607	4.795	8.102	4.039	6.908	1.073
105	625	8.418	4.269	6.705	3.600	1.338
97	660	8.818	8.730	6.416	7.263	1.658
98	662	8.264	4.459	6.939	4.055	1.842
99	664	5.006	8.841	3.899	7.696	1.803
103	666	8.886	8.264	6.778	7.031	1.676

(e) Propane/*cyclo*-propane

Methoxyls were generated in mixtures of propane and cyclopropane for 1 to 2 hours. In the subsequent analysis, the alkanes were separated from each other and from the products of the reaction by using split columns. Column 1 and 2 were both activated alumina (mesh, 25-52; weight, 20 g. ; length, 75 cm.). The columns were maintained at room temperature and the flow rate was initially 35 cc./min. Nitric oxide was vented to atmosphere for 11 minutes, then column 2 was bypassed. The flow rate increased to 60 cc./min., and in a further 14 minutes all the cyclopropane was eluted. Column 2 was reconnected and the propane was eluted in 10 minutes. The analysis was completed in 40 minutes.

The results are shown in Table 9 and from the Arrhenius plot (Figure 9).

$\text{Log } A_{\text{propane}} - \log A_{\text{cyclopropane}} = 0.63 \pm 0.25 \text{ log mole}^{-1}\text{cc. sec.}^{-1}$

$E_{\text{propane}} - E_{\text{cyclopropane}} = 1100 \pm 700 \text{ cal./mole}$

and $k_{\text{propane}}/k_{\text{cyclopropane}} = 1.70$ at 350°C.

Table 9.

Propane/Cyclopropane

Run	Temp. °A	C_3H_8(cc.) initial	C_3H_6(cc.) initial	C_3H_8(cc.) final	C_3H_8(cc.) final	k_p/k_{cp}
76	594	8.175	8.065	5.659	6.290	1.490
77	599	7.903	3.478	5.355	2.804	1.807
80	601	5.035	8.730	3.339	6.519	1.407
87	643	7.645	4.389	4.977	3.477	1.835
88	655	4.912	8.288	3.262	6.665	2.015
75	662	8.318	7.936	5.601	6.290	1.701
74	665	8.770	8.457	5.720	6.513	1.627

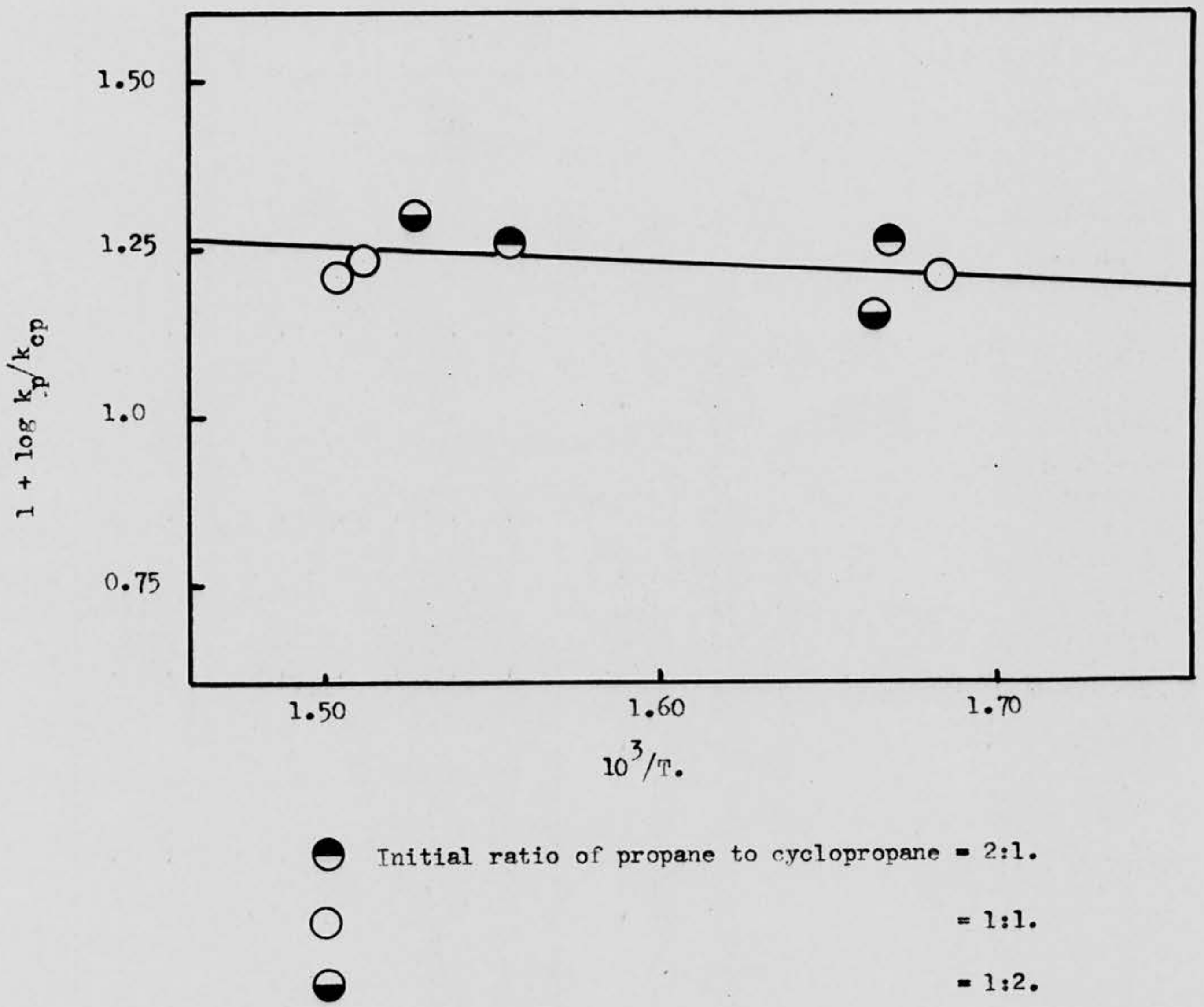


Figure 9. PROPANE/CYCLOPROPANE.

(iii) Experiments using dimethyl peroxide as radical source

(a) Ethane/propane

Methoxyls were generated in mixtures of ethane, propane and nitric oxide in the cyclic flow system for 20 minutes. In the subsequent analysis, ethane, propane and nitric oxide were separated from each other and from the products of the reaction by split columns. Column 1 was poisoned alumina (Mesh, 25-32; weight, 40 g. ; length, 150 cm.), and was maintained at room temperature. Column 2 was activated charcoal (mesh 25-32; weight, 5 g. ; length, 20 cm.), and was maintained at 78°C. The flow rate was initially 20 cc./min. Nitric oxide was vented for 13 minutes, then column 2 was bypassed. The flow rate increased to 35 cc./min., and between 22 minutes and 34 minutes all the propane was eluted. The charcoal column was reconnected and the ethane was eluted in 17 minutes. The analysis was completed in 52 minutes.

The results are shown in Table 10, and from the Arrhenius plot (Figure 10).

$$\text{Log } A_{\text{propane}} - \log A_{\text{ethane}} = -0.239 \log \text{mole}^{-1} \text{cc. sec.}^{-1}$$

$$E_{\text{propane}} - E_{\text{ethane}} = -1830 \text{ cal./mole}$$

$$k_{\text{propane}}/k_{\text{ethane}} = 3.367 \text{ at } 250^{\circ}\text{C.}$$

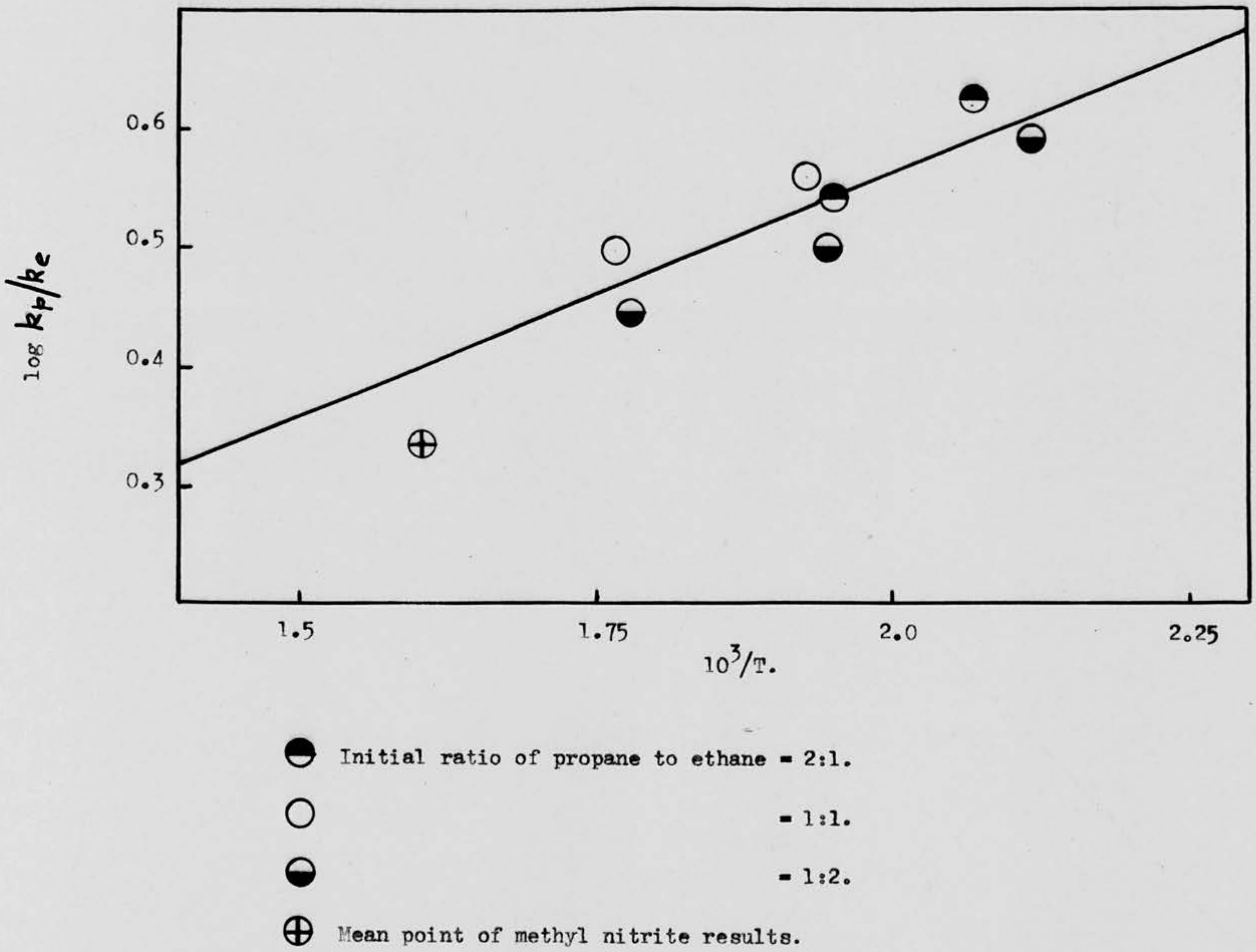


Figure 10. PROPANE/ETHANE

Table 10.

Propane/Ethane

Run	Temp. °A	C_3H_8(cc.) initial	C_2H_6(cc.) initial	C_3H_8(cc.) final	C_2H_6(cc.) final	NO (cc.) final	$k_p k_e$
235	472	3.972	8.337	1.144	6.060	14	3.904
234	483	8.153	3.904	4.922	3.463	14	4.198
230	513	7.964	6.524	4.933	4.026	14	3.461
231	514	3.915	8.128	2.036	6.624	14	3.159
232	518	7.650	8.121	3.769	6.683	14	3.631
238	563	3.904	7.891	2.435	6.667	14	2.790
239	566	7.898	8.183	5.380	7.244	14	3.151

(b) Propane/<u>n</u>-butane

Methoxyls were generated in mixtures of propane, <u>n</u>-butane and nitric oxide in the cyclic flow system for about 25 minutes. In the subsequent analysis, propane, <u>n</u>-butane and nitric oxide were separated from each other and from the products of the reaction by a column of poisoned alumina (mesh, 25-52; weight, 20 g. ; length, 75 cm.). The column was maintained at room temperature and the flow rate was 45 cc./min. Nitric oxide was vented for 5 minutes. The retention times of propane and <u>n</u>-butane were 8 minutes and 27 minutes respectively. The analysis was completed in 35 minutes.

The results are shown in Table 11 and from the Arrhenius plot (Figure 11).

$\text{Log } A_{\text{propane}} - \log \underline{n}\text{-butane} = 0.751 \log \text{mole}^{-1} \text{cc. sec.}^{-1}$

$E_{\text{propane}} - E_{\underline{n}\text{-butane}} = 2300 \text{ cal./mole}$

$k_{\text{propane}} / k_{\underline{n}\text{-butane}} = 0.623 \text{ at } 250^{\circ}\text{C}$.

Table 11.

Propane/n-butane

Run	Temp. °A	C_3H_8(cc.) initial	C_4H_{10}(cc.) initial	C_3H_8(cc.) final	C_4H_{10}(cc.) final	NO (cc.) initial	$k_p k_{nb}$
171	466	8.193	3.988	5.205	1.430	12.5	0.442
170	469	3.664	8.021	1.781	2.073	12.5	0.515
169	513	3.662	8.237	1.714	2.282	14	0.583
168	513	7.859	3.028	2.980	0.635	14	0.621
166	518	7.964	7.964	4.024	2.496	14	0.588
158	562	4.190	8.385	2.268	3.770	14	0.769
155	562	8.034	4.378	3.618	1.356	14	0.680

(c) Propane/i-butane

Methoxyls were generated in mixtures of propane, i-butane and nitric oxide for about 30 minutes. In the subsequent analysis propane, i-butane and nitric oxide were separated from each other and from the products of the reaction by using split

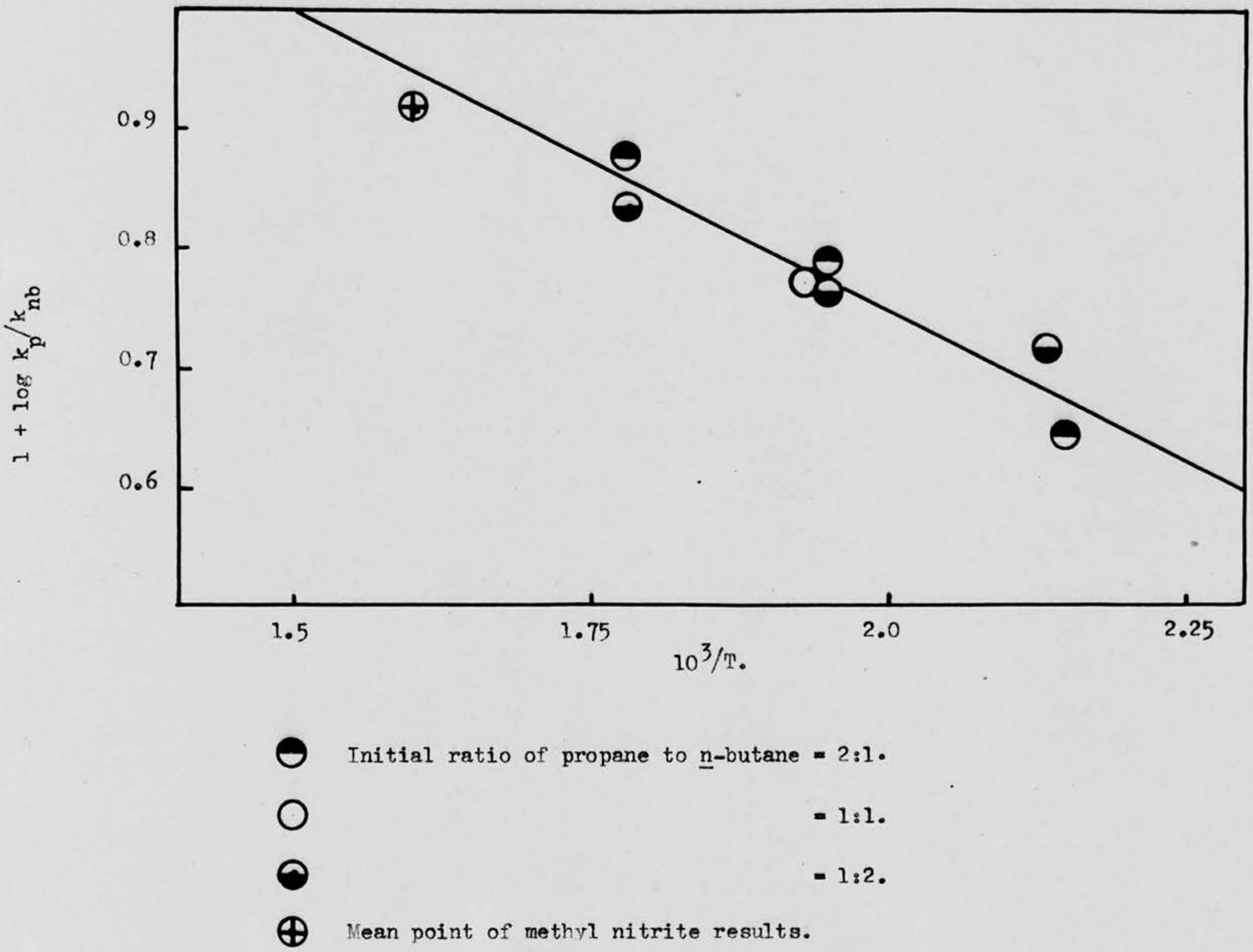


Figure 11. PROPANE/n-BUTANE

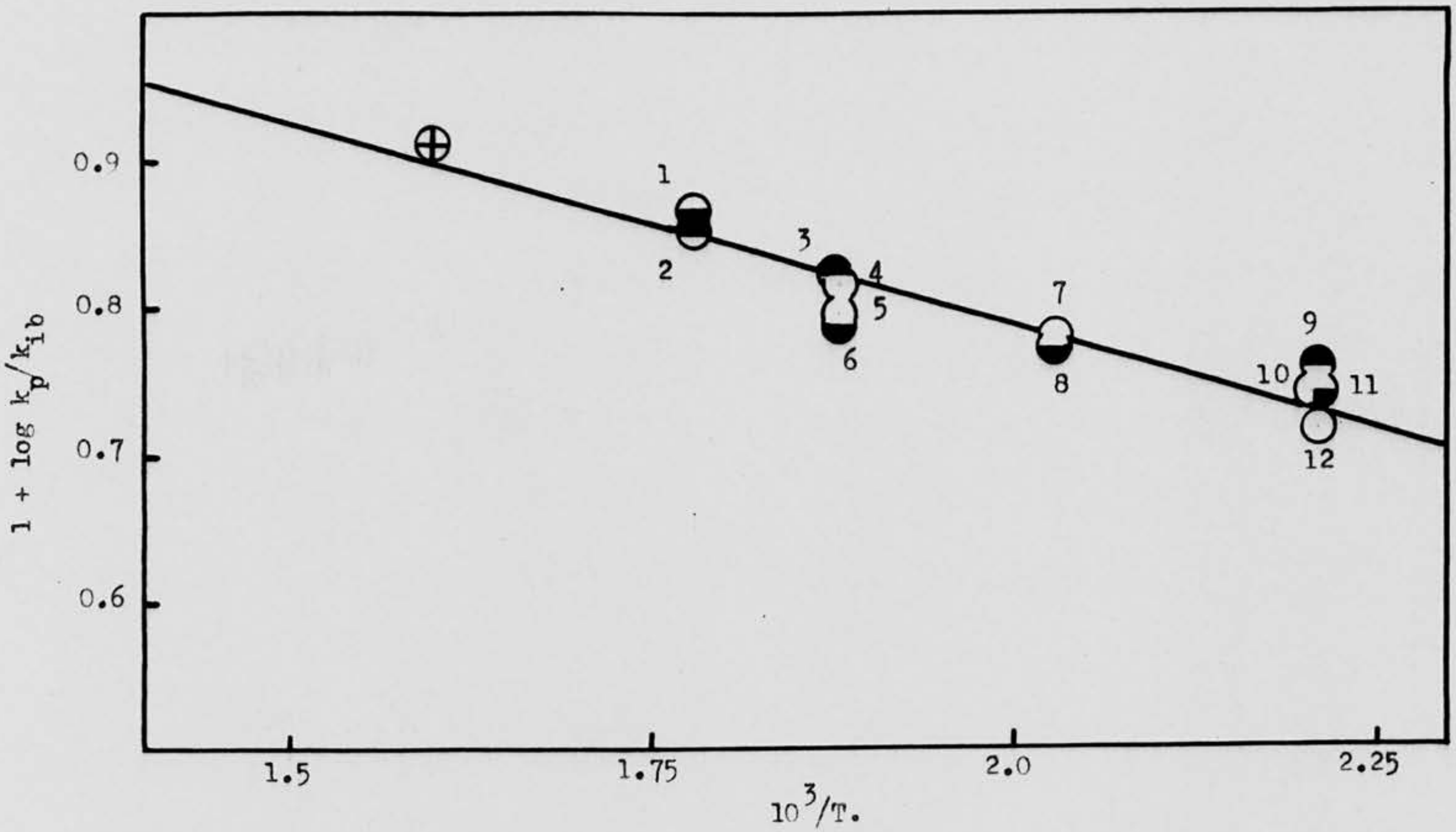
columns. Column 1 and 2 were both poisoned alumina (mesh 25-52; weight, 20 g. ; length, 75 cm.). The columns were maintained at room temperature and the flow rate was initially 30 cc./min. Nitric oxide was vented to atmosphere for 11 minutes then column 2 was bypassed. The flow rate increased to 42 cc./min., and in a further ten minutes all the i-butane was eluted. Column 2 was reconnected and the propane was eluted in 10 minutes. The analysis was completed in 35 minutes.

The results are shown in Table 12, and from the Arrhenius plot (Figure 12).

$$\text{Log } A_{\text{propane}} - \log A_{\underline{\text{i}}\text{-butane}} = 0.269 \text{ log mole}^{-1}\text{cc. sec.}^{-1}$$

$$E_{\text{propane}} - E_{\underline{\text{i}}\text{-butane}} = 1110 \text{ cal./mole}$$

$$k_{\text{propane}}/k_{\underline{\text{i}}\text{-butane}} = 0.642 \text{ at } 250^{\circ}\text{C} .$$



◓ Initial ratio of propane to i-butane = 2:1 (runs 2, 3, 9).

○ = 1:1 (runs 4, 5, 7, 10, 12).

◒ = 1:2 (runs 1, 6, 8, 11).

⊕ Mean point of methyl nitrite results.

Figure 12. PROPANE/i-BUTANE.

Table 12

Propane/i-butane

Run	Temp. °A	C_3H_8(cc.) initial	C_4H_{10}(cc.) initial	C_3H_8(cc.) final	C_4H_{10}(cc.) final	NO (cc.) initial	$k_p k_{ib}$
138	453	8.314	7.324	4.093	1.863	14	0.517
139	453	7.709	3.875	4.395	1.434	14	0.565
140	454	3.715	7.941	1.600	1.729	11	0.553
137	454	7.778	7.900	4.088	2.439	14	0.548
141	493	7.973	8.245	2.878	1.499	14	0.598
142	493	4.048	11.68	1.397	1.922	16	0.589
125	532	7.964	7.900	4.771	3.595	12.5	0.652
126	533	9.189	8.658	4.742	2.974	12.5	0.618
127	533	4.704	8.110	2.013	2.013	14	0.609
128	533	8.788	4.551	3.712	1.234	12.5	0.661
156	562	8.847	4.394	5.152	2.057	14	0.712
157	562	3.810	8.766	1.758	3.020	14	0.726

(d) Propane/neopentane

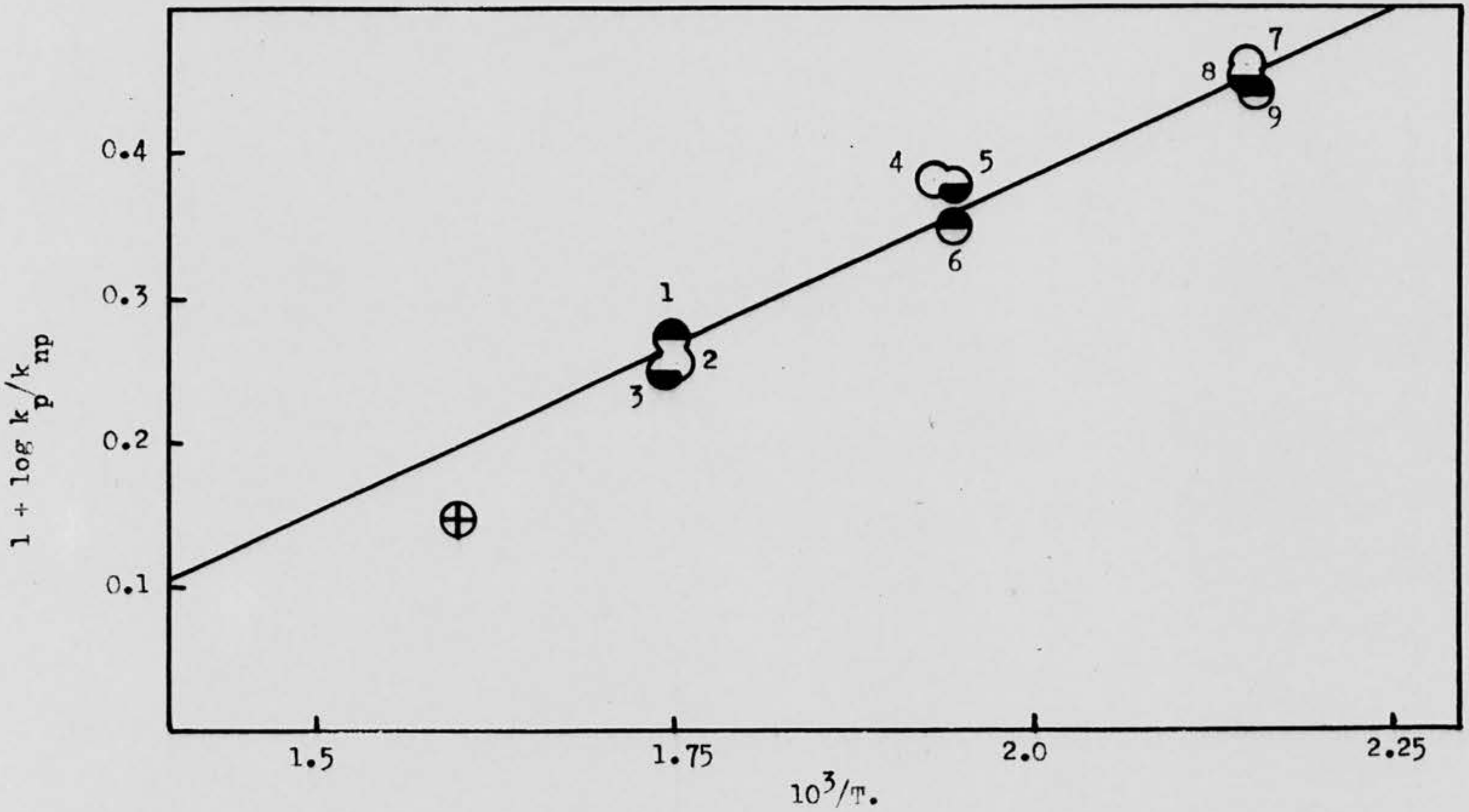
Methoxyls were generated in mixtures of propane, neopentane and nitric oxide in the cyclic flow system for about 30 minutes. In the subsequent analysis, propane, neopentane and nitric oxide were separated from each other and from the products of the reaction by a column of poisoned alumina (mesh, 25-52; weight, 20 g. ; length, 75 cm.). The column was maintained at room temperature and the flow rate was initially 30 cc./min. (one bubbler). Nitric oxide was vented for 7 minutes. The retention time of the propane was 10 minutes. After all the propane had been eluted (14 minutes) the flow rate was increased to 42 cc./min. (two bubblers). Consequently, the neopentane was speeded up, and its retention time was reduced to 40 minutes. The analysis was completed in 50 minutes.

The results are shown in Table 13 and from the Arrhenius plot (Figure 13).

$$\log A_{\text{propane}} - \log A_{\text{neopentane}} = -0.548 \log \text{mole}^{-1}\text{cc. sec.}^{-1}$$

$$E_{\text{propane}} - E_{\text{neopentane}} = -2130 \text{ cal./mole}$$

$$k_{\text{propane}}/k_{\text{neopentane}} = 2.198 \text{ at } 250^{\circ}\text{C}.$$



◓ Initial ratio of propane to neopentane = 2:1 (runs 1, 6, 9).

○ = 1:1 (runs, 2, 4, 7).

◒ = 1:2 (runs 3, 5, 8).

⊕ Mean point of methyl nitrite results.

Figure 13. PROPANE/NEOPENTANE

Table 13

Propane/Neopentane

Run	Temp. °A	C_3H_8 (cc.) initial	C_5H_{12} (cc.) initial	C_3H_8 (cc.) final	C_5H_{12} (cc.) final	NO (cc.) initial	k_p/k_{np}
187	462	8.072	4.077	4.236	3.221	12	2.736
186	465	7.721	8.328	2.558	5.702	12	2.917
189	465	3.725	8.509	1.135	5.591	12	2.842
184	513	3.984	8.638	0.646	3.843	12	2.393
185	513						
183	517	8.044	8.722	2.478	5.343	12	2.408
176	571	8.638	8.418	5.636	6.628	12	1.786
178	571	8.136	3.571	3.742	2.354	12	1.867
177	572	3.571	8.678	1.489	5.314	12	1.781

(e) Propane/cyclopropane

Methoxyls were generated in mixtures of propane, cyclopropane and nitric oxide in the cyclic flow system for about 30 minutes. In the subsequent analysis, propane, cyclopropane and nitric oxide were separated from each other and from the products of the reaction by a column of poisoned alumina (mesh, 25-52; weight, 20 g. ; length, 75 cm.). The column was maintained at room temperature and the flow rate was 30 cc./min. Nitric oxide was vented for 6 minutes. The retention times of propane and cyclopropane were 10 minutes and 16 minutes respectively. No propylene was detected in the products. The analysis was completed in 35 minutes.

Cyclopropane proved to be very unreactive so only two runs were done. The results are shown in Table 14.

Table 14.

Propane/Cyclopropane

Run	Temp. °A	C_3H_8(cc.) initial	C_3H_6(cc.) initial	C_3H_8(cc.) final	C_3H_6(cc.) final	NO (cc.) initial	k_p/k_{cp}
175	569	8.061	4.026	3.828	3.709	11	5
174	571	2.685	8.233	1.829	7.612	11	7

(iv) Method of Calculating Arrhenius Parameters and Probable Errors

The relative activation energies and A factors were calculated in the following way:-

Let $1/T$ be the independant variable x, and let $\log k_1/k_2$ be the dependant variable y. Then the arithmetic means of the n values of x is $\bar{x} = \frac{\sum x}{n}$. Similarly $\bar{y} = \frac{\sum y}{n}$. Further, $X = x-\bar{x}$, and $Y = y-\bar{y}$

By the theory of Least Squares, the line giving the closest fit to the experimental points is

$$(y-\bar{y}) = b(x-\bar{x}) \text{ where } b = \frac{\sum XY}{\sum X^2}$$

$$\text{i.e.} \quad y = a(\pm P_a) + b(\pm P_b)x$$

where P_a and P_b are the probable errors in a and b respectively, such that there is a 50% probability that the line will lie between these limits. In these experiments $a = \log A_1 - \log A_2$ and $b = -(E_1 - E_2)/2.303R$.

$$P_a = 0.6745\sqrt{\frac{\sum d_i^2 \sum x_i^2}{n(n-2)\sum X^2}} \quad \text{and} \quad P_b = 0.6745\sqrt{\frac{\sum d_i^2}{(n-2)\sum X^2}}$$

$\sum d_i^2$ may be calculated from $\sum(y_{observed} - y_{calculated})^{\frac{1}{2}}$

or $\sum d_i^2 = \sum X^2 \left[\frac{\sum Y^2}{\sum X^2} - \left(\frac{\sum XY}{\sum X^2}\right)^2\right]$

Example: Propane/Cyclopropane/Methyl Nitrite

Run No.	x $10^3/T$	y $1 + \log k_p/k_c$	$x-\bar{x}$ X	$y-\bar{y}$ Y	y calc.	d = y-y calc.
76	1.684	1.21	+0.096	-0.02	1.21	0.0
77	1.669	1.26	+0.081	+0.02	1.21	0.05
80	1.664	1.15	+0.076	-0.08	1.21	0.06
87	1.555	1.26	-0.033	+0.03	1.24	0.02
88	1.527	1.30	-0.061	+0.07	1.24	0.06
75	1.511	1.23	-0.077	0	1.25	0.02
74	1.504	1.21	-0.084	-0.02	1.25	0.04

$\sum x = 11.114$ $\sum y = 8.62$ $\sum X^2 = 0.03935$

$\bar{x} = 1.588$ $\bar{y} = 1.23$ $\sum XY = 0.00996$

$$m = \frac{0.00996}{0.03935}$$

$$= -0.25$$

$(y-1.23) = -0.25(x-1.588)$

i.e. $y = 1.63 - 0.25x$

at $x = 1.50$, $y = 1.25$ and at $x = 1.70$, $y = 1.20$.

Errors

$$\sum d_i^2 = 0.0101, \quad \sum x_i^2 = 17.69$$

$$P_a = 0.6745 \sqrt{\frac{0.0101 \times 17.69}{5 \times 7 \times 0.03935}} \qquad P_b = 0.6745 \sqrt{\frac{0.0101}{5 \times 0.03935}}$$

$$= 0.25 \qquad\qquad = 0.15$$

Check

$$P_a = P_b \sqrt{\frac{\sum x_i}{n}}$$

$$= 0.15 \sqrt{\frac{17.69}{7}}$$

$$= 0.25$$

$$= P_a$$

$$\therefore \quad y = 1.63(\pm 0.25) - 0.25(\pm 0.15)x$$

i.e. $1 + \log k_p/k_c = 1.63(\pm 0.25) - 0.25(\pm 0.15)10^3/T$

i.e. $\log A_{\text{propane}} - \log A_{\text{cyclopropane}} = 0.63(\pm 0.25)$

and $-(E_{\text{propane}} - E_{\text{cyclopropane}}) = -0.25(\pm 0.15) \times 10^3 \times 2.303R$ cal.

i.e. $E_{\text{propane}} - E_{\text{cyclopropane}} = 1100 \pm 700$ cal.

At 350°C, i.e. $x = 1.605$, $y = 1.23$

i.e. $1 + \log k_p/k_c = 1.23$

i.e. $k_p/k_c = 1.70$ at 250°C.

DISCUSSION

A. The Accuracy of the Results

The relative rate constants were calculated from the equation

$$\frac{k_1}{k_2} = \frac{\log (R_1H) \text{ initial} - \log (R_1H) \text{ final}}{\log (R_2H) \text{ initial} - \log (R_2H) \text{ final}} .$$

The results obtained using dimethyl peroxide were much more reproducible than these using methyl nitrite. With the former the error was of the order of ± 5% and with the latter it was nearer ±30%.

The reason for the larger error was that methyl nitrite was an inefficient source of methoxyl. For every 100 molecules of methyl nitrite pyrolysed, only about 5 molecules of alkane were attacked. This contributed to two sources of error. Firstly, large quantities of nitric oxide, and a substance thought to be nitrous oxide were produced. These interfered with the analysis and increased the error in (RH) final. Secondly, the total amount of alkanes removed was small. Hence the difference between log (RH) initial and log (RH) final was small and the relative error was large.

For each pair of alkanes, runs were done with one alkane absent to ensure that in the chromatographic analysis no product was eluted with the same retention time as the other alkane.

The relative rate constants were independent of nitric oxide concentration and did not vary significantly when the ratio of the initial concentrations of alkanes was varied from 2:1 to 1:2. Further, with the exception of cyclopropane, the mean point of the methyl nitrite results always lay close to the line obtained by extrapolating the dimethyl peroxide plot. This is good evidence that the abstracting radical in both cases was methoxyl.

Because of their greater accuracy, the Arrhenius parameters and relative rate constants obtained with dimethyl peroxide were used in the calculations made in the later sections of this thesis.

B. Transfer Reactions

Although transfer reactions of the type

$$A + BC = AB + C \qquad (1)$$

have received more attention than any other radical reaction, the factors which govern the rates and the activation energies of these reactions are not well understood. The calculation of A factors from transition state theory has been more successful. Unfortunately the present experimental results are not sufficiently accurate for the comparison with calculated values to be meaningful. However it seems certain that any large differences in the rates at which two radicals react with a compound can be ascribed to a difference in the activation energies.

In reaction (1), a bond is broken and another is formed. If a series of reactions is studied in which group B remains the same but C is varied, then the bond which is being formed (A-B) will be the same in each case. It seems reasonable to attribute the difference in rates and activation energies to the difference in the properties of the B-C, B-C , B-C .... bonds.

At the outset, it must be stated that our present knowledge of the rates and activation energies of these reactions, and especially of bond properties, is fragmentary. The complete calculation of the activation energy of a transfer reaction by quantum mechanics has only been possible in the simplest case of the attack of a hydrogen atom on a hydrogen molecule. In trying to understand the factors which govern the rates of transfer reactions, some assumptions must be made. Often the main justification for these assumptions is the interesting nature of the results obtained.

One of the most important attempts to relate activation energies to bond properties was made by Polanyi and co-workers[29,30]. They studied the reactions of sodium atoms with alkyl halides

$$\mathrm{Na} + \mathrm{RX} = \mathrm{NaX} + \mathrm{R} \qquad (2)$$

and suggested that where there is no resonance stabilisation in the transition complex, or a constant amount of stabilisation throughout a series,

$$E = \alpha\Delta H + \text{constant}$$

where E is the activation energy, ΔH is the heat of reaction and α has a value between 0 and 1.

Polanyi deduced that α was 0.27 for the reaction of sodium with alkyl halides, and Trotman-Dickenson[31] proposed that α was 0.5 for the reactions of methyl with alkanes. Neither the activation energies nor the C-Cl and C-H bond strengths are very accurately known and therefore these values of α must be interpreted with caution.

The rate constants are directly determined and are therefore more reliable than activation energies. Trotman-Dickenson[32] has shown that the logarithms of the rate constants at 254°C for 17 hydrogen abstraction reactions of methyl and trifluoromethyl fall on a pair of parallel straight lines of unit slope. This indicates that the same factors determine the rate constants of the reaction of the two radicals.

A barrier to progress is that the rate constants of hydrogen abstraction reactions have been determined for most radicals (including methoxyl), for the attack on the whole alkane molecule. In molecules which contain only one type of C-H bond e.g. ethane, this is not a limitation. But in molecules such as propane the experimental rate constant is an average value for the attack on the individual primary and secondary bonds.

The rate constants and activation energies for the attack on alkane molecules and the values calculated from them for the attack by methoxyls on individual C-H bonds will be discussed in the next two sections.

C. Hydrogen Abstraction by Methoxyl from Alkane Molecules

The relative activation energies for hydrogen abstraction from alkane molecules are of limited theoretical significance but it is of interest to compare the methoxyl results with those obtained for other radicals.

Table 1.

Activation energies relative to ethane for hydrogen abstraction from alkane molecules.

Alkane	Attacking Radical			
	Cl	CF_3	CH_3	CH_3O
Ethane	0	0	0	0
Propane	- 0.1	- 1.3	- 2.3	- 1.8
n-butane	- 0.3	- 2.4	- 2.1	- 4.1
i-butane	- 0.3	- 2.8	- 2.9	- 1.1
Neopentane	- 0.1	+ 0.1	- 0.2	- 0.3
References	33, 34	33, 35	33, 43	this work

The activation energies are in kcal.

From Table 1 emerges the general pattern of hydrogen abstraction from alkane molecules. The activation energies for the attack on ethane and neopentane are similar. These alkanes contain only primary hydrogen atoms. The activation energies are less for those alkanes containing secondary and tertiary hydrogen atoms. In addition, the difference in activation energies over the series of alkanes is much greater for trifluoromethyl, methyl and methoxyl than for chlorine.

The results shown in Table 1 are not inconsistent with those obtained by Wijnen[13] for the hydrogen abstraction from methyl acetate by methyl and methoxyl.

$$CH_3 + CH_3COOCH_3 = CH_4 + CH_2COOCH_3 \quad (3)$$

$$CH_3O + CH_3COOCH_3 = CH_3OH + CH_2COOCH_3 \quad (4)$$

$E_3 = 10$ kcal. and $E_4 = 5\text{-}9$ kcal.

Few similar activation energy determinations have been reported for any other alkoxyl radical. Brook[36] has determined the difference between the activation energy of hydrogen abstraction by t-butoxyl with that for the decomposition of t-butoxyl for 2:3 dimethyl butane, 2:3 dimethyl hexane, methyl cyclohexane, toluene and tetralin.

$$(CH_3)_3CO + RH = (CH_3)_3COH + R \quad (5)$$

$$(CH_3)_3CO = (CH_3)_2CO + CH_3 \quad (6)$$

Gray[37] has suggested that the best value for E_6 from determinations by several workers is 13±2 kcal. E_5 can then be calculated by subtraction. The results are shown in Table 2 together with comparable results for methyl[38].

$$CH_3 + RH = CH_4 + R \quad (7)$$

Table 2.

Hydrogen abstraction by t-butoxyl

Alkane	E_5-E_6	E_5	E_7
2:3 dimethyl butane	-7	6	7
2:3 dimethyl hexane	-8	5	
methyl cyclohexane	-7.5	5.5	
toluene	-11	2	8
tetralin	-11	2	

The units of E are kcal.

The results for toluene and 2:3 dimethyl butane are interesting. The C-H bond in the methyl group of the former is weaker than the tertiary C-H bond in the latter and so t-butoxyl follows the expected trend.

The absolute activation energies for hydrogen abstraction by methoxyl from ethane, propane, n-butane, i-butane and neopentane could be calculated if the activation energy for the attack on any one of them was known. Unfortunately, no such determinations have been reported. However, if the series was extended by measuring the relative activation energy for methane/ethane mixtures, and if the activation energy for the hydrogen abstraction from methane was known, the absolute activation energies for the other five alkanes could be calculated. The activation energy for hydrogen abstraction from methane could be calculated from the activation energy of the back reaction, (8), and the heat of reaction

$$CH_3 + CH_3OH = CH_4 + CH_3O \qquad (8)$$

The heat of reaction could be obtained from the known heats of formation. In practice, it would be extremely difficult to measure E_8 because side reactions would also produce methane. It should be simpler to measure E_9

$$CD_3 + CD_3OH = CD_3H + CD_3O \qquad (9)$$

and it is reasonable to assume that $E_8 = E_9$.

D. Hydrogen Abstraction from Primary, Secondary and Tertiary C-H Bonds.

The rate factors of hydrogen abstraction reactions have been determined for most radicals (including methoxyl) for the attack on the whole alkane molecule. In alkanes which contain only one type of C-H e.g. ethane, this is not a limitation as the rate factors for a single bond may be obtained by dividing by the number of bonds in the molecule, which in this case is 6.

However in a molecule such as propane there is less justification for assuming all the bonds to be equivalent. It is very probable that the primary and secondary bonds react at different rates. In order to get some idea of how the secondary bonds react it is assumed that the primary bonds in ethane and propane react at the same rate.

Some evidence for this assumption is provided by the work of Knox and Nelson[34] on the hydrogen abstraction reactions of chlorine atoms.

Table 3.

Hydrogen Abstraction from Alkanes by Chlorine Atoms

Type of bond attacked	Alkane	$10^{-13}k$ per H atom at 25°C
primary	ethane	0.26
primary	propane	0.31
primary	n-butane	0.37
primary	i-butane	0.33
primary	neopentane	0.30
secondary	propane	1.14
secondary	n-butane	1.40
tertiary	i-butane	1.64

The method of calculating the relative rate of attack at 250°C by methoxyl at primary, secondary and tertiary C-H bonds is shown below:-

alkane	relative rate constant	number of primary hydrogen atoms	relative rate constant per primary hydrogen atom
ethane	0.30	6	0.30/6 = 0.050
neopentane	0.46	12	0.46/12 = 0.038

therefore the average rate of attack on primary hydrogen atoms is 0.044.

alkane	relative rate constant	number of primary hydrogen atoms	number of secondary hydrogen atoms	relative rate constant per secondary hydrogen atom
propane	1.00	6	2	$(1.00-6 \times 0.044)/2 = 0.37$
<u>n</u>-butane	1.61	6	4	$(1.61-6 \times 0.044)/4 = 0.34$

therefore the average rate of attack on secondary hydrogen atoms is 0.36.

alkane	relative rate constant	number of primary hydrogen atoms	number of tertiary hydrogen atoms	relative rate constant per tertiary hydrogen atom
<u>i</u>-butane	1.56	9	1	$(1.56-9 \times 0.044) = 1.16$

therefore the rate of attack on tertiary hydrogen atoms is 1.16.

	Primary	Secondary	Tertiary
Relative Rate Constants at 250°C	0.044	0.36	1.16
that is	1	8	26

It is of interest to compare these results with those we have calculated for other radicals.

Table 4.

Relative rate constants for X + RH = XH + R

Typical D(R-H)	100	94	89			
Radical X	prim.	sec.	tert.	Temp. °C	D(X-H)	Ref.
F	1	1.2	1.4	-	134	39
Cl	1	3	3	250	102	34
Oxid.	1	4	11	350	-	40
CF_3	1	6	36	182	103	33
CH_3O	1	8	26	250	100	this work
CH_3	1	7	50	182	101	33
Br	1	250	6,300	98	86	41

D(R-H) and D(X-H) in kcal., and are obtained from references 14 and 42. "Oxid." is the radical or radicals responsible for the chain propagating step in oxidations, and the relative rate constants were calculated from the results of competitive oxidations of ethane/propane and propane/i-butane mixtures.

From Table 4 it may be deduced that in general the less selective a radical, the more reactive it is. Thus fluorine, which is very unselective, has a negligible activation energy for the attack on primary, secondary and tertiary hydrogen atoms, and in this case the relative rate constants are the relative A factors. The great selectivity shown by bromine is due to the large activation energies for hydrogen abstraction which in turn are due to the endothermicity of the reactions.

It is of interest to compare the relative rate constants of chlorine with those for trifluoromethyl, methoxyl and methyl. The thermochemistry of the reactions of all four radicals is similar as the strengths of the bonds being formed (H-X) are approximately the same in each case. It seems probable that the greater reactivity of chlorine is due at least in part to its greater electronegativity or electron affinity.

It is not possible to distinguish between the selectivities of trifluoromethyl, methoxyl and methyl and consequently it seems reasonable to conclude that these radicals show comparable reactivity.

REFERENCES

(Abbreviations for periodicals as given in World List of Scientific Periodicals, Butterworths Scientific Publications, London, 1952).

1. Steacie, E.W.R.; J. chem. Soc., 1956, 3986.

2. Gray, P.; Trans. Faraday Soc., 1956, 52, 344.

3. Steacie, E.W.R. and Shaw, G.T.; Proc. roy. Soc., 1934, A146, 388.

4. Appin, A., Chariton, J. and Todes, O.; Acta phys.-chim., URSS, 1936, 5, 655.

5. Hanst, P.L. and Calvert, J.G.; J. phys. Chem., 1959, 63, 104.

6. Gray, P. and Williams, A.; Special Publiciations No. 9, p. 98, The Chemical Society, London, 1957.

7. Steacie, E.W.R. and Rosenberg, S.; J. chem. Phys., 1936, 4, 223.

8. Steacie, E.W.R.; Atomic and Free Radical Reactions, p. 239, Rheinhold Publishing Corp., New York, 1954.

9. Carter, A.G. and Travers, M.W.; Proc. roy. Soc., 1937, A158, 495.

10. Swarc, M.; Chem. Rev., 1950, 47, 75.

11. Hinshelwood, C.N. and Askey, P.J.; Proc. roy. Soc., 1927, A115, 215.

12. Rice, F.O. and Herzfeld, K.F.; J. Amer. chem. Soc., 1934, 56, 284.

13. Wijnen, M.H.J., J. chem. Phys., 1957, 27, 710.

14. Gray, J.A. and Style, D.W.; Trans. Faraday Soc., 1952, 48, 1137.

15. Wijnen, M.H.J.; J. chem. Phys., 1958, 28, 271 and 939.

16. Heller, C.A.; J. chem. Phys., 1958, 28, 1255.

17. Kerr, J.A. and Trotman-Dickenson, A.F.; in the press.

18. Kerr, J.A. and Trotman-Dickenson, A.F.; J. Soc. chem. Ind., Lond., (Chem. and Ind.), 1959, 125.

19. Rust, F.F., Seubold, F.H. and Vaughan, W.E.; J. Amer. chem. Soc., 1950, 72, 338.

20. McBay, H.C. and Tucker, O; J. org. Chem., 1954, 19, 869.

21. Gomer, R. and Kistiakowsky, G.B.; J. chem. Phys., 1951, 19. 85.

22. Trotman-Dickenson, A.F. and Steacie, E.W.R.; J. chem. Phys., 1950, 18, 1097.

23. Kornblum, N. and de la Mare, H.E.; J. Amer. chem. Soc., 1952, 74, 3079.

24. Miller, D.M. and Steacie, E.W.R.; J. chem. Phys., 1951, 19, 73.

25. Phillips, C.; Gas Chromatography, p.27, Butterworths Scientific Publications, London, 1956.

26. Trotman-Dickenson, A.F.; Gas Kinetics, p. 199, Butterworths Scientific Publications, London, 1955.

27. Maass, O.; J. Amer. chem. Soc., 1919, 41, 53.

28. Margenau, H. and Murphy, G.M.; The Mathematics of Physics and Chemistry, p. 502, D. Van Nostrand Company Inc., New York, 1943.

29. Evans, M.G. and Polanyi, M.; Trans. Faraday Soc., 1938, 34, 11.

30. Butler, E.T. and Polanyi, M.; Trans. Faraday Soc., 1943, 39, 19.

31. Trotman-Dickenson, A.F.; Disc. Faraday Soc., 1951, 10, 111.

32. Trotman-Dickenson, A.F.; J. Soc. chem. Ind. Lond., (Chem. and Ind.), 1957, 1243.

33. Trotman-Dickenson, A.F.; Free Radicals, p. 65, Methuen and Co. Ltd., London, 1959.

34. Knox, J.H. and Nelson, R.L.; Trans. Faraday Soc., 1959, 55, 937.

35. Pritchard, G.O., Pritchard, H.O., Schiff, H.I. and Trotman-Dickenson, A.F.; Trans. Faraday Soc., 1956, 52, 849.

36. Brook, J.H.T.; Trans. Faraday Soc., 1957, 53, 327.

37. Gray, P., and Williams, A.; Chem. Rev., 1959, 59, 239.

38. Trotman-Dickenson, A.F.; Gas Kinetics, p. 200, Butterworths Scientific Publiciations, London, 1955.

39. Fettis, G.C. and Trotman-Dickenson, A.F.; in the press.

40. Knox, J.H., Smith, R.F. and Trotman-Dickenson, A.F.; Trans. Faraday Soc., 1958, 54, 1509.

41. Fettis, G.C. and Trotman-Dickenson, A.F.; in the press.

42. Cottrell, T.L.; The Strengths of Chemical Bonds, p. 270, Butterworths Scientific Publiciations, London, 1958.

43. Rice, F.O. and Vanderslice, T.A.; J. Amer. chem. Soc., 1958, 80, 291.

Reprinted from Proceedings of the Chemical Society, February, 1959, page 61

The Reactions of Methoxyl Radicals

By R. SHAW and A. F. TROTMAN-DICKENSON
(CHEMISTRY DEPARTMENT, THE UNIVERSITY, EDINBURGH)

SEVERAL workers[1] have shown that methoxyl radicals, produced by the decomposition of peroxides, will abstract hydrogen atoms from large molecules by reaction (1).

$$CH_3{\cdot}O + R^1H = CH_3{\cdot}OH + R^1 \quad \ldots\ldots(1)$$

They obtained a rough measure of the relative reactivities of the compounds by determining the proportion of methoxyl radicals that formed methanol. Values of k_1 could not be deduced from these observations because the competing reactions were ill-defined. These rate constants are of interest because alkoxyl radicals may play a part in the gas-phase oxidation of hydrocarbons. Furthermore, few series of transfer reactions, which are important theoretically because of their simplicity, have been investigated. None of those that have been studied in the gas phase involve identifiable oxygen-containing radicals.

The relative rate of attack of methoxyl radicals on two hydrocarbons has been found by determining the amounts of each removed from a mixture by the radicals.[2] The rate constant of reaction (2) may then be related to that of reaction (1) by the equation:

$$CH_3{\cdot}O + R^2H = CH_3{\cdot}OH + R^2 \quad \ldots\ldots(2)$$

$$\frac{k_1}{k_2} = \frac{\log[R^1H]_{\text{initial}} - \log[R^1H]_{\text{final}}}{\log[R^2H]_{\text{initial}} - \log[R^2H]_{\text{final}}}$$

Accurately measured quantities of two hydrocarbons were circulated by an automatic Toepler pump through a system containing traps, a reaction vessel in an electric furnace, and capillaries to control the rates of flow. Methyl nitrite, which was the source of methoxyl, was bled into the stream just ahead of the reaction vessel. Between 300° and 400° the methyl nitrite rapidly decomposes, a proportion of the molecules forming methoxyl radicals and nitric oxide. Some of these methoxyl radicals abstracted hydrogen from a hydrocarbon, yielding methanol and an alkyl radical which reacted with the nitric oxide. More nitric oxide was sometimes added to ensure that none of the alkyl radicals reacted with hydrocarbons; it had no effect on the value of k_1/k_2. A cold trap placed after the reaction vessel reduced the concentration of the less-volatile products. At the end of a run the products were condensed in a trap at $-183°$. The residual hydrocarbons were then determined by gas chromatography with a Janak detector and an alumina column whose selective affinity for polar oxygenated products made the present work possible. The value of k_1/k_2 did not alter when the concentrations of hydrocarbons were varied between 1:2 and 2:1.

The results can be expressed in terms of the Arrhenius parameters and rate constant for propane as follows:

Hydrocarbon	Runs	log A	E (cal.mole^{-1})	$k(350°)$
Ethane	18	$+0{\cdot}08 \pm 0{\cdot}23$	1200 ± 700	0·46
Propane	—	0	0	1
*cyclo*Propane	7	—	—	0·59
n-Butane	5	—	—	1·21
*iso*Butane	18	$-0{\cdot}38 \pm 0{\cdot}17$	-1300 ± 500	1·24

These results show that methoxyl is rather unselective and suggest that it has a reactivity midway between that of a methyl radical and a chlorine atom.[3] The reactions of other hydrocarbons will be studied in due course.

The accuracy of the results is as high as that of most of the information available on transfer reactions of radicals. It cannot be readily improved because of the restricted temperature range and because methyl nitrite in the presence of nitric oxide is not a very efficient source of methoxyl radicals. A large quantity of nitric oxide is formed while a reasonable fraction of the hydrocarbons is consumed. Its presence interferes with the analysis. It is hoped to overcome this difficulty and at the same time to extend the temperature range greatly by using other sources of methoxyl radicals.

We are indebted to the Institute of Petroleum for a grant.

(*Received, January 6th*, 1959.)

---

[1] McBay and Tucker, *J. Org. Chem.*, 1954, **19**, 869; McBay, Tucker, and Milligan, *ibid.*, 1954, **19**, 1003; Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1950, **72**, 338.

[2] Pritchard, Pyke, and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629; Knox, Smith and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509.

[3] Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955; Knox and Nelson, *Trans. Faraday Soc.*, in the press.