THE COMPETITIVE CHLORINATION
OF HYDROCARBONS.

Thesis
submitted for the degree of
Doctor of Philosophy.

by
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ACKNOWLEDGEMENTS.

The author wishes to thank Dr. John H. Knox for his continued advice and encouragement during the course of this research and Professors J.P. Kendall and E.L. Hirst for the provision of equipment and laboratory facilities.

Thanks are also due to Dr. A.F. Trotman-Dickenson for many helpful suggestions and to Dr. D.M.W. Anderson for infra-red analyses.

The author is indebted to the Department of Scientific and Industrial Research for the provision of a maintenance allowance.
PREFACE.

The reactions of chlorine with hydrogen and hydrocarbons have been widely studied and it is well established that they are chain reactions involving very long chains. There is general agreement as to the chain initiating and propagating steps but still considerable disagreement as to the chain terminating steps. The modern trend in kinetics has been away from the establishment of mechanism in detail and towards the determination of Arrhenius parameters for elementary reactions such as those involved in chain propagation.

The present work was aimed at determining accurately the rate constants for the attack of chlorine atoms on different hydrocarbons (reaction (1))

\[ \text{Cl}^* + \text{H}_2 \text{H} \rightarrow \text{R}^* + \text{H}_2\text{Cl} \]  

and on different positions in the same hydrocarbon. This has been accomplished by employing a competitive technique in which reaction products are analysed for products characteristic of the initial chlorine atom attack. Absolute rate constants for each hydrocarbon are then found, if the absolute value for at least one of the substances studied is known. In this work the rate constant for the chlorine atom attack on hydrogen, which is reasonably well established, has been used as the standard value and all other absolute rate constants are obtained from this.

The activation energies obtained from the rate constants have been explained in a qualitative manner, while the A factors have been used to test transition state theory.
INTRODUCTION.

Of the reactions of chlorine, by far the most extensively studied is that with hydrogen, and out of the mass of information only the features relevant to the present study are mentioned. The reactions of chlorine with hydrocarbons, particularly in the gas phase, have been less widely studied although much important work on chlorinations in solution has been carried out.

(1) The reaction with hydrogen.

(a) Mechanism. The photochemical combination of hydrogen and chlorine was first observed by Cruikshank in 1801. The reaction was studied quantitatively by Draper (1841 - 45) and Bunsen & Roscoe (1855 - 59). Draper showed that the commencement of the reaction was accompanied by an increase of volume at constant pressure. This phenomenon, known as the 'Draper effect', has since been shown to be due to the heat evolved in the chemical reaction. Bunsen & Roscoe subjected hydrogen - chlorine mixtures to the action of light of known intensity for varying periods of time, and showed that the amount of reaction depended on the light absorbed. These workers also observed an 'induction period', which has since been shown to be due to the presence of nitrogenous impurities such as ammonia. No such induction period is observed with pure hydrogen and chlorine. Oxygen also acts as an inhibitor but if present in sufficient quantity simply slows down the reaction throughout without delaying the start.

At the beginning of the 20th century a large amount of quantitative information was accumulated mainly by Bodenstein and his co-workers. Many of the early results were irreproducible and led to erroneous/
erroneous conclusions. For example, several workers reported that carefully dried hydrogen and chlorine would not combine, but this is now known to be due to impurities introduced in the drying process. It was only by following up such leads that the correct mechanism was eventually obtained.

Bodenstein used a static system and followed the photochemical reaction by pressure measurements. He found that, in the presence of oxygen,

\[ R_{\text{HCl}} = k \frac{I_{\text{abs.}}}{(\text{Cl}_2)^2/(\text{O}_2)} \]

while the activity of illuminated chlorine did not last more than \( \frac{1}{1600} \) second.

Bodenstein first thought that the chlorine and hydrogen combined bimolecularly and that the effect of light in initiating the reaction was either to ionise the chlorine molecule or to produce an excited molecule. However the discovery that the quantum efficiency of the reaction was very high led him to propose a chain mechanism (1913). The propagating steps were

\[ \text{Cl}_2 + \varepsilon \rightarrow \text{Cl}_2' \]
\[ \text{Cl}_2' + \text{H}_2 \rightarrow 2\text{HCl} + \varepsilon \]

At this time, the ionic chain scheme seemed plausible since the bond strength in the chlorine molecule was believed to be about 100 k. cal., making the photolysis in visible light impossible. The \( D(\text{Cl} - \text{Cl}) \) value is now known to be 57 k. cal.

It was Nernst (1919) who suggested the existence of an atomic chain of the type

\[ \text{Cl}' + \text{H}_2 \rightarrow \text{HCl} + \text{H}' \]
\[ \text{H}' + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}' \]

after/
after the initial photolysis of a chlorine molecule. By this scheme were explained quantum yields of 10 in the absence of oxygen and in light of wave length 4800° A or less.

The chief difficulty in interpreting the results of the hydrogen - chlorine reaction is their contradictory nature e.g. Bodenstein found that both

\[ R_{\text{HCl}} = k_{\text{abs}} \left( \frac{(\text{Cl}_2)}{(\text{O}_2)} \right) \quad \text{and} \quad R_{\text{HCl}} = k_{\text{abs}} \left( \frac{(\text{Cl}_2)^2}{(\text{O}_2)} \right) \]

applied depending on the chlorine pressures, while other workers disagreed on the effect of hydrogen chloride on the overall reaction.

The mechanism which has proved most satisfactory for the reaction in the presence of oxygen is that first proposed by Gohring. However, for the reaction in the absence of oxygen, which is of interest in the present work, Bodenstein and Unger proposed the following scheme -

\[
\begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2\text{Cl}^\cdot \\
\text{Cl}^\cdot + \text{H}_2 & \rightarrow \text{HCl} + \text{H}^\cdot \\
\text{H}^\cdot + \text{Cl}_2 & \rightarrow \text{HCl} + \text{Cl}^\cdot \\
\text{H}^\cdot + \text{HCl} & \rightarrow \text{H}_2 + \text{Cl}^\cdot \\
\text{Cl}^\cdot + \text{X} & \rightarrow \text{ClX} \\
\text{H}^\cdot + \text{X} & \rightarrow \text{HX}
\end{align*}
\]

where X can be the walls or some volatile substance. Using a stationary state treatment

\[
R_{\text{HCl}} = \frac{4I_{\text{abs}} k_5 (\text{Cl}_2)}{X(k_4 \alpha + k_5)}
\]

where \( \alpha = \frac{k_3 (\text{Cl}_2) + k_{-2} (\text{HCl})}{k_2 (\text{H}_2)} \)

\[ = \frac{(\text{Cl})}{(\text{H})}. \]

When/
When the chain termination is predominantly by chlorine atom removal 

\( k_4 \rightarrow k_5 \) and the expression reduces to 

\[
R_{\text{HCl}} = \frac{4I_{\text{abs}} k_2 k_3 (H) (Cl)}{k_4 (X) \left( k_3 (Cl) + k_{-2} (HCl) \right)}
\]

In the absence of any hydrogen chloride inhibition

\[
R_{\text{HCl}} = \frac{4I_{\text{abs}} k_2 (H_2)}{k_4 (X)}
\]

and this agrees with the experimental expression found by Bodenstein & Unger and Potts & Rollefson. Bodenstein & Unger suggested that the principal chain terminating steps were either the diffusion of chlorine atoms to the walls where recombination occurs or the reaction of chlorine atoms with X which is believed to be a chloride or oxychloride of silicon. Potts & Rollefson confirm this belief that X is a volatile substance while they go as far as to suggest that the strong inhibiting effect of hydrogen chloride, reported by Norrish & Ritchie, was due to some other inhibitor.

In the above expression, the temperature coefficient must depend on the \( k_2/k_4 \) ratio and will lead to the activation energy difference \( E_2 - E_4 \)

Other workers have reported that the rate of the hydrogen-chlorine combination is proportional to the square root of the light intensity. Hence the possibility of bimolecular termination must be considered. Although this appears to be of importance only at high concentrations in the hydrogen-chlorine reaction, it is of much greater importance in the chlorination of substances such as chloroform. Three possible bimolecular chain termination steps are

\[
\begin{align*}
\text{Cl} + \text{Cl} + \text{M} & \rightarrow \text{Cl}_2 + \text{M} \quad (6) \\
\text{Cl} + \text{H} + \text{M} & \rightarrow \text{HCl} + \text{M} \quad (7) \\
\text{H} + \text{H} + \text{M} & \rightarrow \text{H}_2 + \text{M} \quad (8)
\end{align*}
\]

Considering/
Considering reactions (1), (2), (-2), (3), (6), (7) and (8)

\[ R_{\text{HCl}} = \frac{2^{3/2} I_{\text{abs}}^{1/2} k_3 (\text{Cl}_2)}{M^{1/2} (k_6 \alpha^2 + k_7 x + k_8)^{1/2}} \]

when \( \alpha \) is large, since \( k_6 = k_7 = k_8 \)

\[ R_{\text{HCl}} = \frac{2^{3/2} I_{\text{abs}}^{1/2} k_2 k_3 (\text{Cl}_2)(\text{H}_2)}{k_6^{1/2} M^{1/2} (k_3(\text{Cl}_2) + k_2(\text{HCl}))} \]

and if hydrogen chloride inhibition is negligible

\[ R_{\text{HCl}} = \frac{2^{3/2} I_{\text{abs}}^{1/2} k_2 (\text{H}_2)}{k_6^{1/2} M^{1/2}} \]

Because of the low quantum efficiency at high pressures, Ritchie and Taylor have suggested that \( \text{Cl}_3 \) is involved in chain termination steps such as

\[
\begin{align*}
\text{Cl}^\cdot + \text{Cl}_2 + \text{M} & \rightarrow \text{Cl}_3^\cdot + \text{M} \\
\text{Cl}^\cdot + \text{Cl}_3 & \rightarrow 2\text{Cl}_2 \\
\text{Cl}_3 & \rightarrow \text{destroyed}.
\end{align*}
\]

The \( \text{Cl}_3 \) complex has been shown to have a relatively long lifetime.

Bodenstein, however, rejects chain terminations involving \( \text{Cl}_3 \).

Although disagreement still exists, the most likely termination processes are

(i) \( \text{Cl}^\cdot + \text{X} \rightarrow \text{CLX} \)

where \( \text{X} \) is volatile, probably a chloride of silicon

(ii) \( \text{Cl}^\cdot + \text{walls} \rightarrow \frac{1}{2} \text{Cl}_2 \)

at low pressures

(iii) \( \text{Cl}^\cdot + \text{Cl}^\cdot + \text{M} \rightarrow \text{Cl}_2 + \text{M} \)

or \( \text{Cl}^\cdot + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3^\cdot + \text{M} \)

at high pressures, where diffusion of the chlorine atoms to the walls is unlikely.

In the/
In the chlorination of hydrogen the recombination of hydrogen atoms is of no importance as a chain terminating process. However, in the chlorination of hydrocarbons and particularly halogenated hydrocarbons, the combination of the alkyl radicals is now known to be the predominant chain termination reaction.

(b) Rate Constants.

In principle activation energies may be derived from a study of the temperature dependence of the thermal or photochemical reactions. For example where the kinetics follow \( R_{\text{HCl}} = kI_{\text{abs}}(H_2) \) the temperature dependence leads to \( E_2 - E_1 \), and when \( R_{\text{HCl}} = kI_{\text{abs}}(H_2)^{1/2} \) a value for \( E_2 - E_6 \) is obtained. However, since the chains of the chlorine - hydrogen combination are very long, trace impurities may have large effects on the rate of the overall process and result in irreproducible rate constants. The pre-1930 workers concentrated mainly on the elucidation of mechanism, but since then more time has been devoted to the temperature dependence of the rate constants of the individual reactions.

\[
\begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2\text{Cl}^- & (1) & \Delta H = +57.1 \\
\text{Cl}^- + \text{H}_2 & \rightarrow \text{HCl} + \text{H}^- & (2) & \Delta H = +1.1 \\
\text{H}^- + \text{Cl}_2 & \rightarrow \text{HCl} + \text{Cl}^- & (3) & \Delta H = -45.1 \\
\text{Cl}^- + \text{X} & \rightarrow \text{ClX} & (4)
\end{align*}
\]

For a description of these results the above mechanism may be regarded as being adequate, being/
being in agreement with experimental results and giving

\[ R_{\text{HCl}} = 4I_{\text{abs}} k_2 (H_2)/k_4 (X) \]

The heat of dissociation of the chlorine molecule is well established as 57.19 k. cal. (see footnote) which is in agreement with the spectroscopic dissociation energy of 57.08 k. cal. Since the bond dissociation energies of the Cl - Cl, H - H and H - Cl bonds are 57.1, 103.2 and 102.1 k. cal, respectively, reaction (2) is slightly endothermic whereas (3) is strongly exothermic.

From the temperature coefficient for the overall rate of hydrogen chloride production Hertel obtained 5.9 ± 0.5 k. cal. while Potts & Rollefson obtained 5.8 k. cal. for \( E_2 - E_4 \). Hence 5.8 k. cal. appears to be the minimum value for \( E_2 \).

The first determination of the absolute value for the rate constant \( k_2 \) was made by Rodebush & Klingelhofer, who found the probability \( W \) of a chlorine atom reacting with a hydrogen molecule at 0°C and 25°C. The chlorine atoms were produced in a high frequency electrodeless discharge and reacted with a stream of hydrogen in a flow system. The degree of dissociation of the chlorine was measured by a Wrede diffusion gauge

\[ W = \frac{\text{HCl formed}}{\text{Cl introduced}} \]

Footnote: Bond strengths and activation energies will be quoted throughout this thesis in k. cal. instead of k. cal. mole. where/
where $z'$ is the average number of collisions between a given chlorine atom and hydrogen molecule in the reaction vessel as calculated from kinetic theory. Rodebush & Klingelhoefer used the relationship $W \propto \frac{1 + E_2}{RT} e^{-E_2/RT}$ and obtained, from the temperature coefficient of $W$, a value for $E_2$ of 6,100 cal. The relationship of $W \propto e^{-E_2/RT}$ gives $E_2 = 5,550$ cal.

Steiner & Rideal also obtained absolute values for $k_2$ from an examination of the ortho-para conversion in hydrogen. This is catalysed by hydrogen chloride.

$$\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$$

or $$\text{H}_2 + \text{Cl} \rightarrow \text{H}_2\text{Cl}$$

where $k_{-2} = k_{-2}' + k_{-2}''$

From work between 628° C and 798° C they obtained $k_{-2}$ values which gave $E_{-2} = 5,200$ cal. These values in combination with the known equilibrium constant for $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$ gave absolute $k_2$ values. These together with Rodebush & Klingelhoefer's results give $E_2 = 5,500$ cal. Steiner & Rideal claim $E_2 = 5,900$ cal. from their own results but the accuracy of this value is poor because of the small temperature range.

Ashmore & Channugam studied the effect of nitrosyl chloride on the thermal hydrogen - chlorine reaction. In addition to the usual reactions (1), (2), (3) and (4) they considered

$\text{NO} + \text{Cl}_2 \rightarrow \text{NOCl} + \text{Cl}$ \hspace{1cm} (9)

$\text{NOCl} \rightarrow \text{NO} + \text{Cl}$ \hspace{1cm} (10)

$\text{Cl} + \text{NOCl} \rightarrow \text{NO} + \text{Cl}_2$ \hspace{1cm} (11)

In The/
In the presence of nitrosyl chloride, the initial rate of the hydrogen-chlorine combination is radically reduced for a short period due to reaction (11). Incidentally this proves that any molecular reaction between hydrogen and chlorine is negligible. A marked acceleration in the production of hydrogen chloride then occurs which can only be explained by an initiation process other than $\text{Cl}_2 \rightarrow 2\text{Cl}$. This is reaction (9). These workers derived an expression for the rate of hydrogen chloride production

$$R_{\text{HCl}} = \alpha (\text{H}_2)(\text{Cl}_2) \frac{(\text{NO})}{(\text{HNO})}$$

where $\alpha = \frac{k_9}{k_2}$. From work at $250^\circ\text{C}$ they obtained $k_2 = 4.8 \times 10^{-6}$ cc. mole sec. This value is in perfect agreement with the other absolute values for $k_2$.

When the results of these three independent methods of determining absolute $k_2$ values are combined.

$$k_2 = 0.8 \times 10^{-14} \exp (-5,500 \pm 200 / \text{RT}) \text{ cc. moles sec.}$$

The rate constant for reaction (3) cannot be obtained as readily as $k_2$. Maximum and minimum values for $E_3$ can, however, be inferred from the available data.

The maximum value of $E_3$ can be obtained from the observation by the majority of workers that hydrogen chloride has no inhibiting effect on the photochemical hydrogen chlorine combination. At room temperature the reverse reaction ($\rightarrow 2$) $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ must be at least a hundred times slower than reaction (3) $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$. Steiner & Hideal showed that $E_{-2} = 5,200$ cal., so that if $A_{-2} \approx A_3$, the maximum value of $E_3$ is $2,500$ cal.
The minimum value of $E_3$ is obtained from the study of the hydrogen - chlorine reaction in the presence of oxygen. In this reaction:

$$H^- + O_2 + M = HO_2 + M$$  \hspace{1cm} (12)

$$Cl^- + O_2 + M = ClO_2 + M$$  \hspace{1cm} (13)

For moderate oxygen pressures, the main termination reaction appears to be (12)

$$R_{HCl} = \frac{2I_{abs} k_3 (O_2)^2}{k_{12} (M)(O_2)}$$

From the temperature coefficient a value for $E_3 - E_{12}$ of $2.0 \text{ k. cal.}$ has been obtained by Hertel. Hoare & Walsh have recently shown that reactions of type (12) where $M = H_2$ almost certainly have negative activation energies. This suggests a minimum value for $E_3$ of $0k. \text{ cal.}$

The activation energies of chain terminating steps (4) and (5) are not known but are probably small. The quadratic termination reactions (6), (7) and (8) have almost certainly zero or slightly negative $E$ values as do most free radical recombination reactions.
(2) The reaction with hydrocarbons.

(a) Mechanism and Rate Constants. The photochemical and thermal chlorinations of alkanes and chloro-alkanes are chain processes involving long chains. By analogy with the chlorination of hydrogen the initiation and propagation steps are

\[ \text{Cl}_2 \xrightarrow{hv \text{ or heat}} 2\text{Cl} \cdot \tag{1} \]
\[ \text{Cl} \cdot + R - H \longrightarrow R \cdot + \text{HCl} \tag{2} \]
\[ R \cdot + \text{Cl}_2 \longrightarrow R \text{Cl} + \text{Cl} \cdot \tag{3} \]

The alternative propagating steps of

\[ \text{Cl} \cdot + R - H \longrightarrow R - \text{Cl} + H \cdot \tag{2a} \]
\[ H \cdot + \text{Cl}_2 \longrightarrow \text{HCl} + \text{Cl} \cdot \tag{3a} \]

are extremely unlikely since (2a) is strongly endothermic. The possible chain terminating steps are

\[ \text{Cl} \cdot + X \longrightarrow \text{ClX} \tag{4} \]
\[ R \cdot + X \longrightarrow RX \tag{5} \]
\[ \text{Cl} + \text{Cl} + M \longrightarrow \text{Cl}_2 + M \tag{6} \]
\[ R \cdot + \text{Cl} \cdot \longrightarrow \text{RCl} \tag{7} \]
\[ R \cdot + R \cdot \longrightarrow R_2 \tag{8} \]

In the photochemical reaction, if the reverse reaction \(-2\) is unimportant and reaction (4) is the only chain terminating step

\[ R_{\text{HCl}} = \frac{2I_{\text{abs}} k_2 (\text{RH})}{k_4 (X)} \]

When quadratic termination is important, the general expression is

\[ R_{\text{RCl}} = \frac{2I_{\text{abs}} k_3 (\text{Cl}_2)}{M^{\frac{1}{2}} (k_6 \alpha^2 + k_7 \alpha + k_8)^{\frac{1}{2}}} \]

where \( \alpha = \frac{k_3 (\text{Cl}_2)}{k_2 (\text{RH})} \)

Hence/
Hence when reaction (6) is all important.

\[
\frac{R_{RCI}}{R} = \frac{\frac{1}{2} I^{\frac{1}{2}} \pi \frac{1}{2} k_2 (RH)}{k_6 \odot \frac{1}{2} M^{\frac{1}{2}}}
\]

whereas when (7) and (8) are predominant

\[
\frac{R_{RCI}}{R} = \frac{2 \pi \frac{1}{2} I^{\frac{1}{2}} \odot \frac{1}{2} k_3 (Cl_2)}{ \left( k_3 k_7 (Cl_2) / k_2 (RH) + k_8 \right)^{\frac{1}{2}}}
\]

For the thermal reaction, the same expressions apply provided \(2I_{abs}\) is replaced by \(k_7 (Cl_2)\).

Inhibition by hydrogen chloride has been recorded in very few cases.

Chlorination of Methane. Pease & Walz examined the thermal chlorination of methane and showed that an equimolar amount of hydrogen chloride was produced for the chlorine consumed. Methyl chloride was the main chloro-alkane with smaller amounts of methylene dichloride, chloroform and carbon tetrachloride. When chlorine was present in excess, the mixtures were explosive. In absence of oxygen they found

\[\frac{R_{CH_4}}{k (Cl_2)(CH_4)}\]

whereas in presence of oxygen:

\[\frac{R_{CH_4}}{k (Cl_2)^{\odot^2} / (O_2)}\]

This suggests that the termination reactions were respectively

\[Cl + X \rightarrow CIX \text{ with } X \text{ constant and } CH_3 + O_2 \rightarrow \text{ inactive products. These rate expressions are similar to those obtained for the hydrogen-chlorine reaction and suggest a close resemblance of mechanism.}\]

This similarity was supported by Jones & Bates in the oxygen rich chlorination of methane. Coehn & Cordes calculated a chain length of 4 in the photochemical reaction.

From/
From their results, Schumacher showed that $E_{2}$ for $\text{CH}_4$ is less than 8 k. cal. Tamura also investigated the photochemical reaction and concluded that $E_{2} < 6.2$ k. cal. He also found that the rate varied with $I_{\text{abs}}^{1/2}$. This observation has been confirmed by Ritchie & Winning although at high intensities the rate varied with $I_{\text{abs}}$. This result implies that at low $I_{\text{abs}}$ quadratic termination occurs while at high $I_{\text{abs}}$ the termination process involves only one chain carrier. This is the reverse of what might have been expected and Ritchie & Winning were forced to propose that

$$\text{Cl}^{-} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_2^{-} + \text{M}$$  \hspace{1cm} (14)
$$\text{Cl}_2^{-} + \text{Cl}_2 \rightarrow 3\text{Cl}_2$$  \hspace{1cm} (15)

operated at high $I_{\text{abs}}$ values, whereas normal quadratic termination occurred at low $I_{\text{abs}}$. The addition of inert gases increased the extent of quadratic termination. There is still, however, some doubt as to the correct interpretation of these results.

Further evidence for the propagating steps are obtained from the work of Bogdandy & Polanyi who initiated methane-chlorine mixtures with sodium vapour. Hydrogen chloride and methyl chloride were produced by

$$\text{Na} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{Cl}^{-}$$
$$\text{Cl}^{-} + \text{CH}_4 \rightarrow \text{CH}_3^{-} + \text{HCl}$$
$$\text{CH}_3^{-} + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^{-} + \text{termination steps}.$$  

\text{Chlorination of Ethane.}
Ethane was chlorinated both thermally and photochemically by Rust & Vaughan. Inhibition of the reaction occurred in the presence of oxygen or olefins while the thermal reaction could be initiated by tetra-ethyl lead at low temperatures. A chain process was suggested and these workers found in the thermal process that

\[ \text{R}_2\text{HCl} = k (\text{C}_2\text{H}_6)(\text{Cl}_2) \]

This suggests that the termination step is 1st order with respect to the chlorine atoms and is possibly their removal on the walls.

Tetra ethyl lead was also shown to initiate the thermal chlorination of propane while a chain length of 10 was recorded by Yuster & Reyerson. These workers showed that packing the reaction vessel reduced the rate and came to the conclusion that chain termination occurred on the walls. The principal products were hydrogen chloride, normal and iso propyl chlorides.

The overall kinetics of the chlorination of aliphatic hydrocarbons is thus still somewhat obscure, but as with the hydrogen-chlorine reaction the uncertainty attaches not to the initiation or propagation reactions but to the chain terminating step. The general scheme of reactions (1), (2) and (3) is well established, (-2) is almost certainly unimportant, while chain termination varies with the reaction conditions and may be any of (4), (6), (7), (8) and (14).
Chlorination of Chloroform. The chlorination of chloroform to carbon tetrachloride has been more exhaustively studied than that of any aliphatic hydrocarbon. The presence of only one hydrogen atom in the molecule ensures no di-substituted products and simplifies the reaction. However in this, as in the other chlorinations discussed, although the initiation and propagating steps are well established, the terminating step is still doubtful.

Schwab and Priess examined the reaction by the discharge tube method and obtained as products, hydrogen chloride, carbon tetrachloride and possibly some hexa chloroethane. Schumacher & Wolff showed that the experimental rate expression was

\[ R_C = kT \cdot (Cl^2)^1 \]

They assumed that the termination process was

\[ 2C\ Cl^2 + Cl = 2C\ Cl_4 \] (16)

and from the temperature coefficient between 50\(^\circ\) and 60\(^\circ\)C calculated that \( E_2 \sim 5k\text{ cal.} \), \( E_2 \sim 4.3 k\text{ cal.} \) and \( E_1 \sim 0 k\text{ cal.} \). Schumacher & Sundhoff revised the value of \( E_2 \) to \( 3k\text{ cal.} \) from studies on the inhibition by alcohol and ammonia of the photo-oxidation of chloroform. If, however, \( E_5 \) is as large as 8 k. cal. it is conceivable that reaction (2) might also occur. Reaction (2) is exothermic to the extent of 12 k. cal. and therefore \( E_2 = 16 - 20 k\text{ cal.} \). Hence reaction (2) is unlikely to be significant in the presence of (3). This was confirmed experimentally by Schumacher & Wolff and also by Winning who found no inhibition by hydrogen chloride in the gas phase. Work in the liquid phase, however, suggests/
suggests that inhibition by hydrogen chloride of the reaction in carbon tetrachloride solution may occur.

Newton & Rollefson have produced fairly convincing evidence that the back reaction \((\sim2)\) does occur to a limited extent in the gas phase photo chlorination of chloroform. It was found that some deutero-chloroform was produced when chloroform was chlorinated in the presence of deuterium chloride. Hence

\[
D\text{ Cl} + C\text{ Cl}_3 \rightarrow C\text{ D Cl}_3 + \text{Cl}.
\]

appears to occur to a certain extent, unless exchange occurs on the walls. Additional evidence for \((12)\) was furnished by the competitive chlorination of chloroform and deutero-chloroform. The results showed that

\[
k_2 \frac{CHCl_3}{CDCl_3}
\]

was not independent of the extent of the reaction. These workers also demonstrated the formation of considerable amounts of hexa chloroethane, indicating that one of the chain terminating steps involves the production of this compound

\[
C\text{ Cl}_3 + C\text{ Cl}_3 \rightarrow C_2\text{ Cl}_6.
\]

The mechanism of the chlorination of chloroform and other chlorinated hydrocarbons has been considerably clarified in recent years by Goldfinger and co-workers. Using a competitive method in which the substitution of chlorine in pentachloroethane was compared with the addition process to tetrachloroethylene

\[
C_2\text{ HCl}_5 + \text{Cl}_2 \rightarrow C_2\text{ Cl}_6 + \text{HCl} \quad n = 0
\]

\[
C_2\text{ Cl}_4 + \text{Cl}_2 \rightarrow C_2\text{ Cl}_6 \quad n = -1.
\]

The/
the chain terminating steps were shown to be
\[ \begin{align*}
C_2 Cl_5^\cdot + Cl^- \rightarrow & \text{ inactive} \\
C \cdot Cl^\cdot + C Cl\cdot \rightarrow & \text{ products.}
\end{align*} \]

The photochlorination of chloroform, alone and in competition
with tetra chloroethylene has been studied between 70\(^\circ\)C and 155\(^\circ\)C. The
mechanism employed was
\[ \begin{align*}
Cl_2 + hv \rightarrow 2Cl^\cdot \quad & \text{(1)} \\
Cl^\cdot + CHCl_3 \rightarrow C Cl_3^\cdot + HCl \quad & \text{(2)} \\
C Cl_3^\cdot + Cl_2 \rightarrow C Cl_4^\cdot + Cl^- \quad & \text{(3)} \\
Cl^\cdot + Cl^- + M \rightarrow Cl_2 + M \quad & \text{(6)} \\
Cl^\cdot + CCl_3^\cdot \rightarrow & \text{ inactive} \quad & \text{(7)} \\
CCl_3^\cdot + CCl_3^\cdot \rightarrow & \text{ products} \quad & \text{(8)}
\end{align*} \]

The reaction was followed photometrically and manometrically. No
thermal reaction was found to occur at these temperatures.

The order of the reaction was calculated by van't Hoff's
method. By plotting log (initial rate) against log (initial chlorine
pressure) the reaction order under the initial conditions was obtained.
This order was found to vary slightly with the
\[ \frac{P (Cl_2)}{P (CHCl_3)} \]
ratio, having a value of \(3/2\) when this ratio was unity. It was
shown that this result could be explained if reactions (2), (3) and
(6) are unimportant
\[ -n Cl_2 = \frac{I_{abs} k_3 (Cl_2)}{k_3 k_7 (Cl_2) / k_2 (CHCl_3) + k_{8,9}} \]

This/
This mechanism explains the experimental facts of the chloroform chlorination such as the production of hexa chloroethane and the variation of the order of the reaction with the chlorine pressure. At high \((\text{Cl}_2) / (\text{HCl}_3)\) ratios, reaction (7) gains in importance as the chain terminating step at the expense of (8). The ratios \(k_2 \frac{k_3}{k_7}\) and \(k_3^2 \frac{1}{k_8}\) have been obtained over a range of temperatures and lead to minimum values for \(E_2\) and \(E_3\) of 6.5 and 5.3 kcal respectively.

Goldfinger and co-workers conclude that the van't Hoff method is a more delicate test of mechanism than the integration methods, partly because the order of a reaction can be followed as the reaction proceeds.

(b) Competitive Chlorinations. The determination of absolute rate constants of the separate reactions involved in the chlorination of hydrocarbons is beset by the following difficulties:

1. doubts as to the precise mechanism of the chain process, in particular the terminating steps and possible back reactions. Depending on the termination reaction the overall rate leads to either \(k_2\) or \(k_3\).

2. the effect of impurities on the chain length, leading to irreproducible overall rates.

3. practical difficulty in maintaining and measuring the chlorine atom concentration.

Many/
Many of these difficulties disappear when measurements are made of the relative rates of chlorination of two hydrocarbons $R_aH$ and $R_bH$ or of two or more positions in the same hydrocarbon. The assumptions must be made that

(a) the chain propagating steps are similar for both chlorinations

\[ R-H + \text{Cl} \rightarrow R^+ + \text{H-Cl} \quad (2) \]

\[ R^+ + \text{Cl}_2 \rightarrow R-\text{Cl} + \text{Cl}^- \quad (3) \]

(b) the chains are reasonably long, i.e. greater than 100 units in length.

(c) no back reactions of type \((-2)\) occur.

The relative rates of hydrogen abstraction by chlorine atoms \((2)\) can be calculated from either the relative amounts of the chlorides subsequently produced by \((3)\) or the relative amounts of the hydrocarbons consumed. In this technique it matters little whether the chlorine atoms are produced photolytically or thermally.

Haas, McBee & Weber were the first to apply this competitive method to the chlorination of aliphatic hydrocarbons. Propane and isobutane were chlorinated thermally between $50^\circ C$ and $600^\circ C$ in a flow system, using high hydrocarbon and chlorine pressures. The mixtures of isomeric propyl and isobutyl chlorides were analysed by fractional distillation. It was shown that the rates of chlorine atom attack on the different carbon-hydrogen bonds available obeyed the law tert $> sec > primary$. From the data available on the ratio of isomeric chlorides produced,
produced, Arrhenius plots of \( \log k_{\text{sec}}/k_{\text{prim}} \) and \( \log k_{\text{tert}}/k_{\text{iso Bu}} \) against \( 1/T^0 \) may be constructed. These plots curve badly and give unreliable results due to the occurrence of extensive polysubstitution, and pyrolysis of products at the higher temperatures. Steiner and Watson used their high temperature results to obtain values for \( (E_2 \text{ prim.} - E_2 \text{ sec}) \) in propane and \( (E_2 \text{ prim} - E_2 \text{ tert}) \) in iso-butane of 1.35 and 1.74 kcal/mole respectively. However, the present work has shown that these values are seriously in error, being much too large.

Chambers and Ubbelohde studied the gas phase photochlorination of various C5 - C8 paraffins. Using a flow system with product analysis they concluded that the overall rate of monochlorination increases with chain length and decreases with chain branching, while for normal paraffins the reactivity of the secondary relative to the primary positions appear to decrease as the chain lengthens, a trend supported by other workers. From results for \( k_{\text{sec}}/k_{\text{prim}} \) per H atom in \( \text{n-hexane at } 86^\circ \text{C and } 238^\circ \text{C}, \) values for \( (E \text{ prim.} - E \text{ sec}) \) of 900 kcal/mole and \( A_{\text{sec}}/A_{\text{prim.}} \) of unity may be calculated.

Pritchard, Pyke and Trotman-Dickenson studied the chlorination of the following mixtures: hydrogen-methane, methane-methyl chloride, methane-ethane, ethane-ethyl chloride, ethane-propane, ethane-iso butane, ethane-neopentane and ethane-cyclopentane. These mixtures of hydrocarbons were sealed in small bulbs together with chlorine, thermostated and illuminated. The hydrocarbon uptake in each case was measured using a controlled temperature still, and gave results for the relative rates of chlorine atom/
atom attack on each molecule as a whole. The main defect of this method is that no differentiation can be made between chlorine atom attack at different positions in the same molecule.

Using a value for $k_2$ of hydrogen obtained from the results of other workers, the absolute rate constants for each alkane or alkyl chloride were obtained. It was found that the activation energies decreased on ascent of the alkane series from 3.85 k. cal. for methane, 1.6 for ethane to 0.7 k. cal. for neo-pentane. An anomalous result occurred in the cases of methyl and ethyl chlorides. The substitution of chlorine for hydrogen in the methane molecule had an activating effect giving $E = 3.4$ k. cal. while the chlorine in ethane had a deactivating effect giving $E = 1.5$ k. cal. These workers found no experimental evidence of any back reaction (-2).

Since (-2) is in competition with (3) it is most likely to occur when $E_2 - E_3$ is low, i.e. when reaction 2 is thermoneutral and the value of $E_2$ is low. Such is the case for neo-pentane and methane. The back reaction (-2) $\text{C}_2\text{H}_5^- + \text{HCl} \rightarrow \text{C}_2\text{H}_4^- + \text{Cl}^-$ has been studied by Cvetanovic and Steacie who photolysed acetone in the presence of hydrogen chloride. Both this and

$$\text{Cl}^- + \text{C}_2\text{H}_3\text{COCH}_3 \rightarrow \text{HCl} + \text{C}_2\text{H}_2\text{COCH}_3$$

occur and from the collision yield at 28°C they estimate that $E_{-2} \ll 5$ k. cals/mole.

Goldfinger and co-workers competed the chlorine substitution in methylene dichloride, chloroform and penta chloro ethane with the addition of chlorine to tetra chloro ethylene. The chlorination of/
of tetra chloro ethylene was studied alone and from the observed lifetime of the reaction chains an absolute value for the rate constant of the termination process $k_{4c} = 10^{11.6 \pm 0.3} \text{cc. mole sec.}$

$$C \text{Cl}_5^- + C \text{Cl}_5^- \rightarrow \text{products} \quad (4c)$$

was obtained. Although many of the activation energies may be obtained absolutely this value is necessary for a knowledge of the absolute $A$ factors for the chlorine attack on the chloro alkanes studied. For methylene dichloride, chloroform and penta chloro ethane the activation energies obtained were $5.5, 6.5$ and $5.4$ k. cal./mole respectively while the corresponding $A$ factors were $10^{14.3}, 10^{14.6}$ and $10^{13.9}$ cc. mole sec. per H atom. The $A$ factor per H atom obtained for ethane by Pritchard, Pyke and Trotman-Dickenson was $10^{13.3}$ cc. mole sec, so that the presence of chlorine atoms in the chloro-alkanes appears to increase the entropy of activation. Goldfinger suggests that this result can be explained if free rotation exists in the activated complex. However, with a large number of chlorine atoms present in the molecule, any free rotation would appear to be unlikely. Considerable doubt must also be placed on the high values of the activation energies obtained, since these are not self consistent (see Ref. 49 in which the data lead to two values for $E_2$ for chloroform of $10.5$ k. cal./mole. and $6.5$ k.cals/mole). In addition to this Knox, in unpublished work, has obtained activation energies for the chlorine attack on methylene dichloride and chloroform in the region of $3.5$ to $4.0$ k. cal.

In the competitive chlorination of chloroform and deuterochloroform, by extrapolation of the $k_{2H} / k_{2D}$ values back to zero reaction,
reaction, Newton & Rollefson obtained
\[
\frac{k_{2H}}{k_{2D}} = 1.4 \pm 0.2 \exp (710 \pm 90/RT)
\]
for
\[
\begin{align*}
C_-H Cl_3^- + Cl^- &\rightarrow C Cl_3^- + HCl & k_{2H} \\
C_-D Cl_3^- + Cl^- &\rightarrow C Cl_3^- + DC1 & k_{2D}
\end{align*}
\]
They showed that the changes in the classical translation, rotation, vibration and electronic partition functions in substituting a D atom for an H atom both in the original molecule and in the activated complex were negligible and hence, assuming a transmission coefficient ratio of unity, \[A \frac{k_{2H}}{k_{2D}}\] should be 1.0. They calculated an activation energy difference on the assumption that it was due to the difference in zero-point energies for the C-H and C-D stretching vibrations which are in the direction of the reaction co-ordinate. This theoretical value of 1,080 cal. can be reduced to 710 cal. if it is assumed that the Cl atom tends to increase the vibration of the H and D atoms in a plane perpendicular to the C-H-Cl line. The C-H frequency must be changed from 1215 cm\(^{-1}\) to 1720 cm\(^{-1}\) and the C-D frequency from 909 cm\(^{-1}\) to 1284 cm\(^{-1}\). If it is assumed that the ratio of the frequency factors is determined by the number of times that the hydrogen and deuterium atoms are moving in a direction favourable for reaction and that this ratio is given by the ratio of the C-H and C-D stretching frequencies then \[A \frac{k_{2H}}{k_{2D}} = 1.33.\]

Hass, McBee & Weber observed that chlorination of hydrocarbons produced roughly similar results if carried out at 300°C in the gas phase or 25°C in the liquid phase. They showed that the relative rates of substitution of primary - secondary - tertiary hydrogen atoms/
atoms by chlorine under these conditions were 1.0 - 3.25 - 4.43. An explanation of the apparently lower specificity of chlorine atom attack in the liquid phase involves the 'cage effect' which is believed to operate in this phase. The present work has shown the results of Hass, et alia to be unreliable and the above conclusion should be regarded with suspicion.

The effects of substituents on the rates of free radical chlorination at the different remaining positions in a hydrocarbon have been studied in the gas phase and to a much greater extent in the liquid phase. Ash & Brown have found it possible to arrange twelve groups in order of decreasing activating effect on adjacent positions in hydrocarbons: 

\[ \text{C}_6\text{H}_5 > \text{C}_2\text{H}_5 > \text{H} > \text{OOC} \cdot \text{C}_2\text{H}_3 > \text{C}_2\text{H}_2\text{Cl} > \text{C}_2\text{H}_3\text{Cl} > \text{SiCl}_3 > \text{CO}_2\text{H} > \text{Cl} > \text{OOC} \cdot \text{Cl} > \text{OOC} \cdot \text{C}_2\text{Cl}_3 > \text{C}_2\text{Cl}_3 > \text{F}_3 \.] 

From an examination of the effect of solvent on the relative reactivities of sixteen different carbon-hydrogen bonds towards atomic chlorine, Russell concluded that two separate effects operate to cause differing reactivities. These are (a) the stability of the incipient hydrocarbon free radicals and (b) the availability of electrons to the carbon-hydrogen bond from the rest of the molecule. When the activation energy of the chlorine atom attack is fairly high (as in \( \text{CH}_4 \)), the \( \text{C} - \text{H} \) bond has to lengthen to a considerable extent for the production of the activated complex \( \text{C} - \cdot \cdot \cdot \text{H} - \cdot \cdot \cdot \text{Cl} \). The magnitude of the bond strength (dependent on the stability of the incipient hydrocarbon radical) influences the activation energy and hence the presence of a chlorine atom in the original molecule will tend to activate the remaining positions because/
because of a general decrease in bond strength. When the activation energy is low, the C - H bond being attacked is not so extended in the activated complex. The activation energy is now determined to a greater extent by the willingness of the rest of the molecule to give electrons to the H - - - Cl bond. This energy will tend to be governed by the inductive I effect, leading to deactivation in the presence of a chlorine atom in the molecule, since chlorine being electronegative has a -I effect.

This explanation resolves the anomalous results for methyl chloride and ethyl chloride as well as conforming to the general conclusions of Ash & Brown.

The method of the present work was outlined by Know who chlorinated methane-ethane mixtures and obtained relative rate constants from the ratios of methyl and ethyl chlorides produced. This value of

\[
\frac{k_{Et}}{k_{Me}} = 3.85 \exp \left(2,810 \pm 45/RT\right)
\]

agrees excellently with the results of Pritchard, Pyke and Trotman-Dickenson. This agreement was encouraging and suggested that the method of product analysis should be extended to those cases beyond the scope of the method involving the examination of hydrocarbon consumption. The analysis of small quantities of isomeric chlorides obtained from a static system was only made possible by the use of gas chromatography.
(3) Theory of Reaction Rates.

The Arrhenius Equation.

Towards the end of the 19th century van't Hoff suggested that the logarithm of the rate constant of a reaction should bear a linear relationship to the reciprocal of the absolute temperature. Arrhenius showed that this was the case for a number of reactions and that

\[ \ln k = \text{constant} - \frac{E}{RT} \]

This gives

\[ k = A e^{-\frac{E}{RT}} \]

where \( A \) and \( E \) are constants characteristic of the reaction, \( R \) is the gas constant and \( T \) is the absolute temperature. Arrhenius suggested that before reaction could take place, the reactant molecules must become activated, and that an equilibrium exists between normal and activated molecules.

The Maxwell - Boltzmann distribution law states that the fraction of molecules in a gas possessing an energy in excess of \( E \)

is proportional to \( e^{-\frac{E}{RT}} \). The value of \( E \) in the Arrhenius equation was thus considered as the energy necessary for the formation of an activated molecule.

Calculation of the Energy of Activation. \( 'E' \)

A possible method of calculating activation energies was proposed by London using the methods of quantum mechanics. He pointed out that since many chemical reactions do not involve any electronic transitions, it is possible to represent the state of an electron by a single function throughout the chemical reaction. London derived an approximate expression for the potential energy of a system of three atoms \( X, Y \) and \( Z \) each having/
having one unpaired $S-$ electron

$$P.E. = A + B + C = \left\{\frac{1}{2}\left[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2\right]\right\}^{1/2}$$

where $A$, $B$ and $C$ are the coulombic interactions of the pairs of electrons on the atoms $X$ and $Y$, $Y$ and $Z$ and $Z$ and $X$ respectively and $\alpha$, $\beta$ and $\gamma$ are the corresponding resonance or exchange energies.

The values of $A$, $B$, $C$, $\alpha$, $\beta$ and $\gamma$ depend on the interatomic distances and hence the $P.E.$ of the system can be calculated for all possible interatomic distances to give a 'potential energy surface' for each $X - - Y - - Z$ angle. Since the reaction

$$X + YZ \rightarrow XY + Z$$

must follow a path over these surfaces, the assumption that most of the systems will follow the easiest path leads to the energy of activation. A further assumption is made that the easiest line of approach of the $X$ atom is along the line of centres of the $Y$ and $Z$ atoms. Thus only one potential energy surface need be considered.

The calculation of the coulombic and exchange energies, however, present difficulties even for the simplest system. This has been attempted by Eyring & Polanyi in the reaction

$$H\cdot + H_{2p} = H_{2o} + H\cdot$$

by the semi-empirical method using the assumption that the coulombic energies are definite fractions of the total coulombic and exchange energies of the two atoms concerned. The fractions will be characteristic of the atoms but are generally between 10 and 20%. The total energies $A + \alpha$, $B + \beta$ and $C + \gamma$ are obtained by supplying spectroscopic data to the/
the appropriate Morse equation.

It is impossible, however, to produce the necessary data for potential energy surfaces of relatively more complicated reactions such as the one under study

\[ \text{Cl}^- + \text{R} - \text{H} \longrightarrow \text{R}^- + \text{H} - \text{Cl}. \]

The progress of this reaction can be indicated by means of a Morse-type graph (Figure 1). Curve 1 is the potential energy diagram of the hydrocarbon \( \text{R} - \text{H} \) where \( d_{\text{H Cl}} = \infty \). Curve 2 is the potential energy diagram of the activated complex where symmetrical stretching of \( \text{R} - \text{H} - \text{Cl} \) occurs. \( d_{\text{H Cl}} \) varies with \( d_{\text{R H}} \). Curve 3 is the potential energy diagram for the repulsion of \( \text{R}^- \) by the molecule \( \text{H Cl} \).

In this \( d_{\text{H Cl}} = \infty \) \( d_{\text{H Cl}} \).

Figure 2 indicates the possible variation of potential energy of the system as the reaction proceeds. The position of highest energy involves a 'transition state' or 'activated complex' and the height of this above the energy of the reactants is the energy of activation \( E \).

Several attempts have been made to relate the activation energies of bimolecular reactions to the strength of the bond which is broken but without much success. This point will be discussed later.

The Collision Theory. In bimolecular reactions, if the \( e^{-E/RT} \) part of the Arrhenius equation indicates the fraction of the total collisions which involves sufficient energy for reaction to occur, then the \( A \) factor should be related to the total number of collisions. From kinetic theory the rate of collisions between \( A \) and \( B \)
and B in the gas phase is

\[ Z = n_A n_B \sigma_{AB}^2 \left[ 8 \pi k T \frac{(m_A + m_B)}{m_A m_B} \right]^{\frac{1}{2}} \text{ molecules cc. sec}^{-1} \]

where \( n_A \) and \( n_B \) are the concentrations in molecules per cc. of the species of molecular masses \( m_A \) and \( m_B \) respectively, \( \sigma_{AB} \) is the mean collision diameter of A and B and \( k \) is the Boltzmann constant.

\[ k = \sigma_{AB}^2 \left[ 8 \pi k T \frac{(m_A + m_B)}{m_A m_B} \right]^{\frac{1}{2}} e^{-E/RT} \text{ molecules cc. sec}^{-1} \]

\[ -E/RT \text{ molecules cc. sec}^{-1} \]

\[ Z \cdot e^{-E/RT} \text{ molecules cc. sec}^{-1} \]

\( Z \) is known as the collision number and is the number of collisions per second when there is only one molecule of each reactant per cc.

The rate constants of many gas phase reactions do conform to the above equation, while reactions in solution and many other gas reactions take place much more slowly, or in a few cases more rapidly than the predicted rate and necessitate the introduction of a 'steric factor' \( P \).

\[ k = P \cdot Z \cdot e^{-E/RT} \]

Theory of Absolute Reaction Rates. Whereas the collision theory of bimolecular reactions does not consider the configuration of the transition state, the theory of absolute reaction rates does and predicts the rate constant from a knowledge of the concentration of activated complexes present.

Consider the formation of the activated complex \( M^+ \)

\[ A + B \rightarrow M \rightarrow \text{products} \]

The/
The rate of the reaction is equal to the concentration of $\mathbf{M}^+$ at the top of the energy barrier multiplied by the frequency of crossing the barrier. Hence rate of reaction = \[ c^+ \cdot \frac{\bar{v}}{\delta} \]

where $c^+$ is the number of complexes in unit volume along a distance $\delta$ at the top of the barrier in the transition state, and $\bar{v}$ the normal translational velocity is assumed to be the mean velocity of crossing. These complexes can be treated as normal molecules having concentration $c^+$ with no vibration in the reaction co-ordinate if

\[ c^+ = c^+ \cdot \left( \frac{2 \pi m^* kT}{\hbar} \right)^{1/2} \delta \]

where \( \left( \frac{2 \pi m^* kT}{\hbar} \right)^{1/2} \delta \) is the partition function for translation in the reaction co-ordinate with $m^*$ the effective mass of the complex. By kinetic theory $\bar{v}$ the mean velocity of crossing the barrier is \( \left( \frac{2kT}{\pi m^*} \right)^{1/2} \) but only half the complexes are moving in the one direction.

\[ \therefore \text{Rate of reaction} = c^+ \cdot \left( \frac{2 \pi m^* kT}{\hbar} \right)^{1/2} \left( \frac{kT}{2\pi m^*} \right)^{1/2} \frac{1}{\delta} \]

\[ = c^+ \cdot \frac{kT}{\hbar} \]

It has been assumed that all complexes passing over the barrier complete the reaction. This is not always the case and a transmission coefficient $\mathcal{K}$ is necessary. For many reactions $\mathcal{K}$ is close to unity.

Since rate of reaction = $k \cdot c_A \cdot c_B$,

\[ k = \frac{kT}{\hbar} \cdot \frac{c^+}{c_A c_B} = \frac{kT}{\hbar} \cdot \mathcal{K}^+ \]

where $K^+$ is the equilibrium constant for the activation process and can be obtained/
be obtained from thermodynamic relationships.

\[- \Delta G^\ddagger = RT \ln K^\ddagger\]

and

\[\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger\]

\[k = \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R - \Delta H^\ddagger/RT}\]

Now

\[\frac{E_{ex}}{RT^2} = \frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_c}{dT}\]

\[E_{ex} = RT + \Delta u^\ddagger = RT + \Delta H^\ddagger - p \Delta V^\ddagger\]

where \(E_{ex}\) is the experimental activation energy obtained from the Arrhenius equation, \(\Delta u^\ddagger\) is the increase in internal energy for the activation process and \(\Delta V^\ddagger\) is the accompanying increase in volume.

\[p \Delta V^\ddagger = \Delta n^\ddagger \cdot R \cdot T\]

for \(\Delta n^\ddagger = -1\) as in \(A + B \rightarrow M^\ddagger\)

\[k = e^{\frac{E_{ex}}{RT}} \cdot \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R}\]

Thus the theory of absolute reaction rates predicts a value for the experimental \(A\) factor of

\[e^{\frac{kT}{h} \cdot e^{\Delta S^\ddagger/R}}\]

This applies to a bimolecular reaction of the type

\[X + Y = Z \rightarrow X - Y + Z\]

which proceeds through a single activation complex. \(\Delta S^\ddagger_{c}\) is the entropy of activation at constant concentration and can be calculated if the entropies of the complex and reactants are known

\[\Delta S^\ddagger = \Delta S^\ddagger_{\text{trans}} + \Delta S^\ddagger_{\text{rot}} + \Delta S^\ddagger_{\text{vib}}\]

Since \(\Delta S^\ddagger_{c}\) depends on temperature the \(A\) factor should be calculated for the mid temperature within the experimental range.
METHOD OF PRESENT WORK AND CALCULATION OF RESULTS.

The object of this work was to determine accurately the relative rate constants for the attack of chlorine atoms on different hydrocarbons and on different carbon-hydrogen bonds in the one molecule.

The mechanism assumed for the chlorination of the hydrocarbons studied is

\[
\text{Cl}_2 + \text{hv} \rightarrow 2 \text{Cl}.
\]  

(1)

\[
\text{Cl}^- + \text{R}_a \rightarrow \text{R}_a^+ + \text{HCl}
\]  

(2a)

\[
\text{R}_a^+ + \text{Cl}_2 \rightarrow \text{R}_a\text{Cl} + \text{Cl}^-. 
\]  

(3a)

+ termination processes.

The rate of removal of the hydrocarbon is

\[-R_{R_a}^\text{H} = k_2a (R_a\text{H})(\text{Cl}^-)\]

If another hydrocarbon is chlorinated simultaneously

\[-R_{R_b}^\text{H} = k_2b (R_b\text{H})(\text{Cl}^-)\]

provided that the chain propagating steps are similar.

Hence

\[
\frac{R_{R_a}^\text{H}}{R_{R_b}^\text{H}} = \frac{k_2a (R_a\text{H})}{k_2b (R_b\text{H})}
\]

\[
= \frac{\frac{d(R_a\text{H})}{dt}}{\frac{d(R_b\text{H})}{dt}} = \frac{d(R_a\text{H})}{d(R_b\text{H})}
\]

Therefore

\[
\frac{\frac{d(R_a\text{H})}{k_2a (R_a\text{H})}}{\frac{d(R_b\text{H})}{k_2b (R_b\text{H})}} = \text{and/}
\]
and by integration

\[ \frac{k_{2a}}{k_{2b}} = \frac{\ln \left( \frac{(R_a H)_i}{(R_a H)_f} \right)}{\ln \left( \frac{(R_b H)_i}{(R_b H)_f} \right)} \]

where \( i \) and \( f \) indicate initial and final concentrations respectively.

If the amount of reaction is small the approximation can be made that

\[ \ln \left( \frac{(R_b H)_i}{(R_b H)_f} \right) = \frac{\Delta (R_b H)}{(R_b H)} \]

Therefore

\[ \frac{k_{2a}}{k_{2b}} = \frac{\Delta (R_a H) \cdot (R_b H)}{\Delta (R_b H) \cdot (R_a H)} \]

If the reaction chains are long, it can be assumed that, for the hydrocarbon removed, an equivalent amount of chloride is produced.

\[ \frac{k_{2a}}{k_{2b}} = \frac{(R_a Cl)(R_b H)}{(R_b Cl)(R_a H)} \]

where \((R_a Cl)\) and \((R_b Cl)\) are the concentrations of chlorination products while \((R_a H)\) and \((R_b H)\) are the initial concentrations of the hydrocarbons.

For chlorination at different points in the one hydrocarbon, leading to different chloride products

\[ \frac{k_{2a}}{k_{2b}} = \frac{(R_a Cl)}{(R_b Cl)} \]

In this work the relative pressures of hydrocarbons in the reaction mixture were measured while the chlorides produced were analysed.
analysed by gas chromatography.

By studying the chlorination of the various mixtures at different temperatures, Arrhenius plots of \( \log_{10} \frac{k_{2a}}{k_{2b}} \) against \( \frac{1}{T^0} \) were obtained.

The method of least squares, in the treatment of these results, gave values for the difference in activation energies \( E_{2b} - E_{2a} \) and the relative 'A factors' \( A_{2a}/A_{2b} \). The experimental A factors depend on the number of similar carbon-hydrogen bonds per molecule, and so relative 'A factors per atom' were obtained by making allowance for this number. The mixtures methane-hydrogen, propane-ethane, n butane-ethane, iso butane-ethane, neo pentane-propane, cyclopropane-ethane and cyclobutane-propane have been chlorinated and together with the previous results for ethane-methane and the absolute rate constant for hydrogen, absolute rate constants for the chlorine attack on the following bonds have been obtained: \( 1^H \) in methane, ethane, propane, n butane, iso butane and neo pentane, \( 2^H \) in propane, n butane, cyclopropane and cyclobutane, and \( 3^H \) in iso butane.
(2) MATERIALS

Hydrogen was obtained from a B.O.G. cylinder. It was dried by passage through phosphorus pentoxide.

Nitrogen was obtained from a B.O.G. cylinder and was stated to be oxygen free.

Chlorine was obtained from an I.C.I. cylinder. The middle fraction was collected and freed from water by distillation from a trap at -80°C to the trap of a 1 litre storage bulb at -194°C.

Methane was obtained from a B.O.G. cylinder. This contained a small amount of ethane which would have caused interference owing to its much higher rate of chlorination. This impurity was removed by pre-chlorination.

A 2 litre bulb containing methane at a pressure of 40 cm Hg and chlorine at a pressure of 4 cm Hg was exposed to sunlight for 12 hours. The chlorides, most of the ethane giving ethyl chloride, were frozen out and the middle fraction of methane was collected in a pump-down trap. The methane was distilled into a trap at -194°C attached to the storage bulb from a trap at -80°C to remove any water.

Ethane was obtained from a B.O.G. cylinder. It contained 1.2% ethylene.

Propene was obtained from a cylinder gifted by I.C.I. This contained 0.6% iso butane and traces of ethane and propylene.

iso Butane was obtained from a cylinder gifted by B.P.

n Butane was obtained from a cylinder gifted by B.P.

iso Pentane was obtained from an ampoule supplied by D.S.I.R., Chemical Research Laboratories, Teddington.

Cyclo Propane was obtained from a B.O.G. (Medicinal) cylinder.
**Cyclo Butane** was prepared by photolysis of cyclopentanone. 12 ml. of cyclopentanone (B.D.H. Lab. Reagent) were sealed in an evacuated 5-l. pyrex bulb, heated to 150° - 200°C in an air bath and illuminated with ultraviolet light from a 250 watt Hg vapour lamp for 7 days. After breaking the seal and pumping off the carbon monoxide, a mixture of ethylene, cyclobutane and butenes was obtained by distillation, leaving behind unreacted cyclopentanone and polymerised material. Pure cyclobutane was obtained by passing the mixture through the analytical gas chromatography column. The identity of cyclobutane was checked by infra-red analysis.

All the above hydrocarbon vapours were freed from water by distillation from a trap at - 80°C to one at - 194°C. In view of the nature of the experiments, small amounts of impurities of the order of 1% would not influence the accuracy of the results, except in the case of methane, and no special steps were taken to purify the reagents further.

**Mercury diphenyl** was obtained as B.D.H. laboratory reagent. This was found to be impure and was purified by fractional sublimation. The impurity possibly diphenyl, sublimed first while the fraction subliming in vacuo between 100 and 120°C was found to be pure mercury diphenyl (m.p. 120°C).

**Hydrogen chloride** was prepared by dropping conc. H₂SO₄ into conc. HCl. The evolved hydrogen chloride was collected in a trap at - 194°C and later freed from water by distillation from a trap at - 80°C.

**Methyl chloride** was obtained from an I.C.I. cylinder.

**Ethyl chloride** was obtained from a B.D.H. (Anesthetic) ampoule.

**Propyl chlorides**

**n-Butyl chlorides** — were obtained as B.D.H. Lab. Reagents.

**iso-Butyl chlorides**
(3) APPARATUS AND PROCEDURE

The chlorinations were carried out in a static system and the analyses were made by means of gas chromatography.

Kinetic System (see Figure 3) The apparatus was evacuated by means of a high-vac. oil pump together with a two stage mercury pump. The reaction vessel (R.V.) was of pyrex glass and had a volume of 82 ml. It possessed an inner thermometer well and a detachable outer jacket. When the vapours from a boiling liquid were used for thermostating the R.V., this outer jacket was used in conjunction with a small water condenser. In this way the whole R.V. acquired a constant temperature except for the small volume between the tap and the main R.V. As this part was made of capillary glass the effect on the reaction in the main R.V. was negligible. The outer jacket was covered with asbestos apart from an illumination 'window'. When a freezing mixture was used to thermostat the R.V. a pyrex, unsilvered Dewer vessel was used to hold the mixture. A pentane thermometer was used to measure the temperatures below 0°C.

The reaction vessel was thermostated by the following methods:

- Acetone + solid CO₂
- 79°C
- Chloroform + solid CO₂
- 68°C
- 50% H₂SO₄ + solid CO₂
- 35°C
- Ice
- 0°C
- Water at room temperature
- +20°C
- Boiling chloroform
- +61°C
- Boiling water
- +100°C
- Boiling chlorobenzene
- +132°C
- Boiling decalin
- +190°C
boiling methylsalicylate + 225°C
boiling H₂SO₄ + 327°C

Illumination: Illumination of the reaction mixture was by means of a 250W'Osram' projection lamp. In order to remove most of the infra-red rays from the light a 10% copper sulphate solution was used. This solution was placed in a round 600 ml. pyrex beaker between the projection lamp and the R.V. To prevent this solution from losing water by evaporation cold water was run through a spiral tube dipping into the solution. This beaker of copper sulphate solution also assisted in focusing the light on the R.V.

Preparation of Reaction Mixture: Silicone high vac. tap grease was used throughout the kinetic system. Chlorine was found to attack this tap grease slowly and so the chlorine was stored at liquid oxygen temperature in the trap attached to a 1 litre storage bulb. Hydrogen and the hydrocarbons were contained in 2 litre storage bulbs while the nitrogen was held in a 5 litre bulb. Chlorination mixtures were prepared in a 100 ml. darkened mixing vessel to prevent any photochemical reaction occurring before the mixture entered the reaction vessel. The pressures of gases in this mixing vessel were measured by means of a Bourdon spoon gauge. This spoon gauge was constructed of pyrex glass and had an optical lever system by which movements of the spoon were transferred to a small mirror which reflected light from a projector back to a centimetre scale. The movements of the spoon were damped by allowing the end of the spoon to dip into di-octyl phthalate. This system was calibrated by means of a mercury manometer and it was found that 1 cm. scale division corresponded/
corresponded to a pressure of 1.11 cm Hg.

Chlorine was first measured into the mixing vessel. The two competing hydrocarbons or hydrogen were then measured into the vessel in the required ratio. This ratio was the only quantity which had to be measured accurately until analysis of the products. The chlorine pressure was, however, measured to give an indication of the amount of chlorides to be expected when analysing. The pressure of the chlorine - hydrocarbon mixture was then increased to ~50 cm Hg. by allowing nitrogen to enter the mixing vessel. After this mixture had come to equilibrium it was allowed to enter the R.V. The tap of the R.V. was closed and the mixture illuminated for 30 minutes. To satisfy the conditions for the equation

\[
\frac{k_{2a}}{k_{2b}} = \frac{(R_C) (R_H)}{(R_{CI}) (R_{H})}
\]

and to ensure that secondary chlorination occurred to the smallest extent possible, the chlorine / hydrocarbons ratio was kept low (generally less than 1/10) where feasible. The presence of nitrogen in the reaction vessel was to ensure that no self heating of the reaction mixture occurred, although this precaution was hardly necessary in view of the low chlorine pressures used. Incidentally the nitrogen would help to decrease the frequency of termination processes on the walls.

**Sampling Procedure.** Two different methods of transferring the products of the reaction from the R.V. to the 'U' tube of the chromatography apparatus were used.

(a) A portion of the contents of the R.V. was allowed to enter the cold finger, the central tube of which was filled with liquid oxygen. After a short time, to/
to allow the hydrocarbons and chlorides to freeze out on the central tube, the nitrogen and hydrogen chloride were pumped off through the chromatography 'U' tube at \(-194^\circ C\). The oxygen in the cold finger was replaced with hot water and the hydrocarbons and chlorides were allowed to distil into the 'U' tube. Complete transfer was effected by pumping through the 'U' tube after most of the material had distilled across.

(b) For less volatile chloride products a simpler method of transfer was used. This simply involved pumping the contents of the R.V. through the 'U' tube at \(-194^\circ C\).

Before either sampling procedure could be carried out after runs at \(-80^\circ C\) it was first necessary to bring the R.V. temperature up to room temperature to remove any of the chlorides which had been frozen out or adsorbed on the walls.

In the chlorination of hydrogen - methane mixtures an additional operation was involved in transferring the products of the reaction to the chromatography section. This was necessary since the product of the chlorination of hydrogen, hydrogen chloride, could not be detected in the analysis. Hydrogen chloride is either irreversibly absorbed by the column packing material or only comes through the column very slowly.

The products of the hydrogen - methane chlorinations were completely transferred to a 'U' tube packed with purified mercury diphenyl. The taps of the 'U' tube were then closed and the tube itself was heated to \(+80^\circ C\) for 5 minutes. It was found that by this technique all the hydrogen chloride present was converted into an equivalent amount of benzene. The products were then distilled into the chromatography 'U' tube. The transfer was completed by pumping through the 'U' tube.
ANALYSIS SECTION.

- Mercury Manometer
- Water Bubbler
- Buffering Vessels
- Thermostated Thermal Conductivity Gauges
- Analytical and Dummy Columns in Heating Jacket
- Needle Valve
- Hydrogen Cylinder

Fig. 4.
Gas Chromatography Apparatus. (See Figure 4) This apparatus was of conventional design having a pressure regulating device, sampling vessel, columns with packing and a detector.

Pressure Regulator. The carrier gas used was hydrogen. This was obtained from a B.o.C. cylinder and was dried through the $P_2O_5$ before passing through a needle valve. The hydrogen stream was then divided into two, part going through the columns and part going into water bubblers where a constant head of water ensured a constant hydrogen pressure. Any irregularities in the pressure caused by the creation of bubbles were evened out by means of 4 buffering vessels before the hydrogen stream entered the sampling vessel.

Sampling Vessel. This consisted of a double 'U' tube, through which the chlorination products could be pumped. By means of two 2-way taps the hydrogen flow prior to entering the columns could either pass through the 'U' tube or by-pass it completely. The products entered the hydrogen stream on being heated to +30°C.

Columns. Two identical columns were used. Through one passed the hydrogen stream after collecting the material for analysis from the 'U' tube, while the other was used as a 'dummy' column to supply hydrogen at a similar pressure to the second thermal conductivity gauge. The columns were of pyrex glass, 6-7 m.m. in internal diameter. The packing consisted of firebrick 25-52 B.S.S. mesh containing 25% w/w di-octyl phthalate. The di-octyl phthalate was evenly distributed on the firebrick by evaporation of a chloroform solution. The columns were both thermostated in a glass jacket which was heated electrically. Thus the separation of products effected on/
on the column could be controlled by

(a) Initial hydrogen pressure
(b) Length of columns
(c) Temperature of columns.

Detector. Thermal-conductivity cells were used throughout the work. A copper block (Fig. 5 is ½ actual size) had two channels drilled in it. Each channel had a tungsten filament, of resistance approximately 10 ohms, stretched along its axis. The carrier gas from each column was passed over a tungsten filament which was incorporated in a Wheatstone Bridge circuit. Each filament (see Fig. 6) was an arm in this circuit and the off-balance current was transferred to a moving-coil galvanometer. Using a projector lamp and a cm. scale the off-balance current was observed visually and could be plotted against time.

In Fig. 6 $G_1$ and $G_2$ represent the filaments of the thermal-conductivity gauges, $G_2$ having the lower resistance. Both $R_1$ and $R_2$ are standard resistances of 10 ohms. $R_4$ is a resistance box of resistances 0 - 8,000 ohms with the moving-coil galvanometer in series. $R_3$ is a variable resistance for zeroing the off-balance current through the galvanometer. The potential of 8 volts was supplied by four accumulators in series.

The sensitivity of the moving coil galvanometer could be varied by means of $R_4$ to suit the quantity of chlorides produced.

The off-balance current, generally observed at 12 second intervals, was plotted against time. The areas of the surfaces enclosed by the peaks and the normal base line were measured with a planimeter, and these indicated the molar concentrations of the various substances present in the chromatogram, provided/
provided that the relative sensitivities were known.

The relative sensitivities of substances under analysis were obtained by analysing known mixtures of authentic samples.

The sensitivities of all the hydrocarbon chlorides studied were identical to within 5% while the methyl chloride and benzene in the methane - hydrogen chlorinations had widely differing sensitivities.

This result is not surprising since hydrogen was used as the carrier gas; and the thermal conductivities of the hydrocarbon chlorides relative to the hydrogen value cannot differ to an appreciable extent.
RESULTS AND EXPERIMENTAL DETAILS.

1. CHLORINATION OF HYDROGEN - METHANE MIXTURES.

The chlorine, methane and hydrogen mixtures were prepared by the usual method, illuminated in the R.V. for the arbitrary time of 30 minutes and then passed into the special trap containing diphenyl mercury. It was found that complete replacement of the total hydrogen chloride by benzene occurred in 5 minutes at 80°C, after which the methyl chloride and benzene were analysed by gas chromatography.

A special method of determining the relative sensitivities of the detector to these substances had to be employed since benzene readily dissolved in tap grease, and this made the preparation of a standard methyl chloride-benzene mixture impossible.

Several runs were carried out in which methane was chlorinated alone. The products were analysed for methyl chloride and hydrogen chloride as before. Assuming that only mono-chlorination has occurred, the peaks for methyl chloride and benzene represent equimolar quantities.

\[
\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}
\]

This method of determining the relative sensitivities of methyl chloride and benzene gave the following results.

Run No./
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Area of Me Cl.</th>
<th>Area of Benzene</th>
<th>Ratio</th>
<th>Area of Me Cl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>1.63</td>
<td>3.08</td>
<td>0.53</td>
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<tr>
<td>46</td>
<td>0.89</td>
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<td>0.47</td>
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<tr>
<td>47</td>
<td>1.81</td>
<td>3.50</td>
<td>0.52</td>
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</tr>
<tr>
<td>48</td>
<td>1.28</td>
<td>2.68</td>
<td>0.48</td>
<td></td>
</tr>
</tbody>
</table>

From these figures the detector is 0.5 times as sensitive towards methyl chloride as to benzene.

Small amounts of methylene dichloride (up to 2%) were formed but were neglected in all calculations.

It was noted that variation of the initial hydrogen-methane ratio did not produce any regular variation in the ratio of the rate constants for that temperature. This suggests that the rate expression used was adequate.

In most runs the initial pressures of hydrogen and methane were chosen so that the ratios of benzene to methyl chloride in the analyses were fairly constant. This ensures that any error in calibration is transferred to the relative A factors rather than the activation energy difference.

The chromatography column was 120 c.m. in length, 6mm. internal diameter, and was packed with 25-52 mesh firebrick (Fosalsil No 6) moistened with 25% w/w of dioctyl phthalate. The operating temperature was 100°C and under these conditions methyl chloride appeared after 2½ minutes while benzene appeared after 10 minutes.

Since/
Since reaction (3) produces an equal amount of hydrogen chloride to that produced by reaction (2)
\[
\text{Cl}^- + \text{H}_2 \rightarrow \text{HCl} + \text{H}^-
\]
\[
\text{H}^- + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}^-
\]
the total amount of hydrogen chloride produced from the chlorination of hydrogen is twice that produced by reaction (2) which is the value necessary for (HCl) in
\[
\frac{k_{\text{Me}}}{k_H} = \frac{(\text{CH}_3 \text{Cl})(\text{H}_2)}{(\text{HCl})(\text{CH}_4)}
\]
\[
= \frac{(\text{H}_2)(\text{CH}_3 \text{Cl})}{(\text{CH}_4)(\frac{1}{2} \text{ total HCl from H}_2)}
\]
while \((\text{total HCl from H}_2) \equiv (\text{total HCl}) - (\text{HCl from CH}_4 \text{ chlorination})\)
The results for the hydrogen-methane chlorinations are given in Tables 1 and 2.
Example of Calculation.

Run 24.  
Temp. of R.V. = 100°C.

Pressures of reactants in mixing vessel.

- **Chlorine** = 0.1 cm Hg.
- **Methane** = 1.0 cm Hg. (CH₄)
- **Hydrogen** = 1.85 cm Hg (H₂)
- **Nitrogen** = 50 cm Hg.

Area of methyl chloride = 1.30 units.
Area of benzene = 6.22 units.

Now methyl chloride is 0.5 times as sensitive as benzene.

∴ Molar ratio of (methyl chloride/total HCl) = 2.60/6.22.

and molar ratio of (methyl chloride/total HCl from H₂) = 2.60/3.62

\[
\frac{(H_2)}{(CH_4)} = \frac{1.85}{1.0} \quad \text{and} \quad \frac{(CH_3 Cl)}{\text{total HCl from H}_2} = \frac{2.60}{1.81}
\]

\[
\frac{k_{Me}}{k_H} = \frac{(H_2)(CH_3 Cl)}{(CH_4)(\frac{1}{2} \text{ total HCl from H}_2)} = 2.66.
\]

where \( k_{Me} \) and \( k_H \) are the rate constants for

\[
\text{Cl}^- + \text{CH}_4 \quad \rightarrow \quad \text{CH}_3^+ + \text{HCl}
\]

and

\[
\text{Cl}^- + \text{H}_2 \quad \rightarrow \quad \text{H}^+ + \text{HCl}
\]

respectively.
<table>
<thead>
<tr>
<th>RUN</th>
<th>° C</th>
<th>(HYDROGEN)</th>
<th>(METHANE) added</th>
<th>(CH&lt;sub&gt;4&lt;/sub&gt;Cl)</th>
<th>log&lt;sub&gt;10&lt;/sub&gt; k&lt;sub&gt;H&lt;/sub&gt;</th>
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<td>5.30</td>
<td>1.68</td>
<td>2.19</td>
<td>1.942</td>
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</table>

* in mole---mole.
By the method of least squares on the complete data, the relative rate constants are

\[
\frac{k_{Me}}{k_H} = 0.30 \pm 0.03 \exp (1650 \pm 60 / RT).
\]

where the errors quoted are for 50% probability. This result agrees well with the result obtained by Pritchard, Pyke and Trotman-Dickenson of

\[
\frac{k_{Me}}{k_H} = 0.322 \exp (1650 / RT).
\]

This is a further example of the good agreement between the two methods of product analysis and hydrocarbon-consumption analysis.

<table>
<thead>
<tr>
<th>RUNS.</th>
<th>(10^3/T^3\alpha)</th>
<th>AVERAGE VALUE OF</th>
<th>(\log_{10} \frac{k_{Me}}{k_H})</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>38,40,41.</td>
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Figure 7 is the Arrhenius plot of the results in Table 1, while the above results are found in Figure 17.
Fig. 7.

Hydrogen / Methane.

Log $K_H / K_M$ vs. $1/T 	imes 10^3$. 

Points represent experimental data.
Note on the method of Least Squares. (For complete method, see Margenau & Murphy - 'The Maths. of Physics and Chemistry.')

For ease of calculation, a modified method of least squares analysis on the results in the Arrhenius plot was used.

1/T^0 \text{A} was chosen as the independent variable \(x\) and \(\log_{10} \frac{k_{2a}}{k_{2b}}\) as the dependent variable \(y\). The means of the \(x\) and \(y\) values were first obtained. These gave the point \((\overline{x}, \overline{y})\) which was assumed to lie on the best straight line through the points.

Where \(x = x - \overline{x}\) and \(y = y - \overline{y}\) the gradient \(m\) of the line giving the closest fit to the experimental points is given by

\[
m = \frac{\sum xy}{\sum x^2}.
\]

From the mean point \((\overline{x}, \overline{y})\) and the gradient \(m\), the Arrhenius parameters were calculated. The probable error \(P_m\) in the gradient \(m\) is

\[
P_m = 0.6745 \sqrt{\frac{\sum d^2}{(n-2) \sum x^2}}
\]

where \(d\) is the deviation of a point from the line in the direction of the \(y\) axis, and

\[
\sum d^2 = \sum x^2 \left[ \frac{\sum y^2}{\sum x^2} - \left( \frac{\sum xy}{\sum x^2} \right)^2 \right]
\]

From \(P_m\) are calculated the 50\% probability limits in the activation energy difference, and from this can be derived the corresponding limits in the relative \(A\) factors.
2. CHLORINATION OF ETHANE - PROPAVE MIXTURES.

The products from ethane + propane chlorinations were analysed for ethyl chloride, primary propyl chloride and secondary propyl chloride.

The chromatography column was 190 cm in length, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 50-55°C. Under these conditions the ethyl chloride appeared after 11 minutes, the sec. propyl chloride after 17 minutes and the pri. propyl chloride after 25 minutes. No other chloride products were observed.

Where $k_{Et}$, $k_{sPr}$ and $k_{pPr}$ are the rate constants of

$$\text{Cl}^{-} + \text{CH}_3\text{-CH}_3 \rightarrow \text{CH}_3\text{CH}_2^* + \text{HCl}$$

$$\text{Cl}^{-} + (\text{CH}_2)_2\text{CH}_2 \rightarrow (\text{CH}_2)_2\text{CH}_2^* + \text{HCl}$$

$$\text{Cl}^{-} + \text{CH}_2\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2^* + \text{HCl}$$

respectively, then

$$\frac{k_{sPr}}{k_{Et}} = \frac{(sPr \text{ Cl})(\text{ethane})}{(St \text{ Cl})(\text{propane})} \quad \frac{k_{pPr}}{k_{Et}} = \frac{(pPr \text{ Cl})(\text{ethane})}{(St \text{ Cl})(\text{propane})}$$

and

$$\frac{k_{sPr}}{k_{pPr}} = \frac{(sPr \text{ Cl})}{(pPr \text{ Cl})}$$

N.B. sPr = secondary propyl, pPr = primary propyl and

Et = ethyl.
Chlorinations were carried out at 321°C but these resulted in irreproducible relative rate constants and sec. propyl chloride/prim. propyl chloride ratios which were much lower than would be expected for this temperature. This suggests that decomposition of the propyl chlorides had occurred and that the secondary chloride had decomposed faster than the primary chloride.

This is probably the explanation of the curvature at high temperatures which occurs in the Arrhenius plots of the results of Hass, McBee and Weber.
Example of Calculation.

Run 18. Temperature = -28°C.

Pressures of reactants in mixing vessel

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Pressure (cm Hg)</th>
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<tr>
<td>Chlorine</td>
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</tr>
<tr>
<td>Ethane</td>
<td>4.35</td>
</tr>
<tr>
<td>Propane</td>
<td>3.00</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>50</td>
</tr>
</tbody>
</table>

Area for ethyl chloride = 2.03 units (Et Cl)

" " s. propyl chloride = 2.18 units (sPr Cl)

" " p. propyl chloride = 1.68 units (pPr Cl)

All these chlorides have the same sensitivity.

\[
\frac{k_{sPr}}{k_{Et}} = \frac{(sPr Cl)(ethane)}{(Et Cl)(propane)} = \frac{2.18}{2.03} \times \frac{4.35}{3.00} = 1.56.
\]

Similarly \( k_{sPr} = 1.20 \).

\( k = 1.0 \) and \( k = 1.30 \).
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<th>(PROPANE) added</th>
<th>AREA EtCl</th>
<th>AREA sPrCl</th>
<th>AREA pPrCl</th>
<th>( \log_{10} k_{sPr} )</th>
<th>( \log_{10} k_{pPr} )</th>
<th>( \log_{10} k_{sPr} )</th>
<th>( \log_{10} k_{pPr} )</th>
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</table>
By the method of least squares on the complete data as
given in table 3, the relative rate constants are

\[
\frac{k_{sPr}}{k_{Et}} = 0.78 \pm 0.012 \exp \left( \frac{360 \pm 10}{RT} \right),
\]

\[
\frac{k_{pPr}}{k_{Et}} = 1.11 \pm 0.025 \exp \left( \frac{40 \pm 10}{RT} \right),
\]

\[
\frac{k_{sPr}}{k_{pPr}} = 0.70 \pm 0.010 \exp \left( \frac{320 \pm 10}{RT} \right).
\]

### Table 4.

<table>
<thead>
<tr>
<th>RUNS.</th>
<th>(10^3/T\ A)</th>
<th>AVERAGE VALUES OF (k_{sPr})</th>
<th>AVERAGE VALUES OF (k_{pPr})</th>
<th>AVERAGE VALUES OF (k_{sPr}/k_{pPr})</th>
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</thead>
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The Arrhenius plots of the results in the above tables
are found in Figures 8 & 9 and Figure 18.
ETHANE / 1\textsuperscript{RY} IN PROPAINE.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure8}
\caption{Graph showing \( \log \frac{K_{PPR}}{K_{ET}} \) vs. \( \frac{1}{T} \times 10^3 \).}
\label{fig:8}
\end{figure}
Fig. 9

Ethane / 2Ry in Propane.

$\log K_{SP} / K_{EF}$ vs $1/T \times 10^3$. 

Data points plotted on a graph showing a linear relationship between $1/T \times 10^3$ and $\log K_{SP} / K_{EF}$.
3. CHLORINATION OF ETHANE - n BUTANE MIXTURES.

The products from ethane + n butane chlorinations were analysed for ethyl chloride, secondary n butyl chloride and primary n butyl chloride.

The chromatography column was 190 cm. in length, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 60 - 65°C. The hydrogen pressure at the start of the columns was 6 cm. Hg. and under these conditions the ethyl chloride appeared after \(3\frac{1}{2}\) minutes, the secondary butyl chloride after 12 minutes and the primary butyl chloride after 18 minutes. No other chloride products were observed.

Where \(k_{snBu}\) and \(k_{pnBu}\) are the rate constants of

\[\begin{align*}
\text{Cl}^- + \text{CH}_3\text{(CH}_2)_2\text{CH}_3 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{HCl} \\
\text{Cl}^- + \text{CH}_3\text{(CH}_2)_2\text{CH}_3 & \rightarrow \text{CH}_3\text{(CH}_2)_2\text{CH}_2 + \text{HCl}
\end{align*}\]

respectively, then

\[\frac{k_{snBu}}{k_{Et}} = \frac{(snBu \text{ Cl})(ethane)}{(Et \text{ Cl})(n \text{ butane})} \quad ; \quad \frac{k_{pnBu}}{k_{Et}} = \frac{(pnBu \text{ Cl})(ethane)}{(Et \text{ Cl})(n \text{ butane})}\]

and

\[\frac{k_{snBu}}{k_{pnBu}} = \frac{(snBu \text{ Cl})}{(pnBu \text{ Cl})}\]

N.B. \(snBu\) = secondary n butyl and \(pnBu\) = primary n butyl.
<table>
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<th>RUN</th>
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<th>(ETHANE) (n-BUTANE) added cm Hg---cm Hg</th>
<th>AREA EtCl</th>
<th>AREA sBuCl</th>
<th>AREA pBuCl</th>
<th>$k_{sBu}$</th>
<th>$k_{pBu}$</th>
<th>$k_{sBu}^{10}$</th>
<th>$k_{pBu}^{10}$</th>
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<td>0.72</td>
<td>1.04</td>
<td>0.53</td>
<td>0.3292</td>
<td>0.0363</td>
<td>0.2927</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>2.56 1.57</td>
<td>1.05</td>
<td>1.54</td>
<td>0.64</td>
<td>0.3860</td>
<td>0.1239</td>
<td>0.2632</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>2.13 1.43</td>
<td>0.85</td>
<td>1.27</td>
<td>0.68</td>
<td>0.3448</td>
<td>0.0734</td>
<td>0.2714</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>2.70 1.42</td>
<td>1.03</td>
<td>1.22</td>
<td>0.64</td>
<td>0.3526</td>
<td>0.0723</td>
<td>0.2801</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>2.45 1.41</td>
<td>0.85</td>
<td>1.08</td>
<td>0.57</td>
<td>0.3441</td>
<td>0.0668</td>
<td>0.2777</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
By the method of least squares on the complete data as given in table 5, the relative rate constants are

\[
\frac{k_{\text{snBu}}}{k_{\text{Et}}} = 0.94 \pm 0.056 \exp \left( \frac{770 \pm 35}{RT} \right).
\]

\[
\frac{k_{\text{pnBu}}}{k_{\text{Et}}} = 0.89 \pm 0.04 \exp \left( \frac{250 \pm 30}{RT} \right).
\]

\[
\frac{k_{\text{snBu}}}{k_{\text{pnBu}}} = 1.05 \pm 0.05 \exp \left( \frac{520 \pm 35}{RT} \right).
\]

\[\text{TABLE 6.}\]

<table>
<thead>
<tr>
<th>RUNS</th>
<th>(10^3/T^o)A</th>
<th>(\log_{10}k_{\text{snBu}})</th>
<th>(\log_{10}k_{\text{pnBu}})</th>
<th>(\log_{10}k_{\text{snBu}}/k_{\text{pnBu}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>29, 31, 32, 33, 36.</td>
<td>4.88</td>
<td>0.6102</td>
<td>0.2065</td>
<td>0.6019</td>
</tr>
<tr>
<td>25, 26, 27, 28.</td>
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<td>0.6965</td>
<td>0.2112</td>
<td>0.4872</td>
</tr>
<tr>
<td>18, 19, 20, 21, 23, 39.</td>
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<td>0.5322</td>
<td>0.1404</td>
<td>0.3917</td>
</tr>
<tr>
<td>3, 6, 8, 9.</td>
<td>2.68</td>
<td>0.4241</td>
<td>0.0872</td>
<td>0.3366</td>
</tr>
<tr>
<td>10, 11, 12, 13, 14.</td>
<td>2.15</td>
<td>0.3513</td>
<td>0.0745</td>
<td>0.2770</td>
</tr>
</tbody>
</table>

The Arrhenius plots of the results in the above tables are found in Figures 10 & 11 and Figure 19.
Fig. 10.

Ethane / 1 Ry in n-Butane.

-log K^PnBu_4/K^t^E

1 / T x 10^3

2.0 3.0 x 10^3

4.0 5.0

30 20 10
4. **CHLORINATION OF ETHANE - iso BUTANE MIXTURES.**

The products from ethane - iso butane chlorinations were analysed for ethyl chloride, tertiary iso butyl chloride and primary iso butyl chloride.

The chromatography column was 190 cm. long, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 60 - 65°C. The hydrogen pressure at the start of the columns was 3 cm. Hg. and under these conditions the ethyl chloride appeared after 7 minutes, the tertiary butyl chloride after 14½ minutes and the primary butyl chloride after 27 minutes. No other chloride products were observed.

Where \( k_{tiBu} \) and \( k_{piBu} \) are the rate constants of

\[
\begin{align*}
\text{Cl}^- + (\text{CH}_3)_2\text{CH} & \rightarrow (\text{CH}_3)_2\text{C}^- + \text{HCl} \\
\text{Cl}^- + (\text{CH}_3)_3\text{CH} & \rightarrow (\text{CH}_3)_3\text{CH}^- + \text{HCl}
\end{align*}
\]

respectively, then

\[
\frac{k_{tiBu}}{k_{Et}} = \frac{(tiBu \text{ Cl})(ethane)}{(Et \text{ Cl})(iso butane)} ; \quad \frac{k_{piBu}}{k_{Et}} = \frac{(piBu \text{ Cl})(ethane)}{(Et \text{ Cl})(iso butane)}
\]

and

\[
\frac{k_{tiBu}}{k_{piBu}} = \frac{(tiBu \text{ Cl})}{(piBu \text{ Cl})} .
\]

The results of runs carried out at 134°C and 194°C were irreproducible and in all cases the tertiary/primary butyl chloride ratios were much lower than would be expected. This suggested that decomposition of the tertiary/
the tertiary butyl chloride was occurring at these temperatures, and this was supported by the fact that if short residence times (2-5 minutes) were used the relative rate constants approached the expected values. Further work at 194°C showed that

(a) a sample of tertiary butyl chloride gave 90% decomposition into iso butene and hydrogen chloride after 30 minutes residence in the reaction vessel.

(b) a ten fold excess of hydrogen chloride prevented this decomposition.

(c) the tertiary/primary chloride ratio from a run carried out in the presence of a ten fold excess of hydrogen chloride was much greater than the expected value if no decomposition had occurred.

(d) a sample of primary iso butyl chloride was partially (ca. 40%) converted into the tertiary chloride after 30 minutes residence in the reaction vessel and in the presence of a ten fold excess of hydrogen chloride. No iso butene was detected.

When runs were carried out at 100°C and 15°C with a chlorine:hydrogen chloride ratio of 1:10, the relative rate constants obtained were identical to those found in the absence of any added hydrogen chloride. This proves that either inhibition by hydrogen chloride is negligible or the production of the tertiary and primary chlorides is inhibited to the same extent. This latter case/
case is highly improbable, so that reaction (-2) is unimportant. 69

Barton & Onyon have shown that the decomposition of tertiary butyl chloride in glass reaction vessels is heterogeneous and only becomes reproducible after coating the walls. They found that extensive decomposition occurred at 137°C. Hence the decomposition of the iso butyl chlorides above 100°C is the obvious explanation of the curvature in the Arrhenius plots from the work of Hass, McBee & Weber on the chlorination of iso butane.

N.B.  \( \text{tiBu} \equiv \text{tertiary iso butyl} \)

\( \text{piBu} \equiv \text{primary iso butyl} \).
<table>
<thead>
<tr>
<th>RUN</th>
<th>T °C</th>
<th>(ETHANE) added (ISOHEXANE)</th>
<th>AREA ETCl</th>
<th>AREA tBuCl</th>
<th>AREA pBuCl</th>
<th>log₁₀ k&lt;sub&gt;Et&lt;/sub&gt;</th>
<th>log₁₀ k&lt;sub&gt;pBuEt&lt;/sub&gt;</th>
<th>log₁₀ k&lt;sub&gt;pBuEt&lt;/sub&gt;</th>
<th>log₁₀ k&lt;sub&gt;pBuEt&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
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<td>1.62 0.87</td>
<td>0.85</td>
<td>0.86</td>
<td>0.97</td>
<td>0.3257</td>
<td>0.3761</td>
<td>T.9479</td>
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</tr>
<tr>
<td>45</td>
<td>&quot;</td>
<td>1.59 0.86</td>
<td>0.85</td>
<td>1.41</td>
<td>0.94</td>
<td>0.4866</td>
<td>0.3104</td>
<td>0.1761</td>
<td>0.0000</td>
</tr>
<tr>
<td>46</td>
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<td>0.95</td>
<td>1.38</td>
<td>1.38</td>
<td>0.4610</td>
<td>0.4610</td>
<td>0.0902</td>
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<tr>
<td>47</td>
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<td>1.33</td>
<td>1.60</td>
<td>1.30</td>
<td>0.4014</td>
<td>0.3111</td>
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<td></td>
</tr>
<tr>
<td>48</td>
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<td>1.49 0.86</td>
<td>1.11</td>
<td>1.35</td>
<td>1.41</td>
<td>0.3288</td>
<td>0.3478</td>
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<tr>
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<td>1.17</td>
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<td>1.23</td>
<td>0.3736</td>
<td>0.3596</td>
<td>0.0136</td>
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<td>38</td>
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<td>0.60</td>
<td>0.58</td>
<td>0.3468</td>
<td>0.3320</td>
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<td>0.69</td>
<td>0.64</td>
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<tr>
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<td>0.96</td>
<td>1.42</td>
<td>1.30</td>
<td>0.3791</td>
<td>0.3410</td>
<td>0.0382</td>
<td></td>
</tr>
<tr>
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<td>1.00</td>
<td>0.4624</td>
<td>0.3160</td>
<td>0.1461</td>
<td></td>
</tr>
<tr>
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<td>-37</td>
<td>1.85 1.05</td>
<td>0.66</td>
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<td>0.76</td>
<td>0.1824</td>
<td>0.3071</td>
<td>T.8751</td>
<td></td>
</tr>
<tr>
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<td>1.65</td>
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<td>0.2732</td>
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</tr>
<tr>
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<td>0.81</td>
<td>0.96</td>
<td>1.31</td>
<td>0.2485</td>
<td>0.3033</td>
<td>T.8648</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>&quot;</td>
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<td>0.90</td>
<td>0.55</td>
<td>0.94</td>
<td>0.0414</td>
<td>0.2742</td>
<td>T.7672</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>&quot;</td>
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<td>0.99</td>
<td>0.81</td>
<td>1.34</td>
<td>0.1199</td>
<td>0.3387</td>
<td>T.7810</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>+2</td>
<td>2.19 2.10</td>
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<td>0.75</td>
<td>1.05</td>
<td>0.1858</td>
<td>0.3314</td>
<td>T.8537</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>&quot;</td>
<td>1.72 2.70</td>
<td>0.66</td>
<td>1.14</td>
<td>2.11</td>
<td>0.0418</td>
<td>0.2902</td>
<td>T.7328</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>&quot;</td>
<td>1.76 2.50</td>
<td>0.76</td>
<td>1.35</td>
<td>2.29</td>
<td>0.0969</td>
<td>0.2365</td>
<td>T.7705</td>
<td></td>
</tr>
<tr>
<td>34</td>
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<td>2.51 2.13</td>
<td>0.88</td>
<td>1.03</td>
<td>1.72</td>
<td>0.1399</td>
<td>0.3624</td>
<td>T.7772</td>
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</tr>
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<td>35</td>
<td>&quot;</td>
<td>1.91 2.09</td>
<td>0.90</td>
<td>0.43</td>
<td>1.37</td>
<td>0.1600</td>
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<td>36</td>
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<td>2.35 2.23</td>
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<td>1.14</td>
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</tr>
<tr>
<td>49</td>
<td>61</td>
<td>2.24 2.75</td>
<td>1.27</td>
<td>1.47</td>
<td>2.80</td>
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</tr>
<tr>
<td>51</td>
<td>&quot;</td>
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<td>2.31</td>
<td>0.9365</td>
<td>0.2961</td>
<td>T.6405</td>
<td></td>
</tr>
</tbody>
</table>
By the method of least squares on the complete data as given in table 7, the relative rate constants are

\[
\frac{k_{tibu}}{k_{Et}} = 0.18 \pm 0.016 \exp (1020 \pm 45 / RT).
\]

\[
\frac{k_{piBu}}{k_{Et}} = 1.30 \pm 0.067 \exp (220 \pm 25 / RT).
\]

\[
\frac{k_{tibu}}{k_{piBu}} = 0.13 \pm 0.01 \exp (800 \pm 40 / RT).
\]

<table>
<thead>
<tr>
<th>RUNS.</th>
<th>(10^3/T^0A)</th>
<th>AVERAGE VALUES OF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(k_{tibu}/k_{Et})</td>
</tr>
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</tr>
<tr>
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<td>0.3921</td>
</tr>
<tr>
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<td>0.1335</td>
</tr>
<tr>
<td>30,31,32,34,35,36.</td>
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<td>0.1104</td>
</tr>
<tr>
<td>49,51,52,53.</td>
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<td>1.2454</td>
</tr>
<tr>
<td>60,61,62,63,64.</td>
<td>2.68</td>
<td>1.8341</td>
</tr>
</tbody>
</table>
Ethane / $1^{RY}$ in iso Butane.
Ethane $3^R_Y$ in iso-Butane.
5. CHLORINATION OF PROPANE - NEO PENTANE MIXTURES.

It had been hoped to compete the chlorination of neopentane against that of ethane, in order to keep the number of intermediates as low as possible when the absolute rate constants were being derived from the absolute value for hydrogen. However, the neopentane interfered with the analysis of ethyl chloride and it was necessary to compete the chlorination of neopentane against that of the primary position in propane. Accordingly, the products from the propane - neopentane chlorinations were analysed for primary propyl chloride and neopentyl chloride.

The chromatography column was 320 cm. long, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 75°C. The hydrogen pressure at the start of the columns was 11 cm. Hg. and under these conditions primary propyl chloride appeared after 11% minutes and neopentyl chloride after 25 minutes.

Where \( k_{pPr} \) and \( k_{neoP} \) are the rate constants of

\[
Cl^- + CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2^- + HCl
\]

and

\[
Cl^- + (CH_3)_4C \rightarrow (CH_3)_2C.CH_2^- + HCl
\]

respectively,

\[
k_{neoP} = \frac{(neoP Cl)(propane)}{k_{pPr}} \frac{(pPr Cl)(neopentane)}
\]

N.B. neoP \( \equiv \) neopentyl and pPr \( \equiv \) primary propyl.
<table>
<thead>
<tr>
<th>RUN</th>
<th>°C</th>
<th>( \frac{\text{PROPANE}}{\text{NEOPENTANE}} ) added cm Hg</th>
<th>AREA ( \text{pFrCl} )</th>
<th>AREA ( \text{neoPeCl} )</th>
<th>( \frac{k_{\text{neoPe}}}{k_{\text{pFr}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>-70</td>
<td>0.96</td>
<td>0.87</td>
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<td>0.3464</td>
</tr>
<tr>
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<td>0.87</td>
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</tr>
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<td>1.97</td>
<td>1.37</td>
<td>0.3043</td>
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<td>1.95</td>
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<td>0.2422</td>
</tr>
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<td>1.70</td>
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</tr>
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<td>1.13</td>
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<td>0.2792</td>
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<td>61</td>
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<td>2.38</td>
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<td>1.53</td>
<td>2.24</td>
<td>2.10</td>
<td>0.2707</td>
</tr>
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</table>
By the method of least squares on the complete data as given in table 9, the rate constant ratio is

\[
\frac{k_{\text{neoFe}}}{k_{\text{pPr}}} = 1.65 \times 10^0 \exp \left( \frac{80 \times 20}{RT} \right).
\]

<table>
<thead>
<tr>
<th>RUNS</th>
<th>36, 37, 40, 41, 42</th>
<th>21, 22, 23, 24, 51, 52, 54</th>
<th>25, 26, 27, 28, 55, 56, 44, 45</th>
<th>38, 39, 43, 46, 47, 48, 49</th>
<th>16, 17, 29, 30, 31, 32, 33</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^3/T A.)</td>
<td>4.92</td>
<td>4.20</td>
<td>3.61</td>
<td>3.00</td>
<td>2.68</td>
</tr>
<tr>
<td>AVERAGE VALUE OF (k_{\text{neoFe}}/k_{\text{pPr}})</td>
<td>0.3177</td>
<td>0.2797</td>
<td>0.2755</td>
<td>0.2790</td>
<td>0.2764</td>
</tr>
</tbody>
</table>

The Arrhenius plots are in Figure 14 and Figure 18.
6. CHLORINATION OF ETHANE - CYCLOPROPANE MIXTURES.

The chlorination of cyclopropane alone was first studied. The chromatography column was 190 cm. long, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 70-75°C. The initial hydrogen pressure was 11 cm. Hg. and under these conditions three products of the chlorination of cyclopropane were observed. Peak A appeared after 3 minutes, peak B after 7 minutes and peak C after 32 minutes. All runs were carried out at 21°C and the results are indicated in the following table.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Area of Peak A</th>
<th>Area of Peak B</th>
<th>Area of Peak C</th>
<th>Area B/Area A</th>
<th>Area C/Area A</th>
<th>(Cl₂)/(C₃H₆)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.73</td>
<td>0.50</td>
<td>0.08</td>
<td>0.68</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
<td>0.46</td>
<td>0.18</td>
<td>0.46</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>6</td>
<td>0.34</td>
<td>0.05</td>
<td>0.03</td>
<td>0.15</td>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td>7</td>
<td>0.67</td>
<td>0.17</td>
<td>0.06</td>
<td>0.25</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>8</td>
<td>0.79</td>
<td>0.11</td>
<td>0.15</td>
<td>0.14</td>
<td>0.19</td>
<td>0.03</td>
</tr>
<tr>
<td>9</td>
<td>0.54</td>
<td>0.02</td>
<td>0.25</td>
<td>0.04</td>
<td>0.19</td>
<td>0.02</td>
</tr>
<tr>
<td>10</td>
<td>0.62</td>
<td>0.04</td>
<td>0.04</td>
<td>0.06</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>12</td>
<td>1.11</td>
<td>0.09</td>
<td>0.09</td>
<td>0.08</td>
<td>0.07</td>
<td>0.03</td>
</tr>
</tbody>
</table>

In run 9 the chlorine-cyclopropane mixture was allowed to remain in the mixing vessel for 15 minutes before the illumination was/
was commenced. In the other runs this period of time varied between 1 and 5 minutes.

Since the ratio Area B/Area A varied directly with the chlorine/cyclopropane ratio, it seemed possible that substance B was formed by chlorination of A, i.e. if peak A corresponds to chloro cyclopropane then peak B is probably a dichloro cyclopropane. A large quantity of substance A was collected as it left the chromatography column and was subjected to infra red analysis. The spectrum obtained was almost identical to that obtained by Slabey for mono chloro cyclopropane.

Since the Area C/Area A ratio bears little relationship to the chlorine/cyclopropane ratio and more especially because of the result from Run 9, a dark reaction was suggested. This could possibly be the addition of chlorine to the cyclopropane with ring rupture to give a dichloro propane. It is rather difficult to see how this could occur in the absence of any free radical substitution, and as yet the dark reaction is not understood.

It was found possible to reduce the formation of substance C to negligible proportions by admitting the chlorine directly to the reaction vessel and illuminating as soon as the cyclopropane was added.

Hence mono chloro cyclopropane was the principal product of the chlorination of cyclopropane when

(a) the 'dark' reaction was prevented in the above manner and

(b) the chlorine/cyclopropane ratio was kept as low as possible/
possible (preferably below .02).

These conditions were maintained throughout the competitive experiments. The chlorine was first placed in the reaction vessel and the ethane-cyclopropane mixture was admitted from the mixing vessel with immediate illumination.

The same column was used in the analysis for ethyl chloride and cyclo propyl chloride with the operating temperature 60°C and an initial hydrogen pressure of 4 cm. Hg. The ethyl chloride appeared after 6 minutes and the cyclopropyl chloride after 14 minutes.

Where $k_{Et}$ and $k_{cPr}$ are the rate constants of:

$$\begin{align*}
\text{Cl}^- + \text{CH}_3 - \text{CH}_3 & \rightarrow \text{CH}_3 \text{CH}_2^- + \text{HCl} \\
\text{Cl}^- + \text{CH}_2 & \rightarrow \text{CH}_2^- + \text{HCl}
\end{align*}$$

respectively,

$$\begin{align*}
k_{cPr} &= \frac{(cPr \text{ Cl})(ethane)}{k_{Et}} = \frac{(Et \text{ Cl})(cyclopropane)}{k_{Et}}
\end{align*}$$

N.B. $Et = \text{ethyl}$ and $cPr = \text{cyclopropyl}$. 
<table>
<thead>
<tr>
<th>RUN</th>
<th>T Θ</th>
<th>ETHANE (CYCLOPROPANE) added</th>
<th>AREA EtCl</th>
<th>AREA cPrCl</th>
<th>k_{Et}</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>21</td>
<td>0.20 10.65</td>
<td>0.85</td>
<td>0.14</td>
<td>3.4771</td>
</tr>
<tr>
<td>42</td>
<td>&quot;</td>
<td>0.27 15.45</td>
<td>0.40</td>
<td>0.08</td>
<td>3.5441</td>
</tr>
<tr>
<td>51</td>
<td>&quot;</td>
<td>0.108 16.75</td>
<td>0.38</td>
<td>0.34</td>
<td>3.3892</td>
</tr>
<tr>
<td>48</td>
<td>61</td>
<td>0.165 17.38</td>
<td>1.48</td>
<td>0.71</td>
<td>3.6580</td>
</tr>
<tr>
<td>49</td>
<td>&quot;</td>
<td>0.165 15.50</td>
<td>0.95</td>
<td>0.38</td>
<td>3.6294</td>
</tr>
<tr>
<td>50</td>
<td>&quot;</td>
<td>0.164 17.36</td>
<td>0.46</td>
<td>0.24</td>
<td>3.6928</td>
</tr>
<tr>
<td>52</td>
<td>100</td>
<td>0.108 16.37</td>
<td>0.39</td>
<td>0.54</td>
<td>3.9609</td>
</tr>
<tr>
<td>53</td>
<td>&quot;</td>
<td>0.140 17.25</td>
<td>0.75</td>
<td>0.96</td>
<td>2.0161</td>
</tr>
<tr>
<td>54</td>
<td>&quot;</td>
<td>0.154 16.53</td>
<td>0.61</td>
<td>0.61</td>
<td>3.9694</td>
</tr>
<tr>
<td>55</td>
<td>&quot;</td>
<td>0.134 16.82</td>
<td>0.90</td>
<td>0.89</td>
<td>3.6965</td>
</tr>
<tr>
<td>45</td>
<td>132</td>
<td>0.193 11.20</td>
<td>0.59</td>
<td>0.33</td>
<td>3.9900</td>
</tr>
<tr>
<td>46</td>
<td>&quot;</td>
<td>0.194 10.75</td>
<td>0.35</td>
<td>0.17</td>
<td>3.9430</td>
</tr>
<tr>
<td>47</td>
<td>&quot;</td>
<td>0.23 16.40</td>
<td>1.16</td>
<td>0.82</td>
<td>3.9969</td>
</tr>
<tr>
<td>60</td>
<td>&quot;</td>
<td>0.184 15.00</td>
<td>1.49</td>
<td>1.43</td>
<td>2.0708</td>
</tr>
<tr>
<td>62</td>
<td>&quot;</td>
<td>0.098 14.10</td>
<td>0.91</td>
<td>1.42</td>
<td>2.0342</td>
</tr>
<tr>
<td>56</td>
<td>192</td>
<td>0.254 13.86</td>
<td>0.82</td>
<td>0.80</td>
<td>2.2630</td>
</tr>
<tr>
<td>58</td>
<td>&quot;</td>
<td>0.161 16.13</td>
<td>1.11</td>
<td>2.44</td>
<td>2.3412</td>
</tr>
<tr>
<td>59</td>
<td>&quot;</td>
<td>0.120 15.85</td>
<td>0.38</td>
<td>0.92</td>
<td>2.2610</td>
</tr>
<tr>
<td>24</td>
<td>220</td>
<td>0.35 11.38</td>
<td>0.29</td>
<td>0.25</td>
<td>4.265</td>
</tr>
<tr>
<td>43</td>
<td>&quot;</td>
<td>0.34 14.23</td>
<td>0.88</td>
<td>1.12</td>
<td>2.4829</td>
</tr>
<tr>
<td>44</td>
<td>&quot;</td>
<td>0.25 13.20</td>
<td>0.38</td>
<td>0.43</td>
<td>2.3263</td>
</tr>
</tbody>
</table>
By the method of least squares on the complete data as given in table 11, the rate constant ratio is

$$\frac{k_{cPr}}{k_{Et}} = 0.56 \pm 0.02 \exp \left( -3,100 \pm 30 / RT \right).$$

<table>
<thead>
<tr>
<th>RUNS</th>
<th>$10^3/T_A$</th>
<th>AVERAGE VALUE OF $\log_{10} \frac{k_{cPr}}{k_{Et}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23,42,51.</td>
<td>3.40</td>
<td>3.4701</td>
</tr>
<tr>
<td>48,49,50.</td>
<td>3.00</td>
<td>3.6601</td>
</tr>
<tr>
<td>52,53,54,55.</td>
<td>2.68</td>
<td>3.9607</td>
</tr>
<tr>
<td>45,46,47,60,62.</td>
<td>2.47</td>
<td>2.0070</td>
</tr>
<tr>
<td>56,58,59.</td>
<td>2.15</td>
<td>2.2884</td>
</tr>
<tr>
<td>24,43,44.</td>
<td>2.03</td>
<td>2.4119</td>
</tr>
</tbody>
</table>

The Arrhenius plots of the results in the above tables are found in Figure 15 and Figure 17.
7. **CHLORINATION OF PROPANE - CYCLOBUTANE MIXTURES.**

The cyclobutane interfered with the analysis of ethyl chloride so that it was necessary to compete the chlorination of cyclobutane against that of the primary position in propane.

The chlorination of cyclobutane produced only one product and this was assumed to be mono chloro cyclobutane. The products of competitive chlorinations were analysed for primary propyl chloride and cyclobutyl chloride.

The chromatography column was 190 cm. long, contained the 80:20 w/w mixture of firebrick and dioctyl phthalate and operated at 60°C. The initial hydrogen pressure was 7 cm. Hg. and under these conditions the *primary* propyl chloride appeared after 6 minutes and the cyclobutyl chloride after 17 minutes.

Where $k_{Pr}$ and $k_{cBu}$ are the rate constants of

$\text{Cl}^- + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^- + \text{HCl}$

and

$\text{Cl}^- + \text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2\text{CH}_2^- + \text{HCl}$

respectively

$$\frac{k_{cBu}}{k_{Pr}} = \frac{(cBu\text{ Cl})(\text{propane})}{(Pr\text{ Cl})(\text{cyclobutane})}$$

N.B. $cBu \equiv$ cyclobutyl and $Pr \equiv$ primary propyl.
<table>
<thead>
<tr>
<th>RUN</th>
<th>T C</th>
<th>(PROPANE) (CYCLOBUTANE) added cm Hg</th>
<th>AREA pPrCl</th>
<th>AREA cBuCl</th>
<th>log&lt;sub&gt;10&lt;/sub&gt; ( \frac{k_{cBu}}{k_{pPr}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>-32</td>
<td>8.49</td>
<td>0.60</td>
<td>0.93</td>
<td>0.5647</td>
</tr>
<tr>
<td>15</td>
<td>&quot;</td>
<td>10.16</td>
<td>1.10</td>
<td>1.54</td>
<td>0.5652</td>
</tr>
<tr>
<td>16</td>
<td>&quot;</td>
<td>8.14</td>
<td>0.80</td>
<td>1.44</td>
<td>0.5888</td>
</tr>
<tr>
<td>17</td>
<td>&quot;</td>
<td>9.22</td>
<td>0.95</td>
<td>1.38</td>
<td>0.5307</td>
</tr>
<tr>
<td>2</td>
<td>+20</td>
<td>8.72</td>
<td>0.71</td>
<td>1.74</td>
<td>0.5769</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>12.68</td>
<td>1.60</td>
<td>1.71</td>
<td>0.5119</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>9.06</td>
<td>1.05</td>
<td>1.60</td>
<td>0.5159</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>9.50</td>
<td>1.05</td>
<td>1.64</td>
<td>0.5432</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>11.15</td>
<td>0.84</td>
<td>1.13</td>
<td>0.5289</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>8.34</td>
<td>0.93</td>
<td>1.60</td>
<td>0.4921</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>8.53</td>
<td>0.95</td>
<td>1.67</td>
<td>0.4835</td>
</tr>
<tr>
<td>18</td>
<td>&quot;</td>
<td>9.20</td>
<td>0.81</td>
<td>1.37</td>
<td>0.5191</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RUNS</th>
<th>( 10^3/T \times A )</th>
<th>AVERAGE VALUE OF ( \log_{10} \frac{k_{cBu}}{k_{pPr}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14,15,16,17</td>
<td>4.15</td>
<td>0.5623</td>
</tr>
<tr>
<td>2, 3,12,13</td>
<td>3.41</td>
<td>0.5370</td>
</tr>
<tr>
<td>4, 5, 6,18</td>
<td>2.68</td>
<td>0.5059</td>
</tr>
</tbody>
</table>

\[
\frac{k_{cBu}}{k_{pPr}} = 2.54 \pm 0.17 \exp \left( 175 \pm 40 / RT \right)
\]

from a least squares analysis of the complete results in Table 13.
Fig. 16.

1RY in Propane / Cyclobutane.

Log $\frac{K_{cb}^n}{K_{pp}^n}$ vs. $\frac{1}{T} \times 10^3$
Fig. 17.

\[ x + \log \frac{KR_{\ell}H}{KR_{c,H}} \]

1.0

0.0

2.0 3.0 4.0 5.0

\( \frac{1}{T} \times 10^3 \).

- \( R_a = H \), \( R_\ell = Me \), \( x = 0 \).
- \( R_a = Et \), \( R_\ell = cPr \), \( x = 3 \).
Fig. 18.

\[ x + \log \left( \frac{K \rho H}{K R_{\rho H}} \right) \]

\[ \frac{1}{T} \times 10^3 \]

- ○ \( R_a = E_T, R_\ell = s P_R \) \( x = 0.3 \)
- ● \( \cdot = E_T, \cdot = p P_R \) \( x = 0.3 \)
- + \( \cdot = p P_R, \cdot = s P_R \) \( x = 0.3 \)
- ● \( \cdot = p P_R, \cdot = \text{neo} P \) \( x = 0.0 \)
- ○ \( \cdot = p P_R, \cdot = c P_R \) \( x = 0.0 \)
Fig. 19

\[ x = \log \left( \frac{K_{RH}}{K_{R^0}} \right) \]

\[ \frac{1}{T} \times 10^3 \]

- \( R_a = Et, R_e = snBu \) \( x = 0.0 \)
- \( = Et, = pnBu \) \( = 0.0 \)
- \( = pnBu, = snBu \) \( = 0.0 \)
- \( = Et, = tiBu \) \( = 1.0 \)
- \( = Et, = piBu \) \( = 1.0 \)
- \( = piBu, = tiBu \) \( = 1.0 \)
DISCUSSION.

(1) **Calculation of absolute rate constants.**

The relative A factors and activation energy differences obtained from the Arrhenius plots are listed in Table 15. The relative rate constants for methane and ethane were obtained by Knox in excellent agreement with the results of Pritchard, Pyke and Trotman-Dickenson. The value for $k_{Et}/k_{Me}$ quoted in Reference 60 is in error, the correct expression being

$$k_{Et}/k_{Me} = 3.85 \exp (2,810 \pm 45 \text{cal/RT}).$$

The relative A factors are those for the chlorine atom attack on all equivalent positions in a molecule. The relative A factors per hydrogen atom (or C-H bond) are obtained by allowing for all equivalent positions in the molecule. Absolute rate constants have been derived from the absolute value for hydrogen.

$$k_H = 0.8 \times 10^{14} \exp (-5,500 \pm 200 \text{cal.mole}^{-1} \text{mole}^{-1} \text{cc sec}^{-1})$$

and are found in Table 16. The errors quoted do not take into account the error in $k$. In all cases (including hydrogen) the absolute A factor per molecule for attack on a particular type of bond is equal to the absolute A factor per hydrogen atom times the number of hydrogen atoms (per molecule) involved in these equivalent bonds.

(2) **Systematic errors.**

While the errors quoted in Tables 15 and 16 represent the/
### Table 15

Relative Rate Constants.

<table>
<thead>
<tr>
<th>Mixture chlorinated</th>
<th>$\frac{A_{Ra}}{A_{Rb}}$ per molecule</th>
<th>$\frac{A_{Ra}}{A_{Rb}}$ per H atom</th>
<th>$E_{Rb} - E_{Ra}$ cal. mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>0.30</td>
<td>0.15 ± 0.015</td>
<td>1650 ± 60</td>
</tr>
<tr>
<td>CH$_3$-H</td>
<td>3.65</td>
<td>2.97 ± 0.16</td>
<td>2310 ± 45</td>
</tr>
<tr>
<td>C$_2$H$_5$-H</td>
<td>1.11</td>
<td>1.11 ± 0.025</td>
<td>40 ± 10</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.78</td>
<td>2.84 ± 0.04</td>
<td>360 ± 10</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.89</td>
<td>0.89 ± 0.04</td>
<td>250 ± 30</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.94</td>
<td>1.41 ± 0.08</td>
<td>770 ± 35</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.30</td>
<td>0.87 ± 0.04</td>
<td>220 ± 25</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.18</td>
<td>1.08 ± 0.10</td>
<td>1100 ± 45</td>
</tr>
<tr>
<td>pri. C$_3$H$_7$-H</td>
<td>1.65</td>
<td>0.02 ± 0.02</td>
<td>80 ± 20</td>
</tr>
<tr>
<td>C$_2$H$_5$-H</td>
<td>0.56</td>
<td>0.56 ± 0.02</td>
<td>-3100 ± 30</td>
</tr>
</tbody>
</table>

The errors quoted in the above table are the 50% probability limits.
### Table 16.

**Absolute Rate Constants.**

<table>
<thead>
<tr>
<th>Type of bond attacked</th>
<th>R--H</th>
<th>$10^{-13} A_R$ per H atom</th>
<th>$E_R$ cal.mole. $^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H--H</td>
<td>4.0</td>
<td>5,500</td>
</tr>
<tr>
<td></td>
<td>CH₃--H</td>
<td>0.6 ± 0.1</td>
<td>3,850 ± 60</td>
</tr>
<tr>
<td>Primary.</td>
<td>C₂H₅--H</td>
<td>1.5 ± 0.2</td>
<td>1,040 ± 75</td>
</tr>
<tr>
<td></td>
<td>pri.C₂H₆--H</td>
<td>1.7 ± 0.2</td>
<td>790 ± 80</td>
</tr>
<tr>
<td></td>
<td>pri.nC₄H₉--H</td>
<td>1.4 ± 0.2</td>
<td>820 ± 80</td>
</tr>
<tr>
<td></td>
<td>pri.iC₄H₉--H</td>
<td>1.3 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>neo C₅H₁₁--H</td>
<td>1.4 ± 0.2</td>
<td>920 ± 80</td>
</tr>
<tr>
<td>Secondary.</td>
<td>sec.C₃H₇--H</td>
<td>3.6 ± 0.5</td>
<td>680 ± 75</td>
</tr>
<tr>
<td></td>
<td>sec.nC₄H₉--H</td>
<td>2.2 ± 0.3</td>
<td>270 ± 80</td>
</tr>
<tr>
<td></td>
<td>cyclo C₂H₅--H</td>
<td>0.9 ± 0.1</td>
<td>4,140 ± 80</td>
</tr>
<tr>
<td></td>
<td>cyclo C₄H₇--H</td>
<td>3.2 ± 0.4</td>
<td>825 ± 85</td>
</tr>
<tr>
<td>Tertiary.</td>
<td>tert.iC₄H₉--H</td>
<td>1.7 ± 0.3</td>
<td>20 ± 90</td>
</tr>
</tbody>
</table>

The errors quoted in the above table are the 50% cumulative probability limits, without consideration of the errors in the $A_R$ and $E_R$ values.
the probability that the best straight lines obtained from the Arrhenius plots are correct, no allowance has been made for the possibility of systematic errors. These may arise from

(a) an error in the absolute $k_\text{H}$ value
(b) errors in the relative sensitivities of the detector towards the various chlorides and benzene.
(c) the solution of certain chlorides in tap-grease. This is most likely in the chlorination of neopentane and the butanes and is reflected in the poorer reproducibility of the results in such cases.
(d) the existence of the back reaction (-2). This is unlikely in view of the absence of any regular variation of the relative rate constants, at any one temperature, with either the hydrocarbon/chlorine or hydrocarbon $A$/hydrocarbon $B$ ratios. Added hydrogen chloride did not affect the chlorination of iso butane at the temperatures at which no decomposition occurred. No evidence for the back reaction (-2) was obtained by Pritchard, Pyke and Trotman-Dickenson.
(e) the thermal decomposition of one or more of the chloride products. All results from work at temperatures at which decomposition was observed were rejected.
(f) bad sampling of products.

The experimental technique was adapted to reduce the possibility of errors from (b), (c) and (f) to a minimum. Apart from (c) and (f) which were probably the greatest sources of error, other/
other errors were due to the measurement of the initial pressures of hydrocarbons and concentrations of the chloride products. Both measurements were carried out with an accuracy of about 2%. 

(3) Values of the Activation Energies.

An examination of the activation energies listed in Table 16 leads to the following generalisations.

1. The activation energies for the chlorine atom attack on the primary positions decrease on ascending the straight chain members of the paraffin series, i.e. methane, ethane, propane and n butane.

2. While increasing chain length leads to lower activation energies, branching of the chains leads to higher values.

3. The activation energies for attack at the secondary positions in propane and n butane are considerably lower than those for the primary positions, there being a difference of 320 cal. for propane and 520 cal. for n butane. This suggests that the primary and secondary values diverge on ascending the paraffin series and is supported by the observation of Chambers & Ubbelohde that 

\( (E_{pri.} - E_{sec.}) \) in n hexane is \( \sim 900 \) cal. These workers found, however, that for the normal C5 - C8 paraffins the reactivity of the secondary positions relative to the primary positions decreased on ascent of the series. It is possible that while the 

\( (E_{pri.} - E_{sec.}) \) values increase on ascending the series, the
$A_{sec}/A_{pri}$ ratios approach unity. These workers in fact quote results for n hexane from which a value for $A_{sec}/A_{pri}$ per H atom of unity may be calculated and this trend is also indicated in our $A_{sec}/A_{pri}$ ratios for propane and n butane of 3.6 and 2.2 respectively.

4. The activation energy for attack at the tertiary position in iso butane is lower than those for the secondary positions studied. The value of $(E_{pri} - E_{tert.})$ in iso butane is 800 cal.

5. The activation energies for methane and cyclopropane are abnormal, that for attack at the so called primary bond in methane being much greater than the other primary attacks and that for the attack on the secondary position in cyclopropane much greater than the other secondary positions.

Recent work by Anson, Fredricks & Tedder on the gas phase chlorination of n butane and iso butane leads to the values

$$k_{snBu}/k_{pnBu} = 1.3 \exp(480 \pm 70 \text{ cal}/RT)$$

and

$$k_{tiBu}/k_{piBu} = 2.1 \exp(540 \pm 70 \text{ cal}/RT)$$

While the n butane results are in good agreement with those obtained in the present work, the iso butane results give an
(\(E_{\text{pri}} - E_{\text{tert}}\)) difference of 540 cal, which is considerably lower than our value of 800 cal. It thus seems possible that 700 cal. is a more reliable value and is not far outside the 50% probability limits of either determination.

An attempt to correlate activation energy with the bond strength of the bond being broken in the course of the reaction was made by Butler & Polanyi for the reactions of sodium atoms with alkyl chlorides. It had been suggested previously that

\[ E = \alpha \Delta H \]

where \(E\) = activation energy, \(\Delta H\) = heat of the reaction and \(\alpha\) lies between 0 and 1, being constant for a series of similar reactions. Although Butler & Polanyi found that \(\alpha\) was constant at about 0.26 where \(H\) values were obtained from the bond strengths of the corresponding iodides, the most recent values for the strengths of carbon - chlorine bonds do not lead to such constancy in \(\alpha\).

Steiner & Watson applied the same reasoning to the reactions of chlorine atoms with propane and iso butane. From the results of Hass, McBee & Weber they showed that for propane

\[ (E_{\text{pri}} - E_{\text{sec}}) = 0.225 (\Delta H_{\text{pri}} - \Delta H_{\text{sec}}) \]

and for iso butane

\[ (E_{\text{pri}} - E_{\text{tert}}) = 0.215 (\Delta H_{\text{pri}} - \Delta H_{\text{tert}}) \]

However, since grave doubts must be cast on any activation energies calculated from Hass, McBee & Webers results, these conclusions are unjustified.
### TABLE 17.

**ACTIVATION ENERGIES AND BOND STRENGTHS.**

<table>
<thead>
<tr>
<th>Bond in R--H</th>
<th>$E_R$ (^{-1}) cal.mole. for Cl attack</th>
<th>$E_R$ (^{-1}) k.cal.mole. for Br attack</th>
<th>$D(R-H)$ (^{-1}) k.cal.mole. at 0°K</th>
<th>$D(R-H)$ from electron impact work alone.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H=H</td>
<td>5,500</td>
<td>17.2</td>
<td>103.2</td>
<td></td>
</tr>
<tr>
<td>CH(_3)=H</td>
<td>3,050</td>
<td>17.8</td>
<td>101.5</td>
<td>102</td>
</tr>
<tr>
<td>C(_2)H(_5)=H</td>
<td>1,040</td>
<td>13.3</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>pri.C(_2)H(_7)=H</td>
<td>1,000</td>
<td></td>
<td>98</td>
<td>99.5</td>
</tr>
<tr>
<td>pri.nC(_4)H(_9)=H</td>
<td>790</td>
<td></td>
<td>101</td>
<td>101</td>
</tr>
<tr>
<td>pri.iC(_4)H(_9)=H</td>
<td>820</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>neOC(_5)H(_11)=H</td>
<td>920</td>
<td>17.8</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>sec.C(_2)H(_7)=H</td>
<td>680</td>
<td></td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>sec.nC(_4)H(_9)=H</td>
<td>270</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cycloC(_3)H(_5)=H</td>
<td>4,140</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cycloC(_4)H(_7)=H</td>
<td>825</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert.iC(_4)H(_9)=H</td>
<td>20</td>
<td>11.4</td>
<td>89</td>
<td>89</td>
</tr>
</tbody>
</table>

The $D(R-H)$ values are taken from reference (9).

$E_R$ for Br attack are quoted in reference (79).
unjustified.

The most recent values for the bond dissociation energies $D(R - H)$ in Table 17 are taken from reference 9 and are based on electron impact and kinetic study evidence. Although the general trend of the activation energies for the attack on $H - H$, $CH_3 - H$, $C_2H_5 - H$, sec $C_3H_7 - H$ and tert $C_4H_9 - H$ is related to the corresponding bond strengths, this relationship is non-linear and breaks down in the cases of pri $C_3H_7 - H$, pri n $C_4H_9 - H$ and neo $C_5H_{11} - H$. Although the bond energies are only accurate to within $\pm 1$ or $2$ k. cal. it is unlikely that any errors in these values can account for the discrepancies.

Invoking the reasoning employed by Russell, an empirical explanation of these activation energies may be advanced. In the cases of hydrogen and methane where the activation energies are relatively high a chlorine atom is not allowed to approach too closely to the hydrogen atom being abstracted and the controlling factor in the formation of the activated complex is the bond energy. In the cases of low activation energies the chlorine atom is allowed a closer approach and the controlling factor is then the availability of electrons to the incipient $H - Cl$ bond from the rest of the hydrocarbon molecule. Hence the magnitude of the low activation energies should depend on the extent of the inductive effect of the remaining hydrocarbon group. From the results of the present work this would suggest that the following are/
are in order of their inductive effects:

\[
\begin{align*}
& (\text{CH}_3)_3 \text{C} \rightarrow \text{CH}_3 \text{CH}_2 \text{CH} \rightarrow \text{CH}_3 \text{CH} \rightarrow \text{CH}_3 \\
& \text{CH}_3 \text{CH}_2 \text{CH}_2 \rightarrow \text{CH}_3 \text{CH}_2 \rightarrow \text{CH}_3 \rightarrow \\
& \text{CH}_3 \text{CH}_2 \rightarrow \text{CH}_3 \rightarrow \text{CH}_3 \
\end{align*}
\]

If methane is considered as the parent of the paraffin series and the formation of the activated complex dependent entirely on the inductive effect of the methyl group, then this effect increases with

1. increasing replacement of the hydrogen atoms in methane by methyl groups.
2. replacement of a methyl group by an ethyl group.
3. replacement of an ethyl group by a secondary propyl or tertiary butyl group.

Rule 1 is well established and can be shown to apply in the carboxylic acids homologous to acetic acid from a study of the pK values for these acids.

Rules 2 and 3 are not well established but in general it can be said that the inductive effect tends to increase as the complexity of \( R \) in \( R - H - Cl \) increases.

Russell has shown that the relative reactivities of primary, secondary and tertiary positions towards chlorine atoms depend not only on the differing inductive effects present but also on the differing bond strengths.

The magnitude of the activation energies \( E_{cPr} \) and \( E_{cBu} \) for/
for chlorine atom attack on the cycloalkanes, cyclopropane and cyclobutane will now be considered. Together with these values for $E_{CP}$ of 4,140 cal. and for $E_{CBu}$ of 825 cal. may be taken the activation energy for attack on cyclopentane $E_{CP}$ of 50 cal. obtained by Fritchard, Pyke & Trotman-Dickenson. In the formation of the $R-H-Cl$ activated complex with subsequent production of a free radical the coordination number of the carbon atom decreases from 4 to 3. Brown has suggested that in small rings the distortion of bond angle is the major source of internal ring strain or $I$ strain. Reactions with a change in coordination number of one of the carbon atoms involved in the ring and which produce additional $I$ strain will be unfavoured.

<table>
<thead>
<tr>
<th>Cycloalkane</th>
<th>Bond present</th>
<th>Theoretical bond $\angle$ for coord. No.4</th>
<th>$\angle$ for coord. No.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\triangle$</td>
<td>$60^\circ$</td>
<td>109.5$^\circ$</td>
<td>120$^\circ$</td>
</tr>
<tr>
<td>$\square$</td>
<td>$90^\circ$</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\diamond$</td>
<td>$108^\circ$</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

From the above table, a change in the coordination number of a ring carbon atom from 4 to 3 results in an increase of $I$ strain in all three cases. Since the strain is originally greatest in cyclopropane the change in coordination number will occur with most difficulty, leading to a high activation energy. The corresponding changes in cyclobutane and cyclopentane will occur with increasing facility and this trend is reflected in the values of
of $E_{tBu}$, $E_{Bu}$ and $E_{Pe}$. Studies of the hydrogen abstraction from a ring carbon atom by methyl radicals show a similar trend and give activation energies of 10.3, 9.3 and 8.5 k. cal. for cyclopropane, cyclobutane and cyclopentane.

The low value for $E_{tBu}$ is of considerable interest. While the temperature dependence of reaction rates are usually given in terms of activation energies ($E_{\text{exp.}}$) the more fundamental concept is $\Delta u_0^+$, the internal energy of activation at absolute zero.

$$\Delta u_0^+ = E_{\text{exp.}} - RT$$

and

$$\Delta u_0^+ = E_{\text{exp.}} - RT - \int_0^\infty \Delta c_v^+ \, dt$$

$\Delta c_v^+$ is the difference between the specific heat of the activated complex and those of the reactants, all at constant volume.

$$\Delta c_v^+ = c_v(\text{HC}) - c_v(\text{RH}) - c_v(\text{Cl})$$

The total specific heat $c_v$ is composed of translation, rotation and vibration terms

$$c_v = c_{v,\text{trans}} + c_{v,\text{rot}} + c_{v,\text{vib}}.$$ 

The $c_{v,\text{trans}}$ and $c_{v,\text{rot}}$ values for the $\text{RH Cl}$ complex and $\text{RH}$ molecule are identical, hence

$$\Delta c_v^+ = c_{v,\text{vib}} (\text{RH Cl}) - c_{v,\text{vib}} (\text{RH}) - c_v (\text{Cl})$$

The specific heat of the chlorine atom is dependent only on translation and is $3/2R$. The difference in the vibrational specific heats/
heats of the complex and hydrocarbon is due mainly to the introduction of new vibrations and from reasoning which will be given later the maximum frequencies are of the order of 200 cm \(^{-1}\) for the doubly degenerate bending and 500 cm \(^{-1}\) for the stretching of the R...H...Cl complex. It has been calculated that these frequencies give rise to internal energy contributions at 300° A of 2 x 0.59 RT and 0.24 RT.

Hence
$$\int_{0}^{300} \Delta C_v \frac{dT}{t} = 2 \times 0.59 \text{ RT} + 0.24 \text{ RT} - 1.5 \text{ RT}$$

$$\Delta u_o^\ddagger = E_{\text{exp}} - 0.9 \text{ RT}$$

$$= E_{\text{exp}} - 500 \text{ cal. mole}^{-1} \text{ at 300° A.}$$

If lower bending and stretching frequencies for the complex had been employed, the value of \(\Delta u_o^\ddagger\) would be even lower.

The internal energy of activation at absolute zero for the chlorine attack on the tertiary position in iso butane thus appears to be negative to the extent of 500 cal. Similar reasoning for the attack on the secondary position in n butane suggests an apparent \(\Delta u_o^\ddagger\) value of -200 cal. These surprising results may be explained in three ways:-

(a) By postulating that \(\Delta u_o^\ddagger\) may in fact have negative values. Negative activation energies are not usually found in bimolecular processes but have been shown to occur in termolecular reactions.

(b) By an overall error in \(E_{\text{tiBu}}\) of 500 cal. assuming \(k_H\) to be correct.

(c) By an overall error in \(E_{\text{tiBu}}\) of 500 cal. assuming \(k_{H}^\ddagger\) to be inaccurate.

Of possibilities (b) and (c) the latter is much more likely and/
and leads to the conclusion that the $E_H$ value used is low. This view is supported by the fact that the results of the individual methods used in the evaluation of $k_H$ all give activation energies higher than 5,500 cal.

The activation energies for the chlorine atom attack on hydrocarbons lie between those for fluorine atom and bromine atom attack. Those for bromine attack are in the range 11 to 18 k. cal. for paraffins whereas fluorine requires little or no activation energy. This is expected since the electronegativity, and hence reactivity, of the chlorine atom is intermediate between those of the fluorine and bromine atoms. Although the activation energies for bromine atom attack are much higher than those for chlorine, the expected linear relationship between activation energies and bond strengths as quoted in Table 17 does not materialise.

(4) Values of the A Factors.

On first inspection the A factors for the attack on the primary positions are fairly constant apart from the cases of hydrogen and methane which cannot in any case be regarded as possessing true primary bonds. The secondary positions in the straight chained alkanes have A factors almost twice those of the corresponding primary positions and the A factor of the tertiary position in iso butane is similar to those of the primary positions. The secondary bond in cyclobutane gives an A factor of the same order as the other secondary positions whereas that for cyclopropane is similar to the case of methane.

As was indicated previously the A factor of a bimolecular reaction/
reaction is dependent on the entropy of activation $\Delta S^\ddagger$ which
in turn is composed of translational, rotational and vibrational
contributions. Whereas the translational and rotational entropies
can be calculated with reasonable certainty from classical partition
functions, the calculation of the vibrational entropy of activation
presents formidable problems since the frequencies of the three
additional vibrations in the activated complex are usually unknown.

Bigeleisen & Wolfsberg evaluated the 'symmetrical'
stretching frequency of the $\text{H} - \text{H} - \text{Cl}$ complex from the known relative
rates of reaction of $\text{H}_2$ and $\text{HT}$ with chlorine atoms at 0°C. Making
a small correction for the bending frequency, their value of 1460 cm
for the stretching frequency gave good agreement with experimental
results. The longitudinal vibration of the central H atom is in the
reaction path and has a zero (or imaginary) frequency.

Using this value of 1460 cm$^{-1}$ for the frequency of the
stretching vibration and the known entropy of activation at 600°A
(obtained from the $A_H$ factor) Pitzer has calculated that the
frequency of the doubly degenerate bending of the $\text{H} - \text{H} - \text{Cl}$ complex
is 540 cm$^{-1}$. Although these frequencies lead to a $\Delta S^\ddagger$ value at
600°A in perfect harmony with the experimental $A_H$ factor the $\Delta S^\ddagger$
value for 300°A does not lead to the same measure of agreement
(see Table 18). While 600°A is the mid temperature in the $k_H$
determinations, 300°A is nearer the mid temperature for the work on
the hydrocarbons.

Pitzer also calculated a $\Delta S^\ddagger$ value for the chlorine
attack/
attack on methane on the assumption that the potential energy function in the reaction area was the same for the CH₃ - H - Cl complex as for the H - H - Cl complex. Whereas 0.9 Å and 1.5 Å were used for the H - H and H - Cl distances in H - H - Cl, the C - H length in CH₃ - H - Cl was assumed to be that present in CH₄ while the H - Cl distance was taken as 1.6 Å. This value leads to a theoretical A factor of 0.92 x 10⁻¹³ c.c. mole⁻¹ sec⁻¹ at 400 K which is near the experimental value of 0.6 x 10⁻¹³ c.c. mole⁻¹ sec⁻¹. Allowing for the increased mass and moment of inertia of CH₃ as compared to H, values of 440 cm⁻¹ and 160 cm⁻¹ were obtained for the frequencies of the stretching and bending vibrations of the CH₃ - H - Cl complex.

Wilson & Johnston have calculated theoretical A factors for reactions involving hydrogen abstraction by bromine and methyl radicals. From calculated stretching and bending force constants for the bonds of the activated complexes, the frequencies of the new vibrations have been obtained. These frequencies together with small changes in the original vibrations of the hydrocarbons give the ∆S⁺ₐₗ₉ values quoted in Table 18. These values in combination with ∆S⁺ₜ r a n s, ∆S⁺₉ rot and ∆S⁺₉ sil lead to the theoretical A factors which are in good agreement with experimental values except in the case of the iso butane bromination.

Knox & Trotman-Dickenson attempted to correlate the known relative A factors for chlorine atom reactions with calculated values.
values using the equation

\[
\frac{A_{R_a}}{A_{R_b}} = \left( \frac{M_{R_a} \text{HCl}}{M_{R_a} \text{H}} \right)^{\frac{3}{2}} \times \left( \frac{M_{R_b} \text{HCl}}{M_{R_b} \text{H}} \right)^{\frac{1}{2}} \times \left( \frac{(ABC)_{R_a} \text{HCl}}{(ABC)_{R_a} \text{H}} \right) \times \left( \frac{(ABC)_{R_b} \text{HCl}}{(ABC)_{R_b} \text{H}} \right)
\]

where \( M_s \) are molecular weights and \( (ABC) \) is the product of the moments of inertia about the three principal axes of the molecules. The vibration entropy terms were neglected in these calculations, being assumed to be relatively unimportant. The discrepancies between experimental and calculated \( A \) factors, however, were rather serious.

The \( A \) factors obtained from the present work form a more extended series than were formerly available and Knox & Nelson have attempted to calculate the vibrational contributions to the entropy of activation. The frequencies of the stretching and doubly degenerate bending vibrations have been calculated from Pitzer's values for the \( \text{H} - \text{H} - \text{Cl} \) complex, making due allowance for the changes in the reduced masses and moments of inertia. The vibrational entropy of activation \( \Delta S_{vib}^\neq \) for the chlorine atom attack on hydrocarbons has been assumed to be due solely to these two new vibrational modes and not to changes in the other vibrations of the hydrocarbon molecule. These calculated \( \Delta S_{vib}^\neq \) values are given in Table 18 together with experimental \( \Delta S_{vib}^\neq \) values obtained from the experimental absolute \( A \) factors in combination with calculated \( \Delta S_{\text{trans}}^\neq \) and \( \Delta S_{\text{rot}}^\neq \) values. Also included in this table are the \( \Delta S_{vib}^\neq \) values calculated by Wilson & Johnston for bromine.
### Table 18

**ENTROPIES OF ACTIVATION.**

<table>
<thead>
<tr>
<th>R—H</th>
<th>$\Delta^{+}_{\text{trans}}$ e.u. calc. for Cl.</th>
<th>$\Delta^{+}_{\text{rot}}$ e.u. calc. for Cl.</th>
<th>$\Delta^{+}_{\text{vib}}$ e.u. calc. for Cl.</th>
<th>$\Delta^{+}_{\text{vib}}$ e.u. exp. for Cl.</th>
<th>$\Delta^{+}_{\text{vib}}$ e.u. calc. for CH$_3$ for Br.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$-H</td>
<td>-13.12</td>
<td>6.25</td>
<td>5.9</td>
<td>2.8</td>
<td>3.6</td>
</tr>
<tr>
<td>C$_2$H$_5$-H</td>
<td>-14.26</td>
<td>4.96</td>
<td>7.5</td>
<td>7.1</td>
<td>6.1</td>
</tr>
<tr>
<td>pri.$\text{C}_3\text{H}_7$-H</td>
<td>-14.83</td>
<td>3.45</td>
<td>8.2</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>pri.$\text{nC}_4\text{H}_9$-H</td>
<td>-15.18</td>
<td>3.15</td>
<td>8.7</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>pri.$\text{iC}_4\text{H}_9$-H</td>
<td>-15.18</td>
<td>2.77</td>
<td>8.7</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>neo $\text{C}<em>5\text{H}</em>{11}$-H</td>
<td>-15.41</td>
<td>2.63</td>
<td>9.0</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>sec.$\text{C}_5\text{H}_7$-H</td>
<td>-14.83</td>
<td>3.70</td>
<td>8.2</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>sec.$\text{C}_4\text{H}_9$-H</td>
<td>-15.18</td>
<td>2.74</td>
<td>8.6</td>
<td>10.9</td>
<td>7.0</td>
</tr>
<tr>
<td>cyclo $\text{C}_2\text{H}_5$-H</td>
<td>-14.77</td>
<td>4.05</td>
<td>8.1</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>cyclo $\text{C}_4\text{H}_7$-H</td>
<td>-15.15</td>
<td>3.36</td>
<td>8.5</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>tert.$\text{iC}_4\text{H}_9$-H</td>
<td>-15.18</td>
<td>2.67</td>
<td>8.6</td>
<td>10.5</td>
<td>8.0</td>
</tr>
<tr>
<td>C$_\infty$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.0</td>
</tr>
</tbody>
</table>
bromine and methyl radical attack on hydrocarbons.

Detailed account of Knox & Nelson's calculations.

In reactions of the type

\[ R - H + Cl \rightarrow R...H...Cl \]

\[ \Delta S^\ddagger = \Delta S_{\text{trans}} + \Delta S_{\text{rot}} + \Delta S_{\text{vib}} \]

Now

\[ \Delta S_{\text{trans}} = S_{\text{tr},RHCl} - S_{\text{tr},RH} - S_{\text{tr},Cl} \]

\[ = \frac{3}{2} R \ln \frac{M_{\text{RHCl}}}{M_{\text{RH}}} - S_{\text{tr},Cl} \]

From the Sackur - Tetrode equation:

\[ S_{\text{tr},Cl} = \left( R \{ \frac{5}{2} \ln T + \frac{3}{2} \ln M - \ln \text{Patm} - 1.164 \} \right) \]

\[ = 16.60 \text{ e.u.} \]

where the standard state is 1 mole cm\(^{-1}\) at 298 K.

Also

\[ \Delta S_{\text{rot}}^\ddagger = \frac{1}{2} R \ln \frac{A^* B^* C^*}{ABC} \]

where \(A^* B^* C^*\) and \(ABC\) are the products of the moments of inertia of \(RHCl\) and \(RH\) about the principal axes in these molecules. The bond lengths used in the molecular models were \(H - H = 0.96 \) \(\text{Å}\) and \(C - H = 1.15 \) \(\text{Å}\) in the normal molecules and \(H - H = 1.15 \) \(\text{Å}\), \(C - H = 1.15 \) \(\text{Å}\) and \(H - Cl = 1.45 \) \(\text{Å}\) in the activated complexes.

The value of 1.15 \(\text{Å}\) for the \(H - H\) bond in the activated complex corresponds to the length of a half bond using Pauling formula.

The bond length used for \(H - Cl\) is also that for a half bond but the length of the \(C - H\) bond in the activated complex has not been correspondingly/
## TABLE 19.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mol. Wt.</th>
<th>$\frac{\text{Mol. Wt. - NHCl}}{\text{Mol. Wt. - RH}}$</th>
<th>(ABC)</th>
<th>$\frac{(A \cdot B \cdot C)}{(ABC)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>2</td>
<td></td>
<td></td>
<td>$I_{H_2}^* = 0.48$</td>
</tr>
<tr>
<td>$\text{NHCl}$</td>
<td>37.5</td>
<td>18.7</td>
<td></td>
<td>$I_{H_2\text{Cl}}^* = 7.72$</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>16</td>
<td></td>
<td></td>
<td>$36.1$</td>
</tr>
<tr>
<td>$\text{CH}_4\text{Cl}$</td>
<td>51.5</td>
<td>3.22</td>
<td></td>
<td>$194.0 \times 10^2$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6$</td>
<td>30</td>
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<td></td>
<td>$41.4 \times 10^2$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6\text{Cl}$</td>
<td>65.5</td>
<td>2.18</td>
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<tr>
<td>$\text{C}_2\text{H}_8$</td>
<td>44</td>
<td></td>
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<td>$6.98 \times 10^4$</td>
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<tr>
<td>$\text{pri. C}_3\text{H}_8\text{Cl}$</td>
<td>79.5</td>
<td>1.81</td>
<td></td>
<td>$2.28 \times 10^6$</td>
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<tr>
<td>$\text{sec. C}_3\text{H}_8\text{Cl}$</td>
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<td>$2.94 \times 10^6$</td>
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<tr>
<td>$\text{nC}<em>4\text{H}</em>{10}$</td>
<td>58</td>
<td></td>
<td></td>
<td>$4.22 \times 10^5$</td>
</tr>
<tr>
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<td>93.5</td>
<td>1.61</td>
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<td>$10.1 \times 10^6$</td>
</tr>
<tr>
<td>$\text{sec. nC}<em>4\text{H}</em>{10}\text{Cl}$</td>
<td>93.5</td>
<td>1.61</td>
<td></td>
<td>$6.8 \times 10^6$</td>
</tr>
<tr>
<td>$\text{iC}<em>4\text{H}</em>{10}$</td>
<td>58</td>
<td></td>
<td></td>
<td>$5.8 \times 10^5$</td>
</tr>
<tr>
<td>$\text{pri. iC}<em>4\text{H}</em>{10}\text{Cl}$</td>
<td>93.5</td>
<td>1.61</td>
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<td>$9.45 \times 10^6$</td>
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<td>93.5</td>
<td>1.61</td>
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<tr>
<td>$\text{neo C}<em>5\text{H}</em>{12}$</td>
<td>72</td>
<td></td>
<td></td>
<td>$1.5 \times 10^6$</td>
</tr>
<tr>
<td>$\text{neo C}<em>5\text{H}</em>{12}\text{Cl}$</td>
<td>107.5</td>
<td>1.49</td>
<td></td>
<td>$21.3 \times 10^6$</td>
</tr>
<tr>
<td>$\text{cyclo C}_3\text{H}_6$</td>
<td>42</td>
<td></td>
<td></td>
<td>$2.51 \times 10^4$</td>
</tr>
<tr>
<td>$\text{cyclo C}_3\text{H}_6\text{Cl}$</td>
<td>77.5</td>
<td>1.85</td>
<td></td>
<td>$1.50 \times 10^6$</td>
</tr>
<tr>
<td>$\text{cyclo C}_4\text{H}_8$</td>
<td>56</td>
<td></td>
<td></td>
<td>$17.4 \times 10^4$</td>
</tr>
<tr>
<td>$\text{cyclo C}_4\text{H}_8\text{Cl}$</td>
<td>91.5</td>
<td>1.63</td>
<td></td>
<td>$5.14 \times 10^6$</td>
</tr>
</tbody>
</table>

$\ast \ast = \text{average of expanded and contracted forms.}$
correspondingly lengthened. Any error introduced in using the wrong 
H - H distance in the H - H - Cl complex alters A B C by \( \sim 6\% \) 
per 0.1 \( ^{\circ} \) while in neopentane the error in the C - H distance used 
in the complex affects A B C by \( \sim 4\% \) per 0.1 \( ^{\circ} \). The details 
necessary for the calculation of \( \Delta S^*_{\text{trans}} \) and \( \Delta S^*_{\text{rot}} \) are 
given in Table 19. In all molecular models the C - H - Cl in the 
complex was assumed to be linear.

The frequencies of the vibrations present in the activated 
complexes were derived from Pitzer's values for \( \nu_{\text{st.H}_2\text{Cl}} \) of \( 1460 \text{ cm}^{-1} \) 
and \( \nu_{\text{bend.H}_2\text{Cl}} \) of \( 540 \text{ cm}^{-1} \) by the following methods.

**Stretching vibrations.** The frequencies of the stretching 
vibrations are decreased as the R groups in \( \text{R-H-Cl} \) increase in mass.

\[
\left\{ \frac{\nu_{\text{st.H}_2\text{Cl}}}{\nu_{\text{strHCl}}} \right\}^2 = \left\{ \frac{\mu_{\text{H-Cl}}}{\mu_{\text{R-Cl}}} \right\}^{-1}
\]

where \( \mu \) the reduced mass is given by

\[
\frac{1}{\mu_{\text{R-Cl}}} = \frac{1}{M_R} + \frac{1}{M_{\text{Cl}}}
\]

where \( M \) are the molecular weights of the fragments.

**Bending vibrations.** The frequency of these vibrations is 
given by

\[
\left\{ \frac{\nu_{\text{bend.H}_2\text{Cl}}}{\nu_{\text{bendHCl}}} \right\}^2 = \left\{ \frac{\lambda_{\text{H-Cl}}}{\lambda_{\text{R-Cl}}} \right\}^{-1}
\]

Knox/
Knox & Nelson used the reduced moments of inertia of the fragments about the central H atom as the \( \gamma \) values

\[
i.e. \quad \frac{1}{\gamma_{R...Cl}} = \frac{1}{I_R} + \frac{1}{I_{Cl}}
\]

where \( I_{\#} = I + M_r r^2 \) where \( r \) is the distance of the centre of gravity of the fragment from the central H atom in the complex.

Schlapp has shown that this is inaccurate and that

\[
\frac{1}{\gamma_{R...Cl}} = \frac{1}{J_R} + \frac{1}{J_{Cl}}
\]

where

\[
J_R = I_R + \frac{M_{Cl} + M_H}{M_{Cl} + M_H + M_R} \cdot M_R \cdot a^2
\]

and

\[
J_{Cl} = I_{Cl} + \frac{M_R + M_H}{M_{Cl} + M_H + M_R} \cdot M_{Cl} \cdot b^2
\]

Since \( M_H \) is small compared with \( M_R \) and \( M_{Cl} \), except in the \( H-H-Cl \) complex, these equations reduce to

\[
J_R = I_R + \mu_{R...Cl} \cdot a^2
\]

\[
J_{Cl} = I_{Cl} + \mu_{R...Cl} \cdot b^2
\]

\( a \) and \( b \) are the \( R...H \) and \( H...Cl \) distances in the \( R...H...Cl \) complexes, measuring from the centre of gravity of \( R \) and \( Cl \) to the central H atom.

The entropy values corresponding to particular frequencies are derived from \( \left\{ \frac{E - E_0}{T} \right\} \) and \( \left\{ \frac{F - F_0}{T} \right\} \) values. All entropy calculations were made for \( 298^\circ C \) and the details for \( \Delta S^\#_{vib} \) are given in Table 20. The differences between \( \Delta S^\#_{vib} \) values using/
### Table 20

**Calculation of \( S \) stretching and \( S \) bending for the new vibrational modes of the \( R-H-Cl \) complex.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>((ABC)^{1/2}) or ( L_R )</th>
<th>( a ) Å</th>
<th>( \mu )</th>
<th>( \lambda )</th>
<th>( \Delta s_{at} ) cm(^{-1})</th>
<th>( \Delta s_{be} ) cm(^{-1})</th>
<th>( S_{st} ) at 298 K</th>
<th>( S_{be} ) 0°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{Cl} )</td>
<td>1.15</td>
<td>0.97</td>
<td>1.28</td>
<td>0.91</td>
<td>1460</td>
<td>560</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>( \text{CH}_4\text{Cl} )</td>
<td>3.3</td>
<td>1.15</td>
<td>10.5</td>
<td>23</td>
<td>11.2</td>
<td>440</td>
<td>160</td>
<td>0.8</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6\text{Cl} )</td>
<td>16.2</td>
<td>1.6</td>
<td>16.0</td>
<td>57</td>
<td>21.2</td>
<td>365</td>
<td>115</td>
<td>1.1</td>
</tr>
<tr>
<td>pri.( \text{C}_3\text{H}_8\text{Cl} )</td>
<td>40.7</td>
<td>2.0</td>
<td>19.4</td>
<td>115</td>
<td>30.3</td>
<td>330</td>
<td>97</td>
<td>1.25</td>
</tr>
<tr>
<td>sec.( \text{C}_3\text{H}_8\text{Cl} )</td>
<td>&quot;</td>
<td>1.6</td>
<td>&quot;</td>
<td>90</td>
<td>28.2</td>
<td>&quot;</td>
<td>100</td>
<td>&quot;</td>
</tr>
<tr>
<td>pri.( \text{C}<em>4\text{H}</em>{10}\text{Cl} )</td>
<td>74</td>
<td>2.15</td>
<td>21.8</td>
<td>175</td>
<td>36.4</td>
<td>320</td>
<td>89</td>
<td>1.3</td>
</tr>
<tr>
<td>sec.( \text{C}<em>4\text{H}</em>{10}\text{Cl} )</td>
<td>&quot;</td>
<td>1.6</td>
<td>&quot;</td>
<td>130</td>
<td>34.1</td>
<td>&quot;</td>
<td>91</td>
<td>&quot;</td>
</tr>
<tr>
<td>pri.( \text{iC}<em>4\text{H}</em>{10}\text{Cl} )</td>
<td>83</td>
<td>2.3</td>
<td>&quot;</td>
<td>190</td>
<td>37.2</td>
<td>&quot;</td>
<td>88</td>
<td>&quot;</td>
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<tr>
<td>tert.( \text{iC}<em>4\text{H}</em>{10}\text{Cl} )</td>
<td>&quot;</td>
<td>1.7</td>
<td>&quot;</td>
<td>146</td>
<td>35.0</td>
<td>&quot;</td>
<td>90</td>
<td>&quot;</td>
</tr>
<tr>
<td>neo ( \text{C}<em>5\text{H}</em>{12}\text{Cl} )</td>
<td>115</td>
<td>2.2</td>
<td>23.6</td>
<td>230</td>
<td>41.2</td>
<td>300</td>
<td>83</td>
<td>1.4</td>
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<tr>
<td>cyclo ( \text{C}_5\text{H}_6\text{Cl} )</td>
<td>29</td>
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<td>1.3</td>
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<tr>
<td>( \text{C}_\infty )</td>
<td>35.5</td>
<td>75</td>
<td>245</td>
<td>57</td>
<td>1.8</td>
<td>4.6</td>
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<td></td>
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</tbody>
</table>

**Note:** \( \Delta S_{vib} \) (calculated) = \( S_{st} + S_{be} \times 2 \) since the bending mode is doubly degenerate.
using the two formulae for $\chi_{R...Cl}$ are small.

Comparison of the calculated and experimental $\Delta S_{vib}^*$ values given in Table 16 leads to the conclusion that although the introduction of two new vibrational modes in the activated complex accounts for most of the vibrational entropy of activation in reactions of the type

$$R - H + Cl. \rightarrow R. + H - Cl,$$

in most cases the calculated values are lower than the experimental values suggesting that other contributions to $\Delta S_{vib}^*$ should be considered.

The calculated value for hydrogen is lower than the experimental value because these calculations were made for $298^0A$, the mid-temperature of most Arrhenius plots in the present work whereas Pitzer obtained the vibrational frequencies from the $\Delta S^*$ value at $600^0A$. This discrepancy between calculated and experimental $\Delta S_{vib}^*$ values for hydrogen possibly explains the discrepancies for the hydrocarbons to a certain extent, but the fact that

$$\Delta S_{vib}^*(exp) - \Delta S_{vib}^*(calc)$$

depends from compound to compound is of some significance.

The low experimental vibrational entropy of activation of methane is anomalous and cannot at present be explained. The best agreement between calculated and experimental values is found/
found with ethane and cyclopropane, both relatively simple molecules, while poorest agreement occurs with the secondary positions in propane and n butane and the tertiary position in iso butane.

These facts can be explained if it is assumed that the presence of a chlorine atom in the activated complex has a significant effect on the frequencies of the vibrations in the parent hydrocarbon. In the simple molecules ethane and cyclopropane the lowest vibrational frequencies are of the order of 800 cm\(^{-1}\) and little contribution to \(\Delta S_{vib}^{\neq}\) can be expected. In the higher paraffins low frequency chain deformation vibrations occur and the contribution to \(\Delta S_{vib}^{\neq}\) from changes in those frequencies can be expected to be larger. The greater effect of a chlorine atom in the activated complex on such frequencies when attack occurs at secondary positions as compared to primary positions is not unreasonable.
SUMMARY.

The free radical, long chain competitive chlorination of hydrocarbons has led to accurate relative rate constants for reactions of the type.

$$R - H + Cl. \rightarrow R. + H - Cl \quad k_R$$

Gas chromatography was used to analyse the chloride products from the chlorinations of hydrogen, methane, ethane, propane, n-butane, iso-butane, neopentane, cyclopropane and cyclobutane. Using the established value for $k_H$ obtained by three independent methods, absolute rate constants $k_R$ for all positions in the hydrocarbons studied were determined.

An attempt has been made to correlate the activation energies for the chlorine atom attack on the straight chain alkanes with (a) the bond dissociation energies of the C - H bonds which break in the course of the reaction and (b) the inductive effect of the hydrocarbon molecule which makes available electrons for the incipient H - Cl bond. The former effect predominates in the higher activation energies and the latter in the lower values. The very low value of $E_{tiBu}$ leads to an apparent negative value for $\Delta u_o$. The high value of $E_{cPr}$ is due to the strain present in the cyclopropane ring.

Using the theory of absolute reaction rates theoretical $A$ factors have been considered. It is found that the main contribution to the vibrational entropies of activation are from two new vibrational modes (one being doubly degenerate) of the activated complex $R - H - Cl$. Additional contributions may arise from changes in the low frequency chain deformation vibrations of the more complicated molecules.
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<td>Chem. &amp; Ind. (1955)1631.</td>
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<td>(63) London</td>
<td>Z.Elek. 35(1929)552.</td>
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</tr>
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THE COMPETITIVE CHLORINATION
OF HYDROCARBONS.

Thesis
submitted for the degree of
Doctor of Philosophy.

by
Robert L. Nelson, B.Sc.

University of Edinburgh.

June, 1959.
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ACKNOWLEDGEMENTS.

The author wishes to thank Dr. John H. Knox for his continued advice and encouragement during the course of this research and Professors J.F. Kendall and E.L. Hirst for the provision of equipment and laboratory facilities.

Thanks are also due to Dr. A.F. Trotman-Dickenson for many helpful suggestions and to Dr. D.M.W. Anderson for infra-red analyses.

The author is indebted to the Department of Scientific and Industrial Research for the provision of a maintenance allowance.
PREFACE.

The reactions of chlorine with hydrogen and hydrocarbons have been widely studied and it is well established that they are chain reactions involving very long chains. There is general agreement as to the chain initiating and propagating steps but still considerable disagreement as to the chain terminating steps. The modern trend in kinetics has been away from the establishment of mechanism in detail and towards the determination of Arrhenius parameters for elementary reactions such as those involved in chain propagation.

The present work was aimed at determining accurately the rate constants for the attack of chlorine atoms on different hydrocarbons (reaction 1)

\[ \text{Cl} \cdot + \text{R-H} \rightarrow \text{R} \cdot + \text{H-Cl} \]  

and on different positions in the same hydrocarbon. This has been accomplished by employing a competitive technique in which reaction products are analysed for products characteristic of the initial chlorine atom attack. Absolute rate constants for each hydrocarbon are then found, if the absolute value for at least one of the substances studied is known. In this work the rate constant for the chlorine atom attack on hydrogen, which is reasonably well established, has been used as the standard value and all other absolute rate constants are obtained from this.

The activation energies obtained from the rate constants have been explained in a qualitative manner, while the A factors have been used to test transition state theory.
INTRODUCTION.

Of the reactions of chlorine, by far the most extensively studied is that with hydrogen, and out of the mass of information only the features relevant to the present study are mentioned. The reactions of chlorine with hydrocarbons, particularly in the gas phase, have been less widely studied although much important work on chlorinations in solution has been carried out.

(1) The reaction with hydrogen.

(a) Mechanism. The photochemical combination of hydrogen and chlorine was first observed by Cruikshank in 1801. The reaction was studied quantitatively by Draper (1841–45) and Bunsen & Roscoe (1855–59). Draper showed that the commencement of the reaction was accompanied by an increase of volume at constant pressure. This phenomenon, known as the 'Draper effect', has since been shown to be due to the heat evolved in the chemical reaction. Bunsen & Roscoe subjected hydrogen–chlorine mixtures to the action of light of known intensity for varying periods of time, and showed that the amount of reaction depended on the light absorbed. These workers also observed an 'induction period', which has since been shown to be due to the presence of nitrogenous impurities such as ammonia. No such induction period is observed with pure hydrogen and chlorine. Oxygen also acts as an inhibitor but if present in sufficient quantity simply slows down the reaction throughout without delaying the start.

At the beginning of the 20th century a large amount of quantitative information was accumulated mainly by Bodenstein and his co-workers. Many of the early results were irreproducible and led to erroneous/
erroneous conclusions. For example, several workers reported that care-
fully dried hydrogen and chlorine would not combine, but this is now
known to be due to impurities introduced in the drying process. It was
only by following up such leads that the correct mechanism was eventually
obtained.

Bodenstein used a static system and followed the photochemical
reaction by pressure measurements. He found that, in the presence of
oxygen,

\[ R_{\text{HCl}} = k I_{\text{abs}} \frac{(\text{Cl}_2)^2 / (\text{O}_2)} \]

while the activity of illuminated chlorine did not last more than 1/1600 second.

Bodenstein first thought that the chlorine and hydrogen combined
bimolecularly and that the effect of light in initiating the reaction was
either to ionise the chlorine molecule or to produce an excited molecule.
However the discovery that the quantum efficiency of the reaction was very
high led him to propose a chain mechanism (1913). The propagating steps were

\[ \text{Cl}_2 + \epsilon \rightarrow \text{Cl}_2' \]
\[ \text{Cl}_2' + \text{H}_2 \rightarrow 2\text{HCl} + \epsilon \]

At this time, the ionic chain scheme seemed plausible since the bond strength
in the chlorine molecule was believed to be about 100 k. cal., making the
photolysis in visible light impossible. The D(Cl - Cl) value is now known
to be 57 k. cal.

It was Nernst (1919) who suggested the existence of an atomic
chain of the type

\[ \text{Cl}^- + \text{H}_2 \rightarrow \text{HCl} + \text{H}^- \]
\[ \text{H}^- + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}^- \]

after/
after the initial photolysis of a chlorine molecule. By this scheme were explained quantum yields of 10 in the absence of oxygen and in light of wave length 4300 Å or less.

The chief difficulty in interpreting the results of the hydrogen - chlorine reaction is their contradictory nature e.g. Bodenstein found that both

\[ R_{\text{HCl}} = k \, \text{I}_{\text{abs}} \, \frac{(\text{Cl}_2)/(\text{O}_2)}{\gamma} \quad \text{and} \quad R_{\text{HCl}} = k \, \text{I}_{\text{abs}} \, \left( \frac{(\text{Cl}_2)}{(\text{O}_2)} \right)^2 \]

applied depending on the chlorine pressures, while other workers disagreed on the effect of hydrogen chloride on the overall reaction.

The mechanism which has proved most satisfactory for the reaction in the presence of oxygen is that first proposed by Gohring. However, for the reaction in the absence of oxygen, which is of interest in the present work, Bodenstein and Unger proposed the following scheme -

\[ \begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2\text{Cl}^- \quad (1) \\
\text{Cl}^- + \text{H}_2 & \rightarrow \text{HCl} + \text{H}^- \quad (2) \\
\text{H}^- + \text{Cl}_2 & \rightarrow \text{HCl} + \text{Cl}^- \quad (3) \\
\text{H}^- + \text{HCl} & \rightarrow \text{H}_2 + \text{Cl}^- \quad (-2) \\
\text{Cl}^- + X & \rightarrow \text{ClX} \quad (4) \\
\text{H}^- + X & \rightarrow \text{HX} \quad (5)
\end{align*} \]

where \( X \) can be the walls or some volatile substance. Using a stationary state treatment

\[ R_{\text{HCl}} = \frac{4 \, \text{I}_{\text{abs}} \, k_3 \, (\text{Cl}_2)}{X (k_4 \alpha + k_5)} \]

where \[\alpha = \frac{k_3 \, (\text{Cl}_2) + k_{-2} \, (\text{HCl})}{k_2 \, (\text{H}_2)} = \frac{(\text{Cl})}{(\text{H})}.\]
When the chain termination is predominantly by chlorine atom removal $k_4 \gg k_5$ and the expression reduces to

$$R_{\text{HCl}} = \frac{4I_{\text{abs}}k_2k_3}{k_4(X)(k_3(Cl_2) + k_{-2}(HCl))}$$

In the absence of any hydrogen chloride inhibition

$$R_{\text{HCl}} = \frac{4I_{\text{abs}}k_2(H_2)}{k_4(X)}$$

and this agrees with the experimental expression found by Bodenstein & Unger and Potts & Rollefson. Bodenstein & Unger suggested that the principal chain terminating steps were either the diffusion of chlorine atoms to the walls where recombination occurs or the reaction of chlorine atoms with $X$ which is believed to be a chloride or oxychloride of silicon. Potts & Rollefson confirm this belief that $X$ is a volatile substance while they go as far as to suggest that the strong inhibiting effect of hydrogen chloride, reported by Norrish & Ritchie, was due to some other inhibitor.

In the above expression, the temperature coefficient must depend on the $k_2/k_4$ ratio and will lead to the activation energy difference $E_2 - E_4$

Other workers have reported that the rate of the hydrogen-chlorine combination is proportional to the square root of the light intensity. Hence the possibility of bimolecular termination must be considered. Although this appears to be of importance only at high concentrations in the hydrogen-chlorine reaction, it is of much greater importance in the chlorination of substances such as chloroform. Three possible bimolecular chain termination steps are

$$\text{Cl} + \text{Cl} + M \rightarrow \text{Cl}_2 + M \quad (6)$$
$$\text{Cl} + \text{H} + M \rightarrow \text{HCl} + M \quad (7)$$
$$\text{H} + \text{H} + M \rightarrow \text{H}_2 + M \quad (8)$$

Considering/
Considering reactions (1), (2), (3), (6), (7) and (8)

\[ R_{\text{HCl}} = \frac{2^{3/2} I_{\text{abs}}^{1/2} k_3 (\text{Cl}_2)}{N^1/2 (k_6 \alpha^2 + k_7 \alpha + k_8)^{1/2}} \]

when \( \alpha \) is large, since \( k_6 \approx k_7 \approx k_8 \)

\[ R_{\text{HCl}} = \frac{2^{3/2} I_{\text{abs}}^{1/2} k_2 k_3 (\text{Cl}_2)(\text{H}_2)}{k_6^{1/2} M^{1/2}(k_3(\text{Cl}_2)+k_2(\text{HCl}))} \]

and if hydrogen chloride inhibition is negligible

\[ R_{\text{HCl}} = \frac{2^{3/2} I_{\text{abs}}^{1/2} k_2 (\text{H}_2)}{k_6^{1/2} M^{1/2}} \]

Because of the low quantum efficiency at high pressures, Ritchie & Taylor have suggested that Cl_3 is involved in chain termination steps such as

\[ \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M} \]

\[ \text{Cl} + \text{Cl}_3 \rightarrow 2\text{Cl}_2 \]

\[ \text{Cl}_3 \rightarrow \text{destroyed.} \]

The Cl_3 complex has been shown to have a relatively long lifetime.

Bodenstein, however, rejects chain terminations involving Cl_3. Although disagreement still exists, the most likely termination processes are

(i) \( \text{Cl} + X \rightarrow \text{CLX} \)

where \( X \) is volatile, probably a chloride of silicon

(ii) \( \text{Cl} + \text{walls} \rightarrow \frac{1}{2} \text{Cl}_2 \)

at low pressures

(iii) \( \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_2 + \text{M} \)

or \( \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M} \)

at high pressures, where diffusion of the chlorine atoms to the walls is unlikely.

In the/
In the chlorination of hydrogen the recombination of hydrogen atoms is of no importance as a chain terminating process. However, in the chlorination of hydrocarbons and particularly halogenated hydrocarbons, the combination of the alkyl radicals is now known to be the predominant chain termination reaction.

(b) Rate Constants.

In principle activation energies may be derived from a study of the temperature dependence of the thermal or photochemical reactions. For example where the kinetics follow \( R_{\text{HCl}} = kI_{\text{abs}}(H_2) \) the temperature dependence leads to \( E_2 - E_4 \), and when \( R_{\text{HCl}} = kI_{\text{abs}}(H_2) \) a value for \( E_2 - \frac{1}{2}E_6 \) is obtained. However, since the chains of the chlorine - hydrogen combination are very long, trace impurities may have large effects on the rate of the overall process and result in irreproducible rate constants. The pre-1930 workers concentrated mainly on the elucidation of mechanism, but since then more time has been devoted to the temperature dependence of the rate constants of the individual reactions.

\[
\begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2\text{Cl}^- \\
\text{Cl}^- + \text{H}_2 & \rightarrow \text{HCl} + \text{H} \\
\text{H}^- + \text{Cl}_2 & \rightarrow \text{HCl} + \text{Cl}^- \\
\text{Cl}^- + \text{X} & \rightarrow \text{ClX}
\end{align*}
\]

For a description of these results the above mechanism may be regarded as being adequate, being/
being in agreement with experimental results and giving

$$ R_{\text{HCl}} = 4I_{\text{abs, k}_2} \frac{k_2(H_2)}{k_4 \times (\cdot)} $$

The heat of dissociation of the chlorine molecule is well established as 57.19 k. cal. (see footnote) which is in agreement with the spectroscopic dissociation energy of 57.08 k. cal. Since the bond dissociation energies of the Cl - Cl, H - H and H - Cl bonds are 57.1, 103.2 and 102.1 k. cal, respectively, reaction (2) is slightly endothermic whereas (3) is strongly exothermic.

From the temperature coefficient for the overall rate of hydrogen chloride production Hertel obtained $5.9 \pm 0.5$ k. cal. while Potts & Rollefson obtained 5.8 k. cal. for $E_2 - E_4$. Hence 5.8 k. cal. appears to be the minimum value for $E_2$.

The first determination of the absolute value for the rate constant $k_2$ was made by Rodebush & Klingelhofer, who found the probability $W$ of a chlorine atom reacting with a hydrogen molecule at 0°C and 25°C. The chlorine atoms were produced in a high frequency electrodeless discharge and reacted with a stream of hydrogen in a flow system. The degree of dissociation of the chlorine was measured by a Wrede diffusion gauge

$$ W = \frac{\text{HCl formed}}{\text{Cl introduced}} $$

_Footnote:_ Bond strengths and activation energies will be quoted throughout this thesis in k. cal. instead of k. cal. mole$^{-1}$ where/
where \( z' \) is the average number of collisions between a given chlorine atom and hydrogen molecule in the reaction vessel as calculated from kinetic theory. Rodebush & Klingelhoefer used the relationship

\[ W \propto \left(1 + \frac{E_2}{RT}\right) e^{-E_2/RT} \]

and obtained, from the temperature coefficient of \( W \), a value for \( E_2 \) of 6,100 cal. The relationship of \( W \propto e^{-E_2/RT} \) gives \( E_2 = 5,550 \) cal.

Steiner & Rideal also obtained absolute values for \( k_2 \) from an examination of the orthopara conversion in hydrogen. This is catalysed by hydrogen chloride.

\[ \text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl} \quad k_-^' \]
\[ \text{or} \quad \text{H}_2 + \text{Cl} \rightarrow \quad k_-^" \]

where \( k_- = k_-^' + k_-^" \)

From work between 628° C and 796° C they obtained \( k_- \) values which gave \( E_- = 5,200 \) cal. These values in combination with the known equilibrium constant for \( \text{Cl} + \text{H}_2 = \text{HCl} + \text{H} \) gave absolute \( k_2 \) values. These together with Rodebush & Klingelhoefer's results give \( E_2 = 5,500 \) cal. Steiner & Rideal claim \( E_2 = 5,900 \) cal. from their own results but the accuracy of this value is poor because of the small temperature range.

Ashmore & Chanaugam studied the effect of nitrosyl chloride on the thermal hydrogen - chlorine reaction. In addition to the usual reactions (1), (2), (3) and (4) they considered

\[ \text{NO} + \text{Cl}_2 \rightarrow \text{NO} \text{Cl} + \text{Cl} \quad (9) \]
\[ \text{NOCl} \rightarrow \text{NO} + \text{Cl} \quad (10) \]
\[ \text{Cl} + \text{NOCl} \rightarrow \text{NO} + \text{Cl}_2 \quad (11) \]

In The/
In the presence of nitrosyl chloride, the initial rate of the hydrogen-chlorine combination is radically reduced for a short period due to reaction (11). Incidentally this proves that any molecular reaction between hydrogen and chlorine is negligible. A marked acceleration in the production of hydrogen chloride then occurs which can only be explained by an initiation process other than $\text{Cl}_2 \rightarrow 2\text{Cl}$. This is reaction (9). These workers derived an expression for the rate of hydrogen chloride production

$$R_{\text{HCl}} = \alpha(I_{\text{H}})(\text{Cl}_2) \frac{(\text{NO})}{(\text{NOCl})}$$

where $\alpha = \frac{k_9 k_2}{k_11}$. From work at $250^\circ\text{C}$ they obtained $k_2 = 4.8 \times 10^{-2}$ cc. mole sec. This value is in perfect agreement with the other absolute values for $k_2$.

When the results of these three independent methods of determining absolute $k_2$ values are combined

$$k_2 = 0.8 \times 10^{-14} \exp(-5,500 \pm 200/KT) \text{ cc. moles sec.}$$

The rate constant for reaction (3) cannot be obtained as readily as $k_2$. Maximum and minimum values for $E_3$ can, however, be inferred from the available data.

The maximum value of $E_3$ can be obtained from the observation by the majority of workers that hydrogen chloride has no inhibiting effect on the photochemical hydrogen chlorine combination. At room temperature the reverse reaction (12) $\text{H} \cdot \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ must be at least a hundred times slower than reaction (3) $\text{H} \cdot \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$. Steiner & Hidal showed that $E_{-2} = 5,200$ cal., so that if $A_{-2} \approx A_3$, the maximum value of $E_3$ is 2,500 cal.
The minimum value of $E_3$ is obtained from the study of the hydrogen - chlorine reaction in the presence of oxygen. In this reaction

$$H^* + O_2 + M = HO_2 + M \quad (12)$$

$$Cl^* + O_2 + M = ClO_2 + M \quad (13)$$

For moderate oxygen pressures, the main termination reaction appears to be (12)

$$R_{HCl} = \frac{2I_{abs} k_3 (Cl_2)^2}{k_{12} (M)(O_2)}$$

From the temperature coefficient a value for $E_3 - E_{12}$ of 2.0 kcal. has been obtained by Hertel. Hoare & Walsh have recently shown that reactions of type (12) where $M = H_2$ almost certainly have negative activation energies. This suggests a minimum value for $E_3$ of 0 kcal.

The activation energies of chain terminating steps (4) and (5) are not known but are probably small. The quadratic termination reactions (6), (7) and (8) have almost certainly zero or slightly negative $E$ values as do most free radical recombination reactions.
(2) The reaction with hydrocarbons.

(a) Mechanism and Rate Constants. The photochemical and thermal chlorinations of alkanes and chloro-alkanes are chain processes involving long chains. By analogy with the chlorination of hydrogen the initiation and propagation steps are

\[
\begin{align*}
\text{Cl}_2 & \xrightarrow{\text{hv or heat}} 2\text{Cl}^- \\
\text{Cl}^- + \text{R} & \rightarrow \text{R} + \text{Cl}^- \\
\text{R} + \text{Cl}_2 & \rightarrow \text{RCl} + \text{Cl}^-. 
\end{align*}
\]

The alternative propagating steps of

\[
\begin{align*}
\text{Cl}^- + \text{R} & \rightarrow \text{R} - \text{Cl} + \text{H}^- \\
\text{H}^- + \text{Cl}_2 & \rightarrow \text{HCl} + \text{Cl}^- 
\end{align*}
\]

are extremely unlikely since (2a) is strongly endothermic. The possible chain terminating steps are

\[
\begin{align*}
\text{Cl}^- + \text{X} & \rightarrow \text{ClX} \\
\text{R} + \text{X} & \rightarrow \text{RX} \\
\text{Cl} + \text{Cl} + \text{M} & \rightarrow \text{Cl}_2 + \text{M} \\
\text{R} + \text{Cl}^- & \rightarrow \text{RCl} \\
\text{R} + \text{R}^- & \rightarrow \text{R}_2
\end{align*}
\]

In the photochemical reaction, if the reverse reaction (-2) is unimportant and reaction (4) is the only chain terminating step

\[
R_{\text{HCl}} = \frac{2I_{\text{abs}} k_2 (\text{RH})}{k_4 (X)}
\]

When quadratic termination is important, the general expression is

\[
R_{\text{HCl}} = \frac{1}{M} \left( k_6 \alpha^2 + k_7 \alpha + k_8 \right)^{1/2}
\]

where \( \alpha = \frac{k_3 (\text{Cl}_2)}{k_2 (\text{RH})} \)

Hence/
Hence when reaction (6) is all important,

\[ \frac{1/2}{2} \frac{1/2}{1} \frac{k_2 (RH)}{k_6 \cdot M^{1/2}} \]

whereas when (7) and (8) are predominant

\[ \frac{1/2}{2} \frac{1/2}{1} \frac{k_3 (Cl_2)}{k_2 (RH) + k_8} \]

For the thermal reaction, the same expressions apply provided \( 2I_{\text{abs}} \) is replaced by \( k_1 (Cl_2) \).

Inhibition by hydrogen chloride has been recorded in very few cases.

**Chlorination of Methane.** Pease & Walz examined the thermal chlorination of methane and showed that an equimolar amount of hydrogen chloride was produced for the chlorine consumed. Methyl chloride was the main chloro-alkane with smaller amounts of methylene dichloride, chloroform and carbon tetrachloride. When chlorine was present in excess, the mixtures were explosive. In absence of oxygen they found

\[ -R_{\text{CH}_4} = k (Cl_2)(\text{CH}_4) \]

whereas in presence of oxygen.

\[ -R_{\text{CH}_4} = k (Cl_2)^2 / (O_2) \]

This suggests that the termination reactions were respectively \( Cl + X \rightarrow ClX \) with \( X \) constant and \( CH_3 + O_2 \rightarrow \) inactive products. These rate expressions are similar to those obtained for the hydrogen-chlorine reaction and suggest a close resemblance of mechanism. This similarity was supported by Jones & Bates in the oxygen rich chlorination of methane. Coehn & Corde calculated a chain length of 4 in the photochemical reaction.
From their results, Schumacher showed that $E_2$ for CH$_4$ is less than 8 k. cal. Tamura also investigated the photochemical reaction and concluded that $E_2 \leq 6.2$ k. cal. He also found that the rate varied with $I^{1/2}_{abs}$. This observation has been confirmed by Ritchie & Winning although at high intensities the rate varied with $I_{abs}$. This result implies that at low $I_{abs}$ quadratic termination occurs while at high $I_{abs}$ the termination process involves only one chain carrier. This is the reverse of what might have been expected and Ritchie & Winning were forced to propose that

$$\text{Cl}^- + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_2^- + \text{M}$$  \hspace{1cm} (14)$$

$$\text{Cl}_3^- + \text{Cl}_3 \rightarrow 3\text{Cl}_2$$  \hspace{1cm} (15)

operated at high $I_{abs}$ values, whereas normal quadratic termination occurred at low $I_{abs}$. The addition of inert gases increased the extent of quadratic termination. There is still, however, some doubt as to the correct interpretation of these results.

Further evidence for the propagating steps are obtained from the work of Bogdandy & Polanyi who initiated methane-chlorine mixtures with sodium vapour. Hydrogen chloride and methyl chloride were produced by

$$\text{Na} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{Cl}^-$$

$$\text{Cl}^- + \text{CH}_4 \rightarrow \text{CH}_3^- + \text{HCl}$$

$$\text{CH}_3^- + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^- + \text{Cl}^-$$

Chlorination of Ethane.
Chlorination of Ethane. Ethane was chlorinated both thermally and photochemically by Rust & Vaughan. Inhibition of the reaction occurred in the presence of oxygen or olefins while the thermal reaction could be initiated by tetra-ethyl lead at low temperatures. A chain process was suggested and these workers found in the thermal process that

\[ R_\text{HCl} = k (C_2 H_6)(Cl_2) \]

This suggests that the termination step is 1st order with respect to the chlorine atoms and is possibly their removal on the walls.

Chlorination of Propane. Tetra ethyl lead was also shown to initiate the thermal chlorination of propane while a chain length of 10 was recorded by Yuster & Reyerson. These workers showed that packing the reaction vessel reduced the rate and came to the conclusion that chain termination occurred on the walls. The principal products were hydrogen chloride, normal and iso propyl chlorides.

The overall kinetics of the chlorination of aliphatic hydrocarbons is thus still somewhat obscure, but as with the hydrogen-chlorine reaction the uncertainty attaches not to the initiation or propagation reactions but to the chain terminating step. The general scheme of reactions (1), (2) and (3) is well established, (-2) is almost certainly unimportant, while chain termination varies with the reaction conditions and may be any of (4), (6), (7), (8) and (14).

Chlorination of Chloroform.
Chlorination of Chloroform.

The chlorination of chloroform to carbon tetrachloride has been more exhaustively studied than that of any aliphatic hydrocarbon. The presence of only one hydrogen atom in the molecule ensures no di-substituted products and simplifies the reaction. However in this, as in the other chlorinations discussed, although the initiation and propagating steps are well established, the terminating step is still doubtful.

Schwab and Friess examined the reaction by the discharge tube method and obtained as products, hydrogen chloride, carbon tetrachloride and possibly some hexa chloroethane. Schumacher & Wolff showed that the experimental rate expression was

$$R_C Cl_4 = \frac{1}{2} k \frac{d}{dt} \text{abs (Cl)}_2.$$  

They assumed that the termination process was

$$2C Cl_2 + Cl_2 \longrightarrow 2C Cl_4$$

(16)

and from the temperature coefficient between 50° and 60° calculated that $E_2 \sim 8 \text{k.cal.}$, $E_2 \sim 4.3 \text{k.cal.}$ and $E_16 \sim 0 \text{k.cal.}$ Schumacher & Sundhoff revised the value of $E_2$ to 8 k.cal. from studies on the inhibition by alcohol and ammonia of the photo-oxidation of chloroform. If, however, $E_2$ is as large as 8 k. cal. it is conceivable that reaction (-2) might also occur. Reaction (2) is exothermic to the extent of 12 k.cal. and hence reaction (-2) is unlikely to be significant in the presence of (3). This was confirmed experimentally by Schumacher & Wolff and also by Winning who found no inhibition by hydrogen chloride in the gas phase. Work in the liquid phase, however, suggests/
suggests that inhibition by hydrogen chloride of the reaction in carbon tetrachloride solution may occur.

Newton & Rollefsen have produced fairly convincing evidence that the back reaction \(-2\) does occur to a limited extent in the gas phase photo chlorination of chloroform. It was found that some deuterio-chloroform was produced when chloroform was chlorinated in the presence of deuterium chloride. Hence

\[
D\text{Cl} + C\text{Cl}_2 \rightarrow C\text{DCl}_2 + Cl
\]

appears to occur to a certain extent, unless exchange occurs on the walls. Additional evidence for (12) was furnished by the competitive chlorination of chloroform and deuterio-chloroform. The results showed that

\[
\frac{k_2\text{CHCl}_3}{k_2\text{CDCl}_3}
\]

was not independent of the extent of the reaction. These workers also demonstrated the formation of considerable amounts of hexa chloroethane, indicating that one of the chain terminating steps involves the production of this compound

\[
C\text{Cl}_3 + C\text{Cl}_2 \rightarrow C_2\text{Cl}_6
\]

The mechanism of the chlorination of chloroform and other chlorinated hydrocarbons has been considerably clarified in recent years by Goldfinger and co-workers. Using a competitive method in which the substitution of chlorine in pentachloroethane was compared with the addition process to tetrachloroethylene

\[
\begin{align*}
C_2\text{HCl}_5 + Cl_2 & \rightarrow C_2\text{Cl}_6 + HCl & n = 0 \\
C_2\text{Cl}_4 + Cl_2 & \rightarrow C_2\text{Cl}_6 & n = -1.
\end{align*}
\]
the chain terminating steps were shown to be

\[
\begin{align*}
C_2Cl_5^+ + Cl^- & \rightarrow \text{ inactive} \\
C Cl_7^+ + C Cl_7^+ & \rightarrow \text{ products.}
\end{align*}
\]

The photochlorination of chloroform, alone and in competition with tetra chloroethylene has been studied between 70°C and 155°C. The mechanism employed was

\[
\begin{align*}
Cl_2 + hv & \rightarrow 2Cl^- \quad (1) \\
Cl^- + ClC_1 & \rightarrow C Cl_3^- + HCl \quad (2) \\
C Cl_3^- + Cl_2 & \rightarrow C Cl_4^- + Cl^- \quad (3) \\
Cl^- + Cl^- + M & \rightarrow Cl_2^- + M \quad (6) \\
Cl^- + CCl_3^- & \rightarrow \text{ inactive} \quad (7) \\
CCl_3^- + CCl_3^- & \rightarrow \text{ products} \quad (8)
\end{align*}
\]

The reaction was followed photometrically and manometrically. No thermal reaction was found to occur at these temperatures.

The order of the reaction was calculated by van't Hoff's method. By plotting log (initial rate) against log (initial chlorine pressure) the reaction order under the initial conditions was obtained. This order was found to vary slightly with the

\[
P (Cl_2^-) / P (CHCl_3^-)
\]

ratio, having a value of \( \frac{3}{2} \) when this ratio was unity. It was shown that this result could be explained if reactions (-2), (-3) and (6) are unimportant

\[
-PCl_2^- = \frac{\frac{1}{2} I_{abs} k_3 (Cl_2^-)}{k_3 k_7 (Cl_2^-)/k_2 (CHCl_3^-) + k_8}
\]

This/
This mechanism explains the experimental facts of the chloroform chlorination such as the production of hexa chloroethane and the variation of the order of the reaction with the chlorine pressure. At high (Cl\(_2\)) / (CHCl\(_3\)) ratios, reaction (7) gains in importance as the chain terminating step at the expense of (8). The ratios \(k_2 k_3 / k_7\) and \(k_3^2 / k_8\) have been obtained over a range of temperatures and lead to minimum values for \(E_2\) and \(E_3\) of 6.5 and 5.3 k. cal. respectively.

Goldfinger and co-workers conclude that the van't Hoff method is a more delicate test of mechanism than the integration methods, partly because the order of a reaction can be followed as the reaction proceeds.

(b) Competitive Chlorinations. The determination of absolute rate constants of the separate reactions involved in the chlorination of hydrocarbons is beset by the following difficulties:

1. doubts as to the precise mechanism of the chain process, in particular the terminating steps and possible back reactions. Depending on the termination reaction the overall rate leads to either \(k_2\) or \(k_3\).

2. the effect of impurities on the chain length, leading to irreproducible overall rates.

3. practical difficulty in maintaining and measuring the chlorine atom concentration.
Many of these difficulties disappear when measurements are made of the relative rates of chlorination of two hydrocarbons \( R_a H \) and \( R_b H \) or of two or more positions in the same hydrocarbon. The assumptions must be made that

(a) the chain propagating steps are similar for both chlorinations

\[
R-H + Cl^- \longrightarrow R^- + H-Cl \quad (2)
\]
\[
R^- + Cl_2 \longrightarrow R-Cl + Cl^- \quad (3)
\]

(b) the chains are reasonably long, i.e. greater than 100 units in length.

(c) no back reactions of type (2) occur.

The relative rates of hydrogen abstraction by chlorine atoms (2) can be calculated from either the relative amounts of the chlorides subsequently produced by (3) or the relative amounts of the hydrocarbons consumed. In this technique it matters little whether the chlorine atoms are produced photolytically or thermally.

Hass, McRee & Weber were the first to apply this competitive method to the chlorination of aliphatic hydrocarbons. Propane and iso butane were chlorinated thermally between 50°C and 600°C in a flow system, using high hydrocarbon and chlorine pressures. The mixtures of isomeric propyl and iso butyl chlorides were analysed by fractional distillation. It was shown that the rates of chlorine atom attack on the different carbon-hydrogen bonds available obeyed the law tert> sec> primary. From the data available on the ratio of isomeric chlorides produced,
produced, Arrhenius plots of $\log k_{\text{sec}}/k_{\text{prim}}$ and $\log k_{\text{tert iso Bu}}/k_{\text{prim iso Bu}}$ against $T/T^0$ may be constructed. These plots curve badly and give unreliable results due to the occurrence of extensive polysubstitution, and pyrolysis of products at the higher temperatures. Steiner and Watson used their high temperature results to obtain values for $(E_2 \text{ prim.} - E_2 \text{ sec})$ in propane and $(E_2 \text{ prim} - E_2 \text{ tert})$ in iso-butane of 1.35 and 1.74 k. cals./mole respectively. However, the present work has shown that these values are seriously in error, being much too large. 

Chambers and Ubbelohde studied the gas phase photo-chlorination of various C_5 - C_8 paraffins. Using a flow system with product analysis they concluded that the overall rate of monochlorination increases with chain length and decreases with chain branching, while for normal paraffins the reactivity of the secondary relative to the primary positions appear to decrease as the chain lengthens, a trend supported by other workers. From results for $k_{\text{sec}}/k_{\text{prim}}$ per H atom in n-hexane at 86°C and 238°C, values for $(E \text{ prim.} - E \text{ sec})$ of 900 cals/mole and $A_{\text{sec}}/A_{\text{prim.}}$ of unity may be calculated.

Pritchard, Pyke and Trotman-Dickenson studied the chlorination of the following mixtures: hydrogen-methane, methane-methyl chloride, methane-ethane, ethane-ethyl chloride, ethane-propane, ethane-iso butane, ethane-neopentane and ethane-cyclopentane. These mixtures of hydrocarbons were sealed in small bulbs together with chlorine, thermostated and illuminated. The hydrocarbon uptake in each case was measured using a controlled temperature still, and gave results for the relative rates of chlorine atom/
atom attack on each molecule as a whole. The main defect of this method is that no differentiation can be made between chlorine atom attack at different positions in the same molecule.

Using a value for $k_2$ of hydrogen obtained from the results of other workers, the absolute rate constants for each alkane or alkyl chloride were obtained. It was found that the activation energies decreased on ascent of the alkane series from 3.85 k. cal. for methane, 1.0 for ethane to 0.7 k. cal. for neo-pentane. An anomalous result occurred in the cases of methyl and ethyl chlorides. The substitution of chlorine for hydrogen in the methane molecule had an activating effect giving $E = 3.4$ k. cal. while the chlorine in ethane had a deactivating effect giving $E = 1.5$ k. cal. These workers found no experimental evidence of any back reaction (-2).

Since (-2) is in competition with (3) it is most likely to occur when $E_2 - E_3$ is low, i.e. when reaction 2 is thermoneutral and the value of $E_2$ is low. Such is the case for neo-pentane and methane. The back reaction (-2) \( \text{CH}_3^* + \text{HCl} \rightarrow \text{CH}_4 + \text{Cl}^* \) has been studied by Cvetanovic and Steacie who photolysed acetone in the presence of hydrogen chloride. Both this and \( \text{Cl}^* + \text{CH}_3 \text{COCH}_3 \rightarrow \text{HCl} + \text{CH}_2 \text{COCH}_3 \)

occur and from the collision yield at 28°C they estimate that $E_2 < 5$ k. cals/mole.

Goldfinger and co-workers competed the chlorine substitution in methylene dichloride, chloroform and penta chloro ethane with the addition of chlorine to tetra chloro ethylene. The chlorination of/
of tetra chloro ethylene was studied alone and from the observed lifetime of the reaction chains an absolute value for the rate constant of the termination process \( k_{4c} = 10^{11.6 \pm 0.3} \text{ cc. mole sec.} \)

\[
C\text{Cl}_5^- + C\text{Cl}_5^- \rightarrow \text{products}
\]

was obtained. Although many of the activation energies may be obtained absolutely this value is necessary for a knowledge of the absolute A factors for the chlorine attack on the chloro alkanes studied. For methylene dichloride, chloroform and penta chloro ethane the activation energies obtained were 5.5, 6.5 and 5.4 k. cal./mole respectively while the corresponding A factors were \(10^{14.3} \) and \(10^{13.9} \) cc. mole sec per H atom. The A factor per H atom obtained for ethane by Pritchard, Pyke and Trotman-Dickenson was \(10^{13.3} \) cc. mole sec, so that the presence of chlorine atoms in the chloro-alkanes appears to increase the entropy of activation. Goldfinger suggests that this result can be explained if free rotation exists in the activated complex. However, with a large number of chlorine atoms present in the molecule, any free rotation would appear to be unlikely. Considerable doubt must also be placed on the high values of the activation energies obtained, since these are not self consistent (see Ref. 49 in which the data lead to two values for \( E_2 \) for chloroform of 10.5 k. cal./mole. and 6.5 k. cal./mole).

In addition to this Knox, in unpublished work, has obtained activation energies for the chlorine attack on methylene dichloride and chloroform in the region of 3.5 to 4.0 k. cal.

In the competitive chlorination of chloroform and deuterochloroform, by extrapolation of the \( k_{2H}/k_{2D} \) values back to zero reaction,
reaction, Newton & Rollefson obtained

\[
\frac{k_{2H}}{k_{2D}} = 1.4 \pm 2 \exp \left(710 \pm 90/RT\right)
\]

for

\[
\begin{align*}
\text{C} \text{H} \text{Cl}_{3} + \text{Cl}^{-} & \rightarrow \text{C} \text{Cl}_{3}^{-} + \text{HCl} & k_{2H} \\
\text{C} \text{D} \text{Cl}_{3} + \text{Cl}^{-} & \rightarrow \text{C} \text{Cl}_{3}^{-} + \text{DCl} & k_{2D}
\end{align*}
\]

They showed that the changes in the classical translation, rotation, vibration and electronic partition functions in substituting a D atom for an H atom both in the original molecule and in the activated complex were negligible and hence, assuming a transmission coefficient ratio of unity, \( A \frac{2H}{2D} \) should be 1.0. They calculated an activation energy difference on the assumption that it was due to the difference in zero-point energies for the C - H and C - D stretching vibrations which are in the direction of the reaction co-ordinate. This theoretical value of 1,080 cal. can be reduced to 710 cal. if it is assumed that the Cl atom tends to increase the vibration of the H and D atoms in a plane perpendicular to the C - Cl line. The C - H frequency must be changed from \(1,215 \text{ cm}^{-1} \) to \(1,720 \text{ cm}^{-1} \) and the C - D frequency from \(909 \text{ cm}^{-1} \) to \(1,234 \text{ cm}^{-1} \). If it is assumed that the ratio of the frequency factors is determined by the number of times that the hydrogen and deuterium atoms are moving in a direction favourable for reaction and that this ratio is given by the ratio of the C - H and C - D stretching frequencies then

\[
A \frac{2H}{2D} = 1.33.
\]

Hass, McClellan & Weber observed that chlorination of hydrocarbons produced roughly similar results if carried out at 300°C in the gas phase or 25°C in the liquid phase. They showed that the relative rates of substitution of primary - secondary - tertiary hydrogen atoms/
atoms by chlorine under these conditions were 1.0 - 3.25 - 4.43. An explanation of the apparently lower specificity of chlorine atom attack in the liquid phase involves the 'cage effect' which is believed to operate in this phase. The present work has shown the results of Hass, et alia to be unreliable and the above conclusion should be regarded with suspicion.

The effects of substituents on the rates of free radical chlorination at the different remaining positions in a hydrocarbon have been studied in the gas phase and to a much greater extent in the liquid phase. Ash & Brown have found it possible to arrange twelve groups in order of decreasing activating effect on adjacent positions in hydrocarbons:

\[ \text{C}_6\text{H}_5 > \text{CH}_3 > \sigma > \text{OOC.C} \text{H}_3 > \text{CH}_2\text{Cl} > \text{CHCl}_2 \text{and SiCl}_3 > \text{Cl} > \text{OOC} > \text{Cl} > \text{OOC} \text{Cl}_3 > \text{Cl}_3 > \text{Cl}_3 > \text{Cl}_3 > \text{F}_3. \]

From an examination of the effect of solvent on the relative reactivities of sixteen different carbon-hydrogen bonds towards atomic chlorine, Russell concluded that two separate effects operate to cause differing reactivities. These are (a) the stability of the incipient hydrocarbon free radicals and (b) the availability of electrons to the carbon-hydrogen bond from the rest of the molecule. When the activation energy of the chlorine atom attack is fairly high (as in \( \text{C}_4\text{H}_4 \)), the C - H bond has to lengthen to a considerable extent for the production of the activated complex C - - H - - - Cl. The magnitude of the bond strength (dependent on the stability of the incipient hydrocarbon radical) influences the activation energy and hence the presence of a chlorine atom in the original molecule will tend to activate the remaining positions because/
because of a general decrease in bond strength. When the activation energy is low, the C – H bond being attacked is not so extended in the activated complex. The activation energy is now determined to a greater extent by the willingness of the rest of the molecule to give electrons to the H – – Cl bond. This energy will tend to be governed by the inductive I effect, leading to deactivation in the presence of a chlorine atom in the molecule, since chlorine being electronegative has a –I effect.

This explanation resolves the anomalous results for methyl chloride and ethyl chloride as well as conforming to the general conclusions of Ash & Brown.

The method of the present work was outlined by Know who chlorinated methane-ethane mixtures and obtained relative rate constants from the ratios of methyl and ethyl chlorides produced. This value of

$$\frac{k_{Et}}{k_{Me}} = 3.85 \exp\left(2,810 \pm 45/RT\right)$$

agrees excellently with the results of Pritchard, Pyke and Trotman-Dickenson. This agreement was encouraging and suggested that the method of product analysis should be extended to those cases beyond the scope of the method involving the examination of hydrocarbon consumption. The analysis of small quantities of isomeric chlorides obtained from a static system was only made possible by the use of gas chromatography.
(3) Theory of Reaction Rates.

**The Arrhenius Equation.**

\[ k = A \cdot e^{-\frac{E}{RT}} \]

Towards the end of the 19th century van't Hoff suggested that the logarithm of the rate constant of a reaction should bear a linear relationship to the reciprocal of the absolute temperature. Arrhenius showed that this was the case for a number of reactions and that

\[ \ln k = \text{constant} - \frac{E}{RT} \]

This gives \( k = A \cdot e^{-\frac{E}{RT}} \) where \( A \) and \( E \) are constants characteristic of the reaction, \( R \) is the gas constant and \( T \) is the absolute temperature. Arrhenius suggested that before reaction could take place, the reactant molecules must become activated, and that an equilibrium exists between normal and activated molecules.

The Maxwell-Boltzmann distribution law states that the fraction of molecules in a gas possessing an energy in excess of \( E \) is proportional to \( e^{-\frac{E}{RT}} \). The value of \( E \) in the Arrhenius equation was thus considered as the energy necessary for the formation of an activated molecule.

**Calculation of the Energy of Activation.**

'E'

A possible method of calculating activation energies was proposed by London using the methods of quantum mechanics. He pointed out that since many chemical reactions do not involve any electronic transitions, it is possible to represent the state of an electron by a single function throughout the chemical reaction. London derived an approximate expression for the potential energy of a system of three atoms \( X, Y \) and \( Z \) each having/
having one unpaired $S^-$ electron

$$\text{P.E.} = A + B + C = \left\{ \frac{1}{2} \left[ (\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2 \right] \right\}^{\frac{1}{2}}$$

where $A$, $B$ and $C$ are the coulombic interactions of the pairs of electrons on the atoms $X$ and $Y$, $Y$ and $Z$ and $Z$ and $X$ respectively and $\alpha$, $\beta$ and $\gamma$ are the corresponding resonance or exchange energies.

The values of $A$, $B$, $C$, $\alpha$, $\beta$ and $\gamma$ depend on the interatomic distances and hence the P.E. of the system can be calculated for all possible interatomic distances to give a 'potential energy surface' for each $X - Y - Z$ angle. Since the reaction

$$X + YZ \rightarrow XY + Z$$

must follow a path over these surfaces, the assumption that most of the systems will follow the easiest path leads to the energy of activation. A further assumption is made that the easiest line of approach of the $X$ atom is along the line of centres of the $Y$ and $Z$ atoms. Thus only one potential energy surface need be considered.

The calculation of the coulombic and exchange energies, however, present difficulties even for the simplest system. This has been attempted by Eyring & Polanyi in the reaction

$$\text{H}^+ + \text{H}_2^0 \rightarrow \text{H}_2^0 + \text{H}^+$$

by the semi-empirical method using the assumption that the coulombic energies are definite fractions of the total coulombic and exchange energies of the two atoms concerned. The fractions will be characteristic of the atoms but are generally between 10 and 20%. The total energies $A + \alpha$, $B + \beta$ and $C + \gamma$ are obtained by supplying spectroscopic data to the/
**Fig. 1.**

Reaction coordinate.

**Fig. 2.**

Reaction coordinate.
the appropriate Morse equation.

It is impossible, however, to produce the necessary data for potential energy surfaces of relatively more complicated reactions such as the one under study

\[ \text{Cl}^- + \text{R} - \text{H} \rightarrow \text{R}^* + \text{H} - \text{Cl}. \]

The progress of this reaction can be indicated by means of a Morse-type graph (Figure 1). Curve 1 is the potential energy diagram of the hydrocarbon \( \text{R} - \text{H} \) where \( d_{\text{H Cl}} = \infty \). Curve 2 is the potential energy diagram of the activated complex where symmetrical stretching of \( \text{R} - \text{H} - \text{Cl} \) occurs. \( d_{\text{H Cl}} \) varies with \( d_{\text{R H}} \). Curve 3 is the potential energy diagram for the repulsion of \( \text{R}^* \) by the molecule \( \text{H Cl} \). In this \( d_{\text{H Cl}} = \delta_{\text{H Cl}} \).

Figure 2 indicates the possible variation of potential energy of the system as the reaction proceeds. The position of highest energy involves a 'transition state' or 'activated complex' and the height of this above the energy of the reactants is the energy of activation \( E \).

Several attempts have been made to relate the activation energies of bimolecular reactions to the strength of the bond which is broken but without much success. This point will be discussed later.

**The Collision Theory.** In bimolecular reactions, if the \( e^{-\frac{E}{RT}} \) part of the Arrhenius equation indicates the fraction of the total collisions which involves sufficient energy for reaction to occur, then the \( A \) factor should be related to the total number of collisions. From kinetic theory the rate of collisions between \text{A} and \text{B}
and B in the gas phase is

\[ Z = n_A n_B \sigma_{AB}^2 \left[ \frac{8\pi k T (m_A + m_B)}{m_A m_B} \right]^{1/2} \text{ molecules cc. sec.} \]

where \( n_A \) and \( n_B \) are the concentrations in molecules per cc. of the species of molecular masses \( m_A \) and \( m_B \) respectively, \( \sigma_{AB} \) is the mean collision diameter of A and B and \( k \) is the Boltzmann constant.

\[ k = \sigma_{AB}^2 \left[ \frac{8\pi k T (m_A + m_B)}{m_A m_B} \right]^{1/2} e^{-E/RT} \text{ molecules cc. sec.} \]

\[ = Z \cdot e^{-E/RT} \text{ molecules cc. sec.} \]

Z is known as the collision number and is the number of collisions per second when there is only one molecule of each reactant per cc.

The rate constants of many gas phase reactions do conform to the above equation, while reactions in solution and many other gas reactions take place much more slowly, or in a few cases more rapidly than the predicted rate and necessitate the introduction of a 'steric factor' \( P \).

\[ k = P \cdot Z \cdot e^{-E/RT} \]

**Theory of Absolute Reaction Rates.** Whereas the collision theory of bimolecular reactions does not consider the configuration of the transition state, the theory of absolute reaction rates does and predicts the rate constant from a knowledge of the concentration of activated complexes present.

Consider the formation of the activated complex \( \mathbf{M}^\ddagger \)

\[ A + B \longrightarrow \mathbf{M}^\ddagger \longrightarrow \text{products.} \]
The rate of the reaction is equal to the concentration of $M^+$ at the top of the energy barrier multiplied by the frequency of crossing the barrier.

Hence rate of reaction $= c_+ \cdot \frac{\bar{r}}{\delta}$

where $c_+$ is the number of complexes in unit volume along a distance $\delta$ at the top of the barrier in the transition state, and $\bar{r}$ the normal translational velocity is assumed to be the mean velocity of crossing.

These complexes can be treated as normal molecules having concentration $c_+$ with no vibration in the reaction co-ordinate if

$$c_+ = c_+ \cdot \frac{(2\pi m^* kT)^{\frac{1}{2}}}{h} \frac{\delta}{\hbar}$$

where $\frac{(2\pi m^* kT)^{\frac{1}{2}}}{h} \frac{\delta}{\hbar}$ is the partition function for translation in the reaction co-ordinate with $m^*$ the effective mass of the complex.

By kinetic theory $\bar{r}$ the mean velocity of crossing the barrier is $\left(\frac{2kT}{\pi m^*}\right)^{\frac{1}{2}}$ but only half the complexes are moving in the one direction.

\[ \therefore \text{Rate of reaction} = c_+ \cdot \frac{(2\pi m^* kT)^{\frac{1}{2}} \delta}{h} \frac{\left(\frac{kT}{2\pi m^*}\right)^{\frac{1}{2}}}{\delta} \]

\[ = c_+ \cdot \frac{kT}{h} \]

It has been assumed that all complexes passing over the barrier complete the reaction. This is not always the case and a transmission coefficient $K$ is necessary. For many reactions $K$ is close to unity.

Since rate of reaction $= k \cdot \frac{c_+ \cdot c_0}{c_A \cdot c_B}$

$$k = \frac{kT}{h} \cdot \frac{c_+}{c_A \cdot c_B} = \frac{kT}{h} \cdot K^*$$

where $K^*$ is the equilibrium constant for the activation process and can be obtained.
be obtained from thermodynamic relationships.

\[-\Delta G^\# = RT \ln K^\#\]

and \[\Delta G^\# = \Delta H^\# - T \cdot \Delta S^\#\]

\[k = \frac{kT}{h} \cdot e \cdot \Delta S^\# / R - \Delta H^\# / RT\]

Now \[
\frac{E_{\text{exp}}}{RT^2} = \frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_c}{dT}
\]

\[E_{\text{exp}} = RT + \Delta u^\# = RT + \Delta H^\# - p \cdot \Delta V^\#\]

where \(E_{\text{exp}}\) is the experimental activation energy obtained from the Arrhenius equation, \(\Delta u^\#\) is the increase in internal energy for the activation process and \(\Delta V^\#\) is the accompanying increase in volume.

\[p \cdot \Delta V^\# = \Delta n^\# \cdot R \cdot T\]

for \(\Delta n^\# = -1\) as in \(A + B \rightarrow M^\#\)

\[k = e^{-\frac{2 \cdot kT}{h} \cdot \Delta S_c^\# / R - E_{\text{exp}} / RT}\]

Thus the theory of absolute reaction rates predicts a value for the experimental \(A\) factor of \(e^{-\frac{2 \cdot kT}{h} \cdot \Delta S_c^\# / R}\).

This applies to a bimolecular reaction of the type

\[X + Y = Z \rightarrow X - Y + Z\]

which proceeds through a single activation complex. \(\Delta S_c^\#\)
is the entropy of activation at constant concentration and can be calculated if the entropies of the complex and reactants are known

\[\Delta S^\# = \Delta S_{\text{trans}}^\# + \Delta S_{\text{rot.}}^\# + \Delta S_{\text{vib.}}^\#\]

Since \(\Delta S_c^\#\) depends on temperature the \(A\) factor should be calculated for the mid temperature within the experimental range.
EXPERIMENTAL.

(1) METHOD OF PRESENT WORK AND CALCULATION OF RESULTS.

The object of this work was to determine accurately the relative rate constants for the attack of chlorine atoms on different hydrocarbons and on different carbon-hydrogen bonds in the one molecule.

The mechanism assumed for the chlorination of the hydrocarbons studied is

\[
\begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2 \text{Cl}, \\
\text{Cl}^- + \text{R}_a \text{H} & \rightarrow \text{R}_a^- + \text{HCl} \quad (2a) \\
\text{R}_a^- + \text{Cl}_2 & \rightarrow \text{R}_a \text{Cl} + \text{Cl}^- \quad (3a) \\
 & + \text{termination processes}. \quad (4)
\end{align*}
\]

The rate of removal of the hydrocarbon is

\[
-\frac{d[R_a\text{H}]}{dt} = k_{2a} (R_a\text{H})(\text{Cl})
\]

If another hydrocarbon is chlorinated simultaneously

\[
-\frac{d[R_b\text{H}]}{dt} = k_{2b} (R_b\text{H})(\text{Cl})
\]

provided that the chain propagating steps are similar.

Hence

\[
\frac{R_{a\text{H}}}{R_{b\text{H}}} = \frac{k_{2a} (R_a\text{H})}{k_{2b} (R_b\text{H})} = \frac{\frac{d(R_a\text{H})}{dt}}{\frac{d(R_b\text{H})}{dt}} = \frac{d(R_a\text{H})}{d(R_b\text{H})}
\]

Therefore

\[
\frac{d(R_a\text{H})}{k_{2a} (R_a\text{H})} = \frac{d(R_b\text{H})}{k_{2b} (R_b\text{H})} \quad \text{and/}
\]
and by integration

\[
\frac{k_{2a}}{k_{2b}} = \frac{\ln \left( \frac{(R_a H)_i}{(R_a H)_f} \right)}{\ln \left( \frac{(R_b H)_i}{(R_b H)_f} \right)}
\]

where \( i \) and \( f \) indicate initial and final concentrations respectively.

If the amount of reaction is small the approximation can be made that

\[
\ln \left( \frac{(R_b H)_i}{(R_b H)_f} \right) \approx \frac{\Delta (R_b H)}{(R_b H)}
\]

Therefore

\[
\frac{k_{2a}}{k_{2b}} = \frac{\Delta (R_a H) \cdot (R_b H)}{\Delta (R_b H) \cdot (R_a H)}
\]

If the reaction chains are long, it can be assumed that, for the hydrocarbon removed, an equivalent amount of chloride is produced.

\[
\frac{k_{2a}}{k_{2b}} = \frac{(R_a Cl)(R_b H)}{(R_b Cl)(R_a H)}
\]

where \((R_a Cl)\) and \((R_b Cl)\) are the concentrations of chlorination products while \((R_a H)\) and \((R_b H)\) are the initial concentrations of the hydrocarbons.

For chlorination at different points in the one hydrocarbon, leading to different chloride products

\[
\frac{k_{2a}}{k_{2b}} = \frac{(R_a Cl)}{(R_b Cl)}
\]

In this work the relative pressures of hydrocarbons in the reaction mixture were measured while the chlorides produced were analysed.
analysed by gas chromatography.

By studying the chlorination of the various mixtures at different temperatures, Arrhenius plots of \( \log_{10} \frac{k_{2a}}{k_{2b}} \) against \( \frac{1}{T^0} \) were obtained.

The method of least squares, in the treatment of these results, gave values for the difference in activation energies \( E_{2b} - E_{2a} \) and the relative 'A factors' \( \frac{A_{2a}}{A_{2b}} \). The experimental A factors depend on the number of similar carbon-hydrogen bonds per molecule, and so relative 'A factors per atom' were obtained by making allowance for this number. The mixtures methane-hydrogen, propane-ethane, n butane-ethane, iso butane-ethane, neo pentane-propane, cyclopropane-ethane and cyclobutane-propane have been chlorinated and together with the previous results for ethane-methane and the absolute rate constant for hydrogen, absolute rate constants for the chlorine attack on the following bonds have been obtained: \( 1^{XY} \) in methane, ethane, propane, n butane, iso butane and neo pentane, \( 2^{XY} \) in propane, n butane, cyclopropane and cyclobutane, and \( 3^{XY} \) in iso butane.
(2) MATERIALS

Hydrogen was obtained from a B.O.G. cylinder. It was dried by passage through phosphorus pentoxide.

Nitrogen was obtained from a B.O.G. cylinder and was stated to be oxygen free.

Chlorine was obtained from an I.C.I. cylinder. The middle fraction was collected and freed from water by distillation from a trap at -30°C to the trap of a 1 litre storage bulb at -194°C.

Methane was obtained from a B.O.G. cylinder. This contained a small amount of ethane which would have caused interference owing to its much higher rate of chlorination. This impurity was removed by pre-chlorination.

A 2 litre bulb containing methane at a pressure of 40 cm Hg and chlorine at a pressure of 4 cm Hg was exposed to sunlight for 12 hours. The chlorides, most of the ethane giving ethyl chloride, were frozen out and the middle fraction of methane was collected in a pump-down trap. The methane was distilled into a trap at -194°C attached to the storage bulb from a trap at -80°C to remove any water.

Ethene was obtained from a B.O.G. cylinder. It contained 1.2% ethylene.

Propene was obtained from a cylinder gifted by I.C.I. This contained 0.6% iso butane and traces of ethane and propylene.

iso Butane was obtained from a cylinder gifted by B.P.

n Butane was obtained from a cylinder gifted by B.P.

neo Pentane was obtained from an ampoule supplied by D.S.I.R., Chemical Research Laboratories, Teddington.

Cyclo Propane was obtained from a B.O.G. (Medicinal) cylinder.
cyclo Butane was prepared by photolysis of cyclopentanone. 12 ml. of cyclopentanone (B.D.H. Lab. Reagent) were sealed in an evacuated 5l. pyrex bulb, heated to 150° - 200°C in an air bath and illuminated with ultra violet light from a 250 watt Hg vapour lamp for 7 days. After breaking the seal and pumping off the carbon monoxide, a mixture of ethylene, cyclobutene and butenes was obtained by distillation, leaving behind unreacted cyclopentanone and polymerised material. Pure cyclobutene was obtained by passing the mixture through the analytical gas chromatography column. The identity of cyclobutene was checked by infra-red analysis.

All the above hydrocarbon vapours were freed from water by distillation from a trap at -80°C to one at -194°C. In view of the nature of the experiments, small amounts of impurities of the order of 1% would not influence the accuracy of the results, except in the case of methane, and no special steps were taken to purify the reagents further.

Mercury diphenyl was obtained as B.D.H. laboratory reagent. This was found to be impure and was purified by fractional sublimation. The impurity possibly diphenyl, sublimed first while the fraction subliming in vacuo between 100 and 120°C was found to be pure mercury diphenyl (m.p. 120°C).

Hydrogen chloride was prepared by dropping conc. H₂SO₄ into conc. HCl. The evolved hydrogen chloride was collected in a trap at -194°C and later freed from water by distillation from a trap at -80°C.

Methyl chloride was obtained from an L.C.L. cylinder.

Ethyl chloride was obtained from a B.D.H. (Anaesthetic) ampoule.

Propyl chlorides
n Butyl chlorides
iso Butyl chlorides
were obtained as B.D.H. Lab. Reagents.
(3) APPARATUS AND PROCEDURE

The chlorinations were carried out in a static system and the analyses were made by means of gas chromatography.

**Kinetic System** (see Figure 3) The apparatus was evacuated by means of a high-vac. oil pump together with a two stage mercury pump. The reaction vessel (R.V.) was of pyrex glass and had a volume of 82 ml. It possessed an inner thermometer well and a detachable outer jacket. When the vapours from a boiling liquid were used for thermostating the R.V., this outer jacket was used in conjunction with a small water condenser. In this way the whole R.V. acquired a constant temperature except for the small volume between the tap and the main R.V. As this part was made of capillary glass the effect on the reaction in the main R.V. was negligible. The outer jacket was covered with asbestos apart from an illumination window. When a freezing mixture was used to thermostat the R.V. a pyrex, unsilvered Dewar vessel was used to hold the mixture. A pentane thermometer was used to measure the temperatures below 0°C.

The reaction vessel was thermostated by the following methods:

- Acetone + solid CO₂ - 79°C
- Chloroform + solid CO₂ - 68°C
- 50% H₂SO₄ + solid CO₂ ~ -35°C
- Ice 0°C
- Water at room temperature ~ +20°C
- Boiling chloroform +61°C
- Boiling water +100°C
- Boiling chlorobenzene +132°C
- Boiling decalin +190°C
boiling methylsalicylate  + 225°C
boiling H₂SO₄  + 327°C

Illumination: Illumination of the reaction mixture was by means of a 250W projection lamp. In order to remove most of the infra-red rays from the light a 10% copper sulphate solution was used. This solution was placed in a round 600 ml pyrex beaker between the projection lamp and the R.V. To prevent this solution from losing water by evaporation cold water was run through a spiral tube dipping into the solution. This beaker of copper sulphate solution also assisted in focusing the light on the R.V.

Preparation of Reaction Mixture. Silicone high vac. tap grease was used throughout the kinetic system. Chlorine was found to attack this tap grease slowly and so the chlorine was stored at liquid oxygen temperature in the trap attached to a 1 litre storage bulb. Hydrogen and the hydrocarbons were contained in 2 litre storage bulbs while the nitrogen was held in a 5 litre bulb. Chlorination mixtures were prepared in a 100 ml darkened mixing vessel to prevent any photochemical reaction occurring before the mixture entered the reaction vessel. The pressures of gases in this mixing vessel were measured by means of a Bourdon spoon gauge. This spoon gauge was constructed of pyrex glass and had an optical lever system by which movements of the spoon were transferred to a small mirror which reflected light from a projector back to a centimetre scale. The movements of the spoon were damped by allowing the end of the spoon to dip into di-0ctyl phthalate. This system was calibrated by means of a mercury manometer and it was found that 1 cm. scale division corresponded/
corresponded to a pressure of 1.11 cm Hg.

Chlorine was first measured into the mixing vessel. The two competing hydrocarbons or hydrogen were then measured into the vessel in the required ratio. This ratio was the only quantity which had to be measured accurately until analysis of the products. The chlorine pressure was, however, measured to give an indication of the amount of chlorides to be expected when analysing. The pressure of the chlorine - hydrocarbon mixture was then increased to ~50 cm Hg. by allowing nitrogen to enter the mixing vessel. After this mixture had come to equilibrium it was allowed to enter the R.V. The tap of the R.V. was closed and the mixture illuminated for 30 minutes. To satisfy the conditions for the equation

$$\frac{k_{2a}}{k_{2b}} = \frac{(R_a C_1) (R_b H)}{(R_a C_1) (R_b H)}$$

and to ensure that secondary chlorination occurred to the smallest extent possible, the chlorine / hydrocarbons ratio was kept low (generally less than 1/10) where feasible. The presence of nitrogen in the reaction vessel was to ensure that no self heating of the reaction mixture occurred, although this precaution was hardly necessary in view of the low chlorine pressures used. Incidentally the nitrogen would help to decrease the frequency of termination processes on the walls.

**Sampling Procedure.** Two different methods of transferring the products of the reaction from the R.V. to the 'U' tube of the chromatography apparatus were used.

(a) A portion of the contents of the R.V. was allowed to enter the cold finger, the central tube of which was filled with liquid oxygen. After a short time, to/
to allow the hydrocarbons and chlorides to freeze out on the central tube, the nitrogen and hydrogen chloride were pumped off through the chromatography "U" tube at -194°C. The oxygen in the cold finger was replaced with hot water and the hydrocarbons and chlorides were allowed to distil into the "U" tube. Complete transfer was effected by pumping through the "U" tube after most of the material had distilled across.

(b) For less volatile chloride products a simpler method of transfer was used. This simply involved pumping the contents of the R.V. through the "U" tube at -194°C.

Before either sampling procedure could be carried out after runs at -80°C it was first necessary to bring the R.V. temperature up to room temperature to remove any of the chlorides which had been frozen out or adsorbed on the walls.

In the chlorination of hydrogen - methane mixtures an additional operation was involved in transferring the products of the reaction to the chromatography section. This was necessary since the product of the chlorination of hydrogen, hydrogen chloride, could not be detected in the analysis. Hydrogen chloride is either irreversibly absorbed by the column packing material or only comes through the column very slowly.

The products of the hydrogen - methane chlorinations were completely transferred to a "U" tube packed with purified mercury diphenyl. The taps of the "U" tube were then closed and the tube itself was heated to +80°C for 5 minutes. It was found that by this technique all the hydrogen chloride present was converted into an equivalent amount of benzene. The products were then distilled into the chromatography "U" tube. The transfer was completed by pumping through the "U" tube.
ANALYSIS SECTION.

Fig. 4.

This is a schematic diagram of an analytical system involving various components such as:

- **Water bubbler**
- **Mercury manometer**
- **Thermocouples and THERMAL CONDUCTIVITY GAUGES**
- **Buffering vessels**
- **Needle valve**
- **Hydrogen cylinder**

The system includes analytical and dummy columns in a heating jacket and is connected from a kinetic system.
**Gas Chromatography Apparatus.** (See Figure 4) This apparatus was of conventional design having a pressure regulating device, sampling vessel, columns with packing and a detector.

**Pressure Regulator.** The carrier gas used was hydrogen. This was obtained from a B.o.C. cylinder and was dried through the $P_2O_5$ before passing through a needle valve. The hydrogen stream was then divided into two, part going through the columns and part going into water bubblers where a constant head of water ensured a constant hydrogen pressure. Any irregularities in the pressure caused by the creation of bubbles were evened out by means of 4 buffering vessels before the hydrogen stream entered the sampling vessel.

**Sampling Vessel.** This consisted of a double 'U' tube, through which the chlorination products could be pumped. By means of two 2-way taps the hydrogen flow prior to entering the columns could either pass through the 'U' tube or by-pass it completely. The products entered the hydrogen stream on being heated to $+80^\circC$.

**Columns.** Two identical columns were used. Through one passed the hydrogen stream after collecting the material for analysis from the 'U' tube, while the other was used as a "dummy" column to supply hydrogen at a similar pressure to the second thermal conductivity gauge. The columns were of pyrex glass, 6-7 m.m. in internal diameter. The packing consisted of firebrick 25-52 B.S.S. mesh containing 25% w/w di-octyl phthalate. The di-octyl phthalate was evenly distributed on the firebrick by evaporation of a chloroform solution. The columns were both thermostated in a glass jacket which was heated electrically. Thus the separation of products effected on/
Fig. 5.

Fig. 6.

8 Volts.
on the column could be controlled by

(a) Initial hydrogen pressure
(b) Length of columns
(c) Temperature of columns.

Detector. Thermal-conductivity cells were used throughout the work. A copper block (Fig. 5 is 1/2 actual size) had two channels drilled in it. Each channel had a tungsten filament, of resistance approximately 10 ohms, stretched along its axis. The carrier gas from each column was passed over a tungsten filament which was incorporated in a Wheatstone Bridge circuit. Each filament (see Fig. 6) was an arm in this circuit and the off-balance current was transferred to a moving-coil galvanometer. Using a projector lamp and a cm. scale the off-balance current was observed visually and could be plotted against time.

In Fig. 6 G1 and G2 represent the filaments of the thermal-conductivity gauges, G2 having the lower resistance. Both R1 and R2 are standard resistances of 10 ohms. R4 is a resistance box of resistances 0 - 8,800 ohms with the moving-coil galvanometer in series. R5 is a variable resistance for zeroing the off-balance current through the galvanometer. The potential of 8 volts was supplied by four accumulators in series.

The sensitivity of the moving coil galvanometer could be varied by means of R₄ to suit the quantity of chlorides produced.

The off-balance current, generally observed at 12 second intervals, was plotted against time. The areas of the surfaces enclosed by the peaks and the normal base line were measured with a planimeter, and these indicated the molar concentrations of the various substances present in the chromatogram, provided/
provided that the relative sensitivities were known.

The relative sensitivities of substances under analysis were obtained by analysing known mixtures of authentic samples.

The sensitivities of all the hydrocarbon chlorides studied were identical to within 5% while the methyl chloride and benzene in the methane – hydrogen chlorinations had widely differing sensitivities.

This result is not surprising since hydrogen was used as the carrier gas; and the thermal conductivities of the hydrocarbon chlorides relative to the hydrogen value cannot differ to an appreciable extent.
RESULTS AND EXPERIMENTAL DETAILS.

1. CHLORINATION OF HYDROGEN - METHANE MIXTURES.

The chlorine, methane and hydrogen mixtures were prepared by the usual method, illuminated in the R.V. for the arbitrary time of 30 minutes and then passed into the special trap containing diphenyl mercury. It was found that complete replacement of the total hydrogen chloride by benzene occurred in 5 minutes at 80°C, after which the methyl chloride and benzene were analysed by gas chromatography.

A special method of determining the relative sensitivities of the detector to these substances had to be employed since benzene readily dissolved in tap grease, and this made the preparation of a standard methyl chloride-benzene mixture impossible.

Several runs were carried out in which methane was chlorinated alone. The products were analysed for methyl chloride and hydrogen chloride as before. Assuming that only mono-chlorination has occurred, the peaks for methyl chloride and benzene represent equimolar quantities.

\[
\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}
\]

This method of determining the relative sensitivities of methyl chloride and benzene gave the following results.

Run No./
From these figures the detector is 0.5 times as sensitive towards methyl chloride as to benzene.

Small amounts of methylene dichloride (up to 2%) were formed but were neglected in all calculations.

It was noted that variation of the initial hydrogen-methane ratio did not produce any regular variation in the ratio of the rate constants for that temperature. This suggests that the rate expression used was adequate.

In most runs the initial pressures of hydrogen and methane were chosen so that the ratios of benzene to methyl chloride in the analyses were fairly constant. This ensures that any error in calibration is transferred to the relative A factors rather than the activation energy difference.

The chromatography column was 120 c.m. in length, 6m.m. internal diameter, and was packed with 25.-52 mesh firebrick (Fosalsil No 6) moistened with 25% w/w of dioctyl phthalate. The operating temperature was 100°C and under these conditions methyl chloride appeared after 2½ minutes while benzene appeared after 10 minutes.
Since reaction (3) produces an equal amount of hydrogen chloride to that produced by reaction (2)

(2)  \[ \text{Cl}^- + \text{H}_2 \rightarrow \text{HCl} + \text{H}^- \]

(3)  \[ \text{H}^- + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}^- \]

the total amount of hydrogen chloride produced from the chlorination of hydrogen is twice that produced by reaction (2) which is the value necessary for \((\text{HCl})\) in

\[
\frac{k_{\text{Me}}}{k_{\text{H}}} = \frac{(\text{CH}_3\text{Cl})(\text{H}_2)}{(\text{HCl})(\text{CH}_4)}
\]

\[
= \frac{(\text{H}_2)(\text{CH}_3\text{Cl})}{(\text{CH}_4)(\frac{2}{3} \text{ total HCl from H}_2)}
\]

while \((\text{total HCl from H}_2) \equiv (\text{total HCl}) - (\text{HCl from CH}_4 \text{ chlorination})\)

The results for the hydrogen-methane chlorinations are given in Tables 1 and 2.
Example of Calculation.

Run 24.  
Temp. of R.V. = 100°C.

Pressures of reactants in mixing vessel.

- Chlorine = 0.1 cm Hg.
- Methane = 1.0 cm Hg. \((\text{CH}_4)\)
- Hydrogen = 1.85 cm Hg \((\text{H}_2)\)
- Nitrogen = 50 cm Hg.

Area of methyl chloride = 1.30 units.
Area of benzene = 6.22 units.

Now methyl chloride is 0.5 times as sensitive as benzene.

\[\text{Molar ratio of } \frac{\text{methyl chloride/total HCl}}{\text{total HCl from } H_2} = \frac{2.60}{6.22}.\]

and molar ratio of \(\frac{\text{methyl chloride/total HCl from } H_2}{\text{total HCl from } H_2} = \frac{2.60}{3.62}\)

\[
\frac{(\text{H}_2)}{(\text{CH}_4)} = \frac{1.85}{1.0} \quad \text{and} \quad \frac{(\text{CH}_3 \text{Cl})}{(\frac{1}{2} \text{ total HCl from } H_2)} = \frac{2.60}{1.81}
\]

\[
\frac{k_{\text{Me}}}{k_{H}} = \frac{(\text{H}_2)(\text{CH}_3 \text{Cl})}{(\text{CH}_4)(\frac{1}{2} \text{ total HCl from } H_2)} = 2.66.
\]

where \(k_{\text{Me}}\) and \(k_{H}\) are the rate constants for

\[
\text{Cl}^- + \text{CH}_4 \longrightarrow \text{CH}_3^+ + \text{HCl}
\]

and

\[
\text{Cl}^- + \text{H}_2 \longrightarrow \text{H}^+ + \text{HCl}
\]

respectively.
<table>
<thead>
<tr>
<th>RUN</th>
<th>T C</th>
<th>(HYDROGEN) ( \text{cm Hg} )</th>
<th>(METHANE) ( \text{cm Hg} ) added</th>
<th>( \frac{1}{2} \text{(HCl)} ) from ( \text{H}_2 ) produced</th>
<th>( \log_{10} K_{\text{H}} )</th>
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<tr>
<td>52</td>
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<td>3.00</td>
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<td>1.00</td>
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<td>2.97</td>
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<td>2.00</td>
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<td>5.55</td>
<td>1.48</td>
<td>0.90</td>
</tr>
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<td>6.05</td>
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<td>1.62</td>
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<td>5.30</td>
<td>1.68</td>
<td>2.19</td>
</tr>
</tbody>
</table>

* in mole --- mole.
By the method of least squares on the complete data, the relative rate constants are

\[ \frac{k_{Me}}{k_H} = 0.30 \pm 0.03 \exp \left( \frac{1650 \pm 60}{RT} \right) \]

where the errors quoted are for 50% probability. This result agrees well with the result obtained by Pritchard, Pyke and Trotman-Dickenson of

\[ \frac{k_{Me}}{k_H} = 0.322 \exp \left( \frac{1650}{RT} \right) \]

This is a further example of the good agreement between the two methods of product analysis and hydrocarbon-consumption analysis.

**Table 2.**

<table>
<thead>
<tr>
<th>RUNS.</th>
<th>(10^3/T_A)</th>
<th>(\text{AVERAGE VALUE OF} ) (\log_{10} k_{Me}/k_H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>52,53,54.</td>
<td>5.13</td>
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<td>21</td>
<td>4.88</td>
<td>1.262</td>
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<tr>
<td>49,51</td>
<td>4.18</td>
<td>0.953</td>
</tr>
<tr>
<td>13,14,15</td>
<td>3.41</td>
<td>0.765</td>
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<tr>
<td>30,31,32,33</td>
<td>3.00</td>
<td>0.592</td>
</tr>
<tr>
<td>23,24,26</td>
<td>2.60</td>
<td>0.444</td>
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<tr>
<td>27,28,29</td>
<td>2.47</td>
<td>0.383</td>
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<tr>
<td>19,35</td>
<td>2.16</td>
<td>0.265</td>
</tr>
<tr>
<td>38,40,41</td>
<td>1.67</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Figure 7 is the Arrhenius plot of the results in Table 1, while the above results are found in Figure 17.
Fig. 7

Hydrogen / Methane

\[ \log \text{K} / \text{K} \]

\[ 1/T \times 10^3 \]
Note on the method of Least Squares. (For complete method, see Margenau & Murphy - 'The Maths. of Physics and Chemistry'.)

For ease of calculation, a modified method of least squares analysis on the results in the Arrhenius plot was used.

1/T°A was chosen as the independent variable x and \(\log_{10} \frac{k_{2a}}{k_{2b}}\) as the dependent variable y. The means of the x and y values were first obtained. These gave the point \((\bar{x}, \bar{y})\) which was assumed to lie on the best straight line through the points.

Where \(x = \bar{x} - \bar{x}\) and \(y = \bar{y} - \bar{y}\) the gradient m of the line giving the closest fit to the experimental points is given by

\[
m = \frac{\sum x y}{\sum x^2}.
\]

From the mean point \((\bar{x}, \bar{y})\) and the gradient m, the Arrhenius parameters were calculated. The probable error \(P_m\) in the gradient m is

\[
P_m = 0.6745 \frac{\sum d^2}{\sqrt{(n-2) \sum x^2}}
\]

where \(d\) is the deviation of a point from the line in the direction of the y axis, and

\[
\sum d^2 = \sum x^2 \left[ \frac{\sum y^2}{\sum x^2} - \left(\frac{\sum xy}{\sum x^2}\right)^2 \right]
\]

From \(P_m\) are calculated the 50% probability limits in the activation energy difference, and from this can be derived the corresponding limits in the relative A factors.
2. **CHLORINATION OF ETHANE - PROPANE MIXTURES.**

The products from ethane + propane chlorinations were analysed for ethyl chloride, primary propyl chloride and secondary propyl chloride.

The chromatography column was 190 cm in length, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 50-55°C. Under these conditions the ethyl chloride appeared after 11 minutes, the sec. propyl chloride after 17 minutes and the pri. propyl chloride after 25 minutes. No other chloride products were observed.

Where $k_{Et}$, $k_{sPr}$ and $k_{pPr}$ are the rate constants of

\[
\begin{align*}
Cl^{-} + CH_{3} - CH_{3} & \rightarrow CH_{3} CH_{2}^{+} + HCl \\
Cl^{-} + (CH_{2})_{2}CH_{2} & \rightarrow (CH_{3})_{2}CH^{+} + HCl \\
Cl^{-} + CH_{2}CH_{2}CH_{2} & \rightarrow CH_{2}CH_{2}CH_{2}^{+} + HCl
\end{align*}
\]

respectively, then

\[
\frac{k_{sPr}}{k_{Et}} = \frac{(sPr\ Cl)(ethane)}{(St\ Cl)(propane)} \quad \frac{k_{pPr}}{k_{Et}} = \frac{(pPr\ Cl)(ethane)}{(St\ Cl)(propane)}
\]

and

\[
\frac{k_{sPr}}{k_{pPr}} = \frac{(sPr\ Cl)}{(pPr\ Cl)}
\]

N.B. $sPr \equiv$ secondary propyl, $pPr \equiv$ primary propyl and $St \equiv$ ethyl.
Chlorinations were carried out at 321°C but these resulted in irreproducible relative rate constants and sec. propyl chloride/prim. propyl chloride ratios which were much lower than would be expected for this temperature. This suggests that decomposition of the propyl chlorides had occurred and that the secondary chloride had decomposed faster than the primary chloride.

This is probably the explanation of the curvature at high temperatures which occurs in the Arrhenius plots of the results of Hass, McBee and Weber.
Example of Calculation.

Run 18.  

Temperature = -28°C.

Pressures of reactants in mixing vessel

- Chlorine = 0.25 cm Hg.
- Ethane = 4.35 cm Hg. (ethane)
- Propane = 3.00 cm Hg. (propane)
- Nitrogen = 50 cm Hg.

Area for ethyl chloride = 2.03 units (Et Cl)
- " s. propyl chloride = 2.18 units (sPr Cl)
- " p. propyl chloride = 1.68 units (pPr Cl)

All these chlorides have the same sensitivity.

\[
\frac{k_{sPr}}{k_{Et}} = \frac{(sPr \text{ Cl})(\text{ethane})}{(Et \text{ Cl})(\text{propane})} = \frac{2.18}{2.03} \times \frac{4.35}{3.00} = 1.56.
\]

Similarly \( \frac{k_{pPr}}{k_{Et}} = 1.20 \).

and \( \frac{k_{pPr}}{k_{sPr}} = 1.30 \).
### Table 3.

<table>
<thead>
<tr>
<th>RUN</th>
<th>°C</th>
<th>(ETHANE) added cm Hg</th>
<th>(PROPANE) added cm Hg</th>
<th>AREA EtCl</th>
<th>AREA sPrCl</th>
<th>AREA pPrCl</th>
<th>log₁₀ kₚPr Et</th>
<th>log₁₀ kₚPr pPr</th>
<th>log₁₀ kₚPr sPr</th>
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<tbody>
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<tr>
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<td>.61</td>
<td>.38</td>
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<td>0.0453</td>
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<td>.38</td>
<td>.25</td>
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<td>2.18</td>
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</table>

321 evidence of propyl chloride decomposition.
By the method of least squares on the complete data as given in table 3, the relative rate constants are

\[
\begin{align*}
\frac{k_{SPR}}{k_{Et}} & = 0.78 \pm 0.012 \ exp \ (360 \pm 10 / RT) \\
\frac{k_{pPR}}{k_{Et}} & = 1.11 \pm 0.025 \ exp \ (40 \pm 10 / RT) \\
\frac{k_{sPR}}{k_{pPR}} & = 0.70 \pm 0.010 \ exp \ (320 \pm 10 / RT).
\end{align*}
\]

<table>
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<tr>
<th>RUNS.</th>
<th>(10^3/T\ A)</th>
<th>(k_{sPR}/k_{Et})</th>
<th>(k_{pPR}/k_{Et})</th>
<th>(k_{SPR}/k_{pPR})</th>
</tr>
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</table>

The Arrhenius plots of the results in the above tables are found in Figures 8 & 9 and Figure 18.
3. **CHLORINATION OF ETHANE - n BUTANE MIXTURES.**

The products from ethane + n butane chlorinations were analysed for ethyl chloride, secondary n butyl chloride and primary n butyl chloride.

The chromatography column was 190 cm. in length, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 60 - 65°C. The hydrogen pressure at the start of the columns was 6 cm. Hg. and under these conditions the ethyl chloride appeared after 3 1/2 minutes, the secondary butyl chloride after 12 minutes and the primary butyl chloride after 18 minutes. No other chloride products were observed.

Where \( k_{snBu} \) and \( k_{pnBu} \) are the rate constants of

\[
\begin{align*}
Cl^- + CH_3(CH_2)_2CH_3 & \rightarrow CH_3CH_2CH(CH_3) + HCl \\
Cl^- + CH_3(CH_2)_2CH_3 & \rightarrow CH_3(CH_2)_2CH_2 + HCl
\end{align*}
\]

respectively, then

\[
\frac{k_{snBu}}{k_{Et}} = \frac{(snBu Cl)(ethane)}{(Et Cl)(n butane)} ; \quad \frac{k_{pnBu}}{k_{Et}} = \frac{(pnBu Cl)(ethane)}{(Et Cl)(n butane)}
\]

and

\[
\frac{k_{snBu}}{k_{pnBu}} = \frac{(snBu Cl)}{(pnBu Cl)}
\]

**N.B.**

\( snBu \equiv \) secondary n butyl and

\( pnBu \equiv \) primary n butyl.
<table>
<thead>
<tr>
<th>RUN</th>
<th>T°C</th>
<th>(ETHANE)</th>
<th>AREA</th>
<th>AREA</th>
<th>AREA</th>
<th>k&lt;sub&gt;sBu&lt;/sub&gt;log&lt;sub&gt;10&lt;/sub&gt;</th>
<th>k&lt;sub&gt;pBu&lt;/sub&gt;log&lt;sub&gt;10&lt;/sub&gt;</th>
<th>k&lt;sub&gt;sBu&lt;/sub&gt;log&lt;sub&gt;10&lt;/sub&gt;</th>
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<tbody>
<tr>
<td></td>
<td></td>
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<td>EtCl</td>
<td>sBuCl</td>
<td>pBuCl</td>
<td>Et&lt;sub&gt;1&lt;/sub&gt;</td>
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</table>
By the method of least squares on the complete data as given in Table 5, the relative rate constants are

\[ \frac{k_{\text{snBu}}}{k_{Et}} = 0.94 \pm 0.056 \exp \left( \frac{770 \pm 35}{RT} \right) \]

\[ \frac{k_{\text{pnBu}}}{k_{Et}} = 0.89 \pm 0.04 \exp \left( \frac{250 \pm 30}{RT} \right) \]

\[ \frac{k_{\text{snBu}}}{k_{\text{pnBu}}} = 1.05 \pm 0.05 \exp \left( \frac{520 \pm 35}{RT} \right) \]

<table>
<thead>
<tr>
<th>RUNS</th>
<th>( \frac{10^{3}}{T^0} )</th>
<th>( \text{log}<em>{10} k</em>{\text{snBu}} )</th>
<th>( \text{log}<em>{10} k</em>{\text{pnBu}} )</th>
<th>( \text{log}<em>{10} k</em>{\text{snBu}} )</th>
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The Arrhenius plots of the results in the above tables are found in Figures 10 & 11 and Figure 19.
Fig. 10.

Ethane / 1 RY in n-Butane

$\log K_{\text{PNBu}}/K_{\text{Et}}$ vs. $1/T \times 10^3$. The graph shows a linear relationship between the logarithm of the ratio of reaction rates and the inverse of temperature.
4. CHLORINATION OF ETHANE - iso BUTANE MIXTURES.

The products from ethane - iso butane chlorinations were analysed for ethyl chloride, tertiary iso butyl chloride and primary iso butyl chloride.

The chromatography column was 190 cm. long, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 60 - 65°C. The hydrogen pressure at the start of the columns was 3 cm. Hg. and under these conditions the ethyl chloride appeared after 7 minutes, the tertiary butyl chloride after 14 1/2 minutes and the primary butyl chloride after 27 minutes. No other chloride products were observed.

Where $k_{tiBu}$ and $k_{piBu}$ are the rate constants of

$$
\text{Cl}^+ \cdot + (CH_3)_3 CH \rightarrow (CH_3)_3 C^- + HCl
\text{Cl}^+ \cdot + (CH_3)_3 CH \rightarrow (CH_3)_2 CH.CH_2^- + HCl
$$

respectively, then

$$
\frac{k_{tiBu}}{k_{Et}} = \frac{(tiBu Cl)(ethane)}{(Et Cl)(iso butane)} ; \frac{k_{piBu}}{k_{Et}} = \frac{(piBu Cl)(ethane)}{(Et Cl)(iso butane)}
$$

and $\frac{k_{tiBu}}{k_{piBu}} = \frac{(tiBu Cl)}{(piBu Cl)}$

The results of runs carried out at 134°C and 194°C were irreproducible and in all cases the tertiary/primary butyl chloride ratios were much lower than would be expected. This suggested that decomposition of the tertiary/
the tertiary butyl chloride was occurring at these temperatures, and this was supported by the fact that if short residence times (2-5 minutes) were used the relative rate constants approached the expected values. Further work at 194°C showed that:

(a) a sample of tertiary butyl chloride gave 90% decomposition into iso butene and hydrogen chloride after 30 minutes residence in the reaction vessel.

(b) a ten fold excess of hydrogen chloride prevented this decomposition.

(c) the tertiary/primary chloride ratio from a run carried out in the presence of a ten fold excess of hydrogen chloride was much greater than the expected value if no decomposition had occurred.

(d) a sample of primary iso butyl chloride was partially (ca. 40%) converted into the tertiary chloride after 30 minutes residence in the reaction vessel and in the presence of a ten fold excess of hydrogen chloride. No iso butene was detected.

When runs were carried out at 100°C and 15°C with a chlorine:hydrogen chloride ratio of 1:10, the relative rate constants obtained were identical to those found in the absence of any added hydrogen chloride. This proves that either inhibition by hydrogen chloride is negligible or the production of the tertiary and primary chlorides is inhibited to the same extent. This latter case/
case is highly improbable, so that reaction \((-2)\) is unimportant.

Barton & Onyon have shown that the decomposition of tertiary butyl chloride in glass reaction vessels is heterogeneous and only becomes reproducible after coating the walls. They found that extensive decomposition occurred at \(137^\circ C\). Hence the decomposition of the iso butyl chlorides above \(100^\circ C\) is the obvious explanation of the curvature in the Arrhenius plots from the work of Hass, McBee & Weber on the chlorination of iso butane.

N.B. \(t^3Bu \equiv \) tertiary iso butyl

\(p^3Bu \equiv \) primary iso butyl.
<table>
<thead>
<tr>
<th>RUN</th>
<th>T°C</th>
<th>(ETHANE) added (iso BUTANE) cm Hg --- cm Hg</th>
<th>AREA EtCl</th>
<th>AREA tBucCl</th>
<th>AREA pBucCl</th>
<th>log_{10} k_{tBu} / k_{Et}</th>
<th>log_{10} k_{pBu} / k_{Et}</th>
<th>log_{10} k_{tBu} / k_{pBu}</th>
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</table>
### TABLE 7. continued.

<table>
<thead>
<tr>
<th>RUNS</th>
<th>10^3/T°</th>
<th>ATOM</th>
<th>k_{tiBu}/k_{Et}</th>
<th>k_{piBu}/k_{Et}</th>
<th>k_{tiBu}/k_{piBu}</th>
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</thead>
<tbody>
<tr>
<td>52</td>
<td>61</td>
<td>1.76</td>
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<td>1.61</td>
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</tr>
<tr>
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<td>100</td>
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<td>2.67</td>
<td>0.80</td>
<td>1.14</td>
</tr>
<tr>
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<td>2.54</td>
<td>1.31</td>
<td>1.46</td>
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<tr>
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<td>0.64</td>
</tr>
<tr>
<td>64</td>
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<td>1.56</td>
<td>2.48</td>
<td>0.70</td>
<td>0.71</td>
</tr>
</tbody>
</table>

By the method of least squares on the complete data as given in table 7, the relative rate constants are

\[
k_{tiBu}/k_{Et} = 0.18 \pm 0.016 \exp\left(\frac{1020 \pm 45}{RT}\right).\]

\[
k_{piBu}/k_{Et} = 1.30 \pm 0.067 \exp\left(\frac{220 \pm 25}{RT}\right).\]

\[
k_{tiBu}/k_{piBu} = 0.13 \pm 0.01 \exp\left(\frac{800 \pm 40}{RT}\right).\]

### TABLE 8.

<table>
<thead>
<tr>
<th>RUNS</th>
</tr>
</thead>
<tbody>
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<td>44,45,46,47,48.</td>
</tr>
<tr>
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<tr>
<td>55,56,57,58,59.</td>
</tr>
<tr>
<td>30,31,32,34,35,36.</td>
</tr>
<tr>
<td>49,51,52,53.</td>
</tr>
<tr>
<td>60,61,62,63,64.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10^3/T°</th>
<th>AK</th>
<th>(\log_{10}k_{tiBu})</th>
<th>(\log_{10}k_{piBu})</th>
<th>(\log_{10}k_{tiBu}/k_{piBu})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.18</td>
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<td>0.3659</td>
<td>0.0390</td>
</tr>
<tr>
<td>4.93</td>
<td></td>
<td>0.3921</td>
<td>0.3430</td>
<td>0.0491</td>
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<td>1.6801</td>
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<tr>
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<td>1.8341</td>
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</table>
Fig 12.

Graph showing the relationship between the logarithm of the equilibrium constant for the reaction of ethane with isobutane and the reciprocal of temperature (1/T).
5. **CHLORINATION OF PROPANE - NEO PENTANE MIXTURES.**

It had been hoped to compete the chlorination of neopentane against that of ethane, in order to keep the number of intermediates as low as possible when the absolute rate constants were being derived from the absolute value for hydrogen. However, the neopentane interfered with the analysis of ethyl chloride and it was necessary to compete the chlorination of neopentane against that of the primary position in propane. Accordingly, the products from the propane - neopentane chlorinations were analysed for primary propyl chloride and neopentyl chloride.

The chromatography column was 320 cm. long, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 75°C. The hydrogen pressure at the start of the columns was 11 cm. Hg. and under these conditions primary propyl chloride appeared after 11½ minutes and neopentyl chloride after 25 minutes.

Where \( k_{\text{pPr}} \) and \( k_{\text{neoP}} \) are the rate constants of

\[
Cl^- + \left(CH_3\right)_2CH_2CH_2 \rightarrow \left(CH_3\right)_2CH_2CH^- + HCl
\]

and

\[
Cl^- + \left(CH_3\right)_3C \rightarrow \left(CH_3\right)_3CCH_2^- + HCl
\]

respectively,

\[
\frac{k_{\text{neoP}}}{k_{\text{pPr}}} = \frac{(\text{neoP Cl})(\text{propane})}{(\text{pPr Cl})(\text{neopentane})}
\]

*N.B. neoP \( \equiv \) neopentyl and pPr \( \equiv \) primary propyl.*
<table>
<thead>
<tr>
<th>RUN</th>
<th>°C</th>
<th>((\text{PROPANE})/\text{NEOPENTANE}) added cm Hg</th>
<th>AREA (\text{pFrCl})</th>
<th>AREA (\text{neoPeCl})</th>
<th>(\log_{10}(k_{\text{neoPe}}/k_{\text{pFr}}))</th>
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</thead>
<tbody>
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<td>0.87</td>
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<td>0.3464</td>
</tr>
<tr>
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<td>0.87</td>
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</tr>
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<td>1.92</td>
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<td>1.70</td>
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<td>RUNS.</td>
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<td>AVERAGE VALUE OF $\log_{10} \frac{k_{\text{neoFe}}}{k_{\text{pPr}}}$</td>
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<td></td>
<td></td>
</tr>
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<td>-----------------</td>
<td>-----------------------------</td>
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</table>

By the method of least squares on the complete data as given in Table 9, the rate constant ratio is

$$\frac{k_{\text{neoFe}}}{k_{\text{pPr}}} = 1.65 \times 0.05 \exp \left( \frac{80}{20 / RT} \right).$$

The Arrhenius plots are in Figure 14 and Figure 16.
$1^{RY}$ in Propane / neo Pentane.

![Graph showing relationship between $\log \frac{K_{neoP}}{K_{Pr}}$ and $\frac{1}{T \times 10^3}$ with data points and a trend line.]

**Fig. 14.**
6. **CHLORINATION OF ETHANE - CYCLOPROPANE MIXTURES.**

The chlorination of cyclopropane alone was first studied. The chromatography column was 190 cm. long, contained the 80:20 w/w mixture of firebrick and di-octyl phthalate and operated at 70-75°C. The initial hydrogen pressure was 11 cm. Hg. and under these conditions three products of the chlorination of cyclopropane were observed. Peak A appeared after 3 minutes, peak B after 7 minutes and peak C after 32 minutes. All runs were carried out at 21°C and the results are indicated in the following table.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Area of Peak A</th>
<th>Area of Peak B</th>
<th>Area of Peak C</th>
<th>Area B</th>
<th>Area C</th>
<th>( \frac{\text{Cl}_2}{\text{C}_3\text{H}_6} )</th>
</tr>
</thead>
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<tr>
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<td>0.08</td>
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<td>0.11</td>
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<td>0.18</td>
<td>0.46</td>
<td>0.18</td>
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<td>0.02</td>
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<td>0.08</td>
<td>0.08</td>
<td>0.07</td>
<td>0.03</td>
</tr>
</tbody>
</table>

In run 9 the chlorine-cyclopropane mixture was allowed to remain in the mixing vessel for 15 minutes before the illumination was/
was commenced. In the other runs this period of time varied between 1 and 5 minutes.

Since the ratio Area B/Area A varied directly with the chlorine/cyclopropane ratio, it seemed possible that substance B was formed by chlorination of A, i.e. if peak A corresponds to chloro cyclopropane then peak B is probably a dichloro cyclopropane. A large quantity of substance A was collected as it left the chromatography column and was subjected to infra red analysis. The spectrum obtained was almost identical to that obtained by Slabey for mono chloro cyclopropane.

Since the Area C/Area A ratio bears little relationship to the chlorine/cyclopropane ratio and more especially because of the result from Run 9, a dark reaction was suggested. This could possibly be the addition of chlorine to the cyclopropane with ring rupture to give a dichloro propane. It is rather difficult to see how this could occur in the absence of any free radical substitution, and as yet the dark reaction is not understood.

It was found possible to reduce the formation of substance C to negligible proportions by admitting the chlorine directly to the reaction vessel and illuminating as soon as the cyclopropane was added.

Hence mono chloro cyclopropane was the principal product of the chlorination of cyclopropane when

(a) the 'dark' reaction was prevented in the above manner and

(b) the chlorine/cyclopropane ratio was kept as low as possible/
possible (preferably below .02).

These conditions were maintained throughout the competitive experiments. The chlorine was first placed in the reaction vessel and the ethane-cyclopropane mixture was admitted from the mixing vessel with immediate illumination.

The same column was used in the analysis for ethyl chloride and cyclopropyl chloride with the operating temperature 60°C and an initial hydrogen pressure of 4 cm. Hg. The ethyl chloride appeared after 6 minutes and the cyclopropyl chloride after 14 minutes.

Where $k_{Et}$ and $k_{cPr}$ are the rate constants of

\[
\text{Cl}^- + \text{CH}_3 - \text{CH}_3 \rightarrow \text{CH}_3 \text{CH}^- + \text{HCl}
\]

\[
\text{Cl}^- + \text{CH}_2 - \text{CH}_2 \rightarrow \text{CH}^- - \text{CH}_2 + \text{HCl}
\]

respectively,

\[
k_{cPr} = \frac{(cPr \text{ Cl})(\text{ethane})}{k_{Et} = \frac{(Et \text{ Cl})(\text{cyclopropane})}

N.B. Et \equiv \text{ethyl and cPr \equiv cyclopropyl.}
<table>
<thead>
<tr>
<th>RUN</th>
<th>T C</th>
<th>(ETHANE) (CYCLOPROPANE) added cm Hg.</th>
<th>AREA EtCl</th>
<th>AREA oPrCl</th>
<th>$\log_{10}k_{Et}$</th>
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<td>$\frac{3.3892}{3.6580}$</td>
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<td>$\frac{3.6294}{3.6928}$</td>
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<td>$\frac{3.9609}{2.0161}$</td>
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<tr>
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<td>0.75</td>
<td>0.96</td>
<td>$\frac{3.9694}{7.9694}$</td>
</tr>
<tr>
<td>54</td>
<td>&quot;</td>
<td>0.154 16.53</td>
<td>0.61</td>
<td>0.61</td>
<td>$\frac{3.9694}{7.9694}$</td>
</tr>
<tr>
<td>55</td>
<td>&quot;</td>
<td>0.134 16.82</td>
<td>0.90</td>
<td>0.89</td>
<td>$\frac{3.9694}{7.9694}$</td>
</tr>
<tr>
<td>45</td>
<td>132</td>
<td>0.193 11.20</td>
<td>0.59</td>
<td>0.33</td>
<td>$\frac{3.9969}{7.9694}$</td>
</tr>
<tr>
<td>46</td>
<td>&quot;</td>
<td>0.194 10.75</td>
<td>0.35</td>
<td>0.17</td>
<td>$\frac{3.9969}{7.9694}$</td>
</tr>
<tr>
<td>47</td>
<td>&quot;</td>
<td>0.23 16.40</td>
<td>1.16</td>
<td>0.82</td>
<td>$\frac{3.9969}{7.9694}$</td>
</tr>
<tr>
<td>60</td>
<td>&quot;</td>
<td>0.184 15.00</td>
<td>1.49</td>
<td>1.43</td>
<td>$\frac{7.0708}{2.0342}$</td>
</tr>
<tr>
<td>62</td>
<td>&quot;</td>
<td>0.098 14.10</td>
<td>0.91</td>
<td>1.42</td>
<td>$\frac{7.0708}{2.0342}$</td>
</tr>
<tr>
<td>56</td>
<td>192</td>
<td>0.254 13.86</td>
<td>0.82</td>
<td>0.80</td>
<td>$\frac{2.2630}{3.3412}$</td>
</tr>
<tr>
<td>58</td>
<td>&quot;</td>
<td>0.161 16.13</td>
<td>1.11</td>
<td>2.44</td>
<td>$\frac{2.2630}{3.3412}$</td>
</tr>
<tr>
<td>59</td>
<td>&quot;</td>
<td>0.120 15.85</td>
<td>0.38</td>
<td>0.92</td>
<td>$\frac{2.2610}{2.2610}$</td>
</tr>
<tr>
<td>24</td>
<td>220</td>
<td>0.35 11.38</td>
<td>0.29</td>
<td>0.25</td>
<td>$\frac{2.4265}{2.4829}$</td>
</tr>
<tr>
<td>43</td>
<td>&quot;</td>
<td>0.34 14.23</td>
<td>0.88</td>
<td>1.12</td>
<td>$\frac{2.4265}{2.4829}$</td>
</tr>
<tr>
<td>44</td>
<td>&quot;</td>
<td>0.25 13.20</td>
<td>0.38</td>
<td>0.43</td>
<td>$\frac{2.3263}{2.3263}$</td>
</tr>
</tbody>
</table>
By the method of least squares on the complete data as given in table 11, the rate constant ratio is

\[
\frac{k_{cPr}}{k_{Et}} = 0.56 \pm 0.02 \exp \left( -3.100 \pm 30 / RT \right).
\]

<table>
<thead>
<tr>
<th>RUNS</th>
<th>(10^3/T_A)</th>
<th>AVERAGE VALUE OF (\log_{10} \frac{k_{cPr}}{k_{Et}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>23, 42, 51</td>
<td>3.40</td>
<td>(3.470)</td>
</tr>
<tr>
<td>48, 49, 50</td>
<td>3.00</td>
<td>(3.660)</td>
</tr>
<tr>
<td>52, 53, 54, 55</td>
<td>2.68</td>
<td>(3.960)</td>
</tr>
<tr>
<td>45, 46, 47, 60, 62</td>
<td>2.47</td>
<td>(2.007)</td>
</tr>
<tr>
<td>56, 58, 59</td>
<td>2.15</td>
<td>(2.288)</td>
</tr>
<tr>
<td>24, 43, 44</td>
<td>2.03</td>
<td>(2.411)</td>
</tr>
</tbody>
</table>

The Arrhenius plots of the results in the above tables are found in Figure 15 and Figure 17.
Fig. 15.

Ethane / Cyclopropane

$\frac{\log K_{cpa}}{K_{p}}$

$\frac{1}{T}$

$2.5 \times 10^3$
7. **CHLORINATION OF PROPANE - CYCLOBUTANE MIXTURES.**

The cyclobutane interfered with the analysis of ethyl chloride so that it was necessary to compete the chlorination of cyclobutane against that of the primary position in propane.

The chlorination of cyclobutane produced only one product and this was assumed to be mono chloro cyclobutane. The products of competitive chlorinations were analysed for primary propyl chloride and cyclobutyl chloride.

The chromatography column was 190 cm. long, contained the 80:20 w/w mixture of firebrick and dioctyl phthalate and operated at 60°C. The initial hydrogen pressure was 7 cm. Hg. and under these conditions the primary propyl chloride appeared after 6 minutes and the cyclobutyl chloride after 17 minutes.

Where $k_{\text{Pr}}$ and $k_{\text{Bu}}$ are the rate constants of

\[
\text{Cl}^- + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^- + \text{HCl}
\]

and

\[
\text{Cl}^- + \text{CH}_2 - \text{CH}_2 \rightarrow \text{CH}_2 - \text{CH}^- + \text{HCl}
\]

respectively

\[
k_{\text{Bu}} = \frac{(\text{Bu Cl})(\text{propane})}{k_{\text{Pr}} = \frac{(\text{Pr Cl})(\text{cyclobutane})}}
\]

N.B. Bu ≡ cyclobutyl and Pr ≡ primary propyl.
TABLE 13.

<table>
<thead>
<tr>
<th>RUN</th>
<th>T (°C)</th>
<th>(PROPANE) (CYCLOBUTANE) added</th>
<th>AREA pPrCl</th>
<th>AREA oBuCl</th>
<th>(\log_{10}\frac{k_{oBu}}{k_{pPr}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>-32</td>
<td>8.49</td>
<td>0.60</td>
<td>0.93</td>
<td>0.5647</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>10.18</td>
<td>1.10</td>
<td>1.54</td>
<td>0.5652</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>8.14</td>
<td>0.80</td>
<td>1.44</td>
<td>0.5888</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>9.22</td>
<td>0.95</td>
<td>1.38</td>
<td>0.5307</td>
</tr>
<tr>
<td>2</td>
<td>+20</td>
<td>8.72</td>
<td>0.71</td>
<td>1.74</td>
<td>0.5769</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>12.68</td>
<td>1.60</td>
<td>1.71</td>
<td>0.5119</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>9.06</td>
<td>1.05</td>
<td>1.60</td>
<td>0.5159</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>9.50</td>
<td>1.05</td>
<td>1.64</td>
<td>0.5432</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>11.15</td>
<td>0.84</td>
<td>1.13</td>
<td>0.5269</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>8.34</td>
<td>0.93</td>
<td>1.60</td>
<td>0.4921</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>8.53</td>
<td>0.95</td>
<td>1.67</td>
<td>0.4835</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>9.20</td>
<td>0.81</td>
<td>1.57</td>
<td>0.5191</td>
</tr>
</tbody>
</table>

TABLE 14.

<table>
<thead>
<tr>
<th>RUNS</th>
<th>(10^3/T)</th>
<th>AVERAGE VALUE OF (\log_{10}\frac{k_{oBu}}{k_{pPr}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>14,15,16,17.</td>
<td>4.15</td>
<td>0.5623</td>
</tr>
<tr>
<td>2, 3,12,13.</td>
<td>3.41</td>
<td>0.5370</td>
</tr>
<tr>
<td>4, 5, 6,18.</td>
<td>2.68</td>
<td>0.5059</td>
</tr>
</tbody>
</table>

\[
\frac{k_{oBu}}{k_{pPr}} = 2.54 \pm 0.17 \exp (175 \pm 40 / RT) \]

from a least squares analysis of the complete results in Table 13.
\[ x + \log \frac{K_{R_{\ell}H}}{K_{R_{a}H}} \]

Fig. 17.

\[ \frac{1}{T} \times 10^3 \]

- \( R_a = H, R_{\ell} = Me \) \( x = 0 \)
- \( R_a = Et, R_{\ell} = cPr \) \( x = 3 \)
Fig. 18

$\frac{x + \log KR_{rH}}{KR_{rH}}$

$1/T \times 10^3$

- $R_a = E_T$, $R_r = sP_R$, $x = 0.3$
- $E_T$, $pP_R$, $x = 0.3$
- $pP_R$, $sP_R$, $x = 0.3$
- $pP_R$, $neoP$, $x = 0.0$
- $pP_R$, $cPr$, $x = 0.0$
$x + \log K_{R' H} / K_{R, H}$ vs $1/\text{T} \times 10^3$. 

- $R_a = \text{Et}, R_e = \text{snBu}$, $x = 0.0$
- $\ldots = \text{Et}, \ldots = \text{pnBu}$, $\ldots = 0.0$
- $\ldots = \text{pnBu}, \ldots = \text{snBu}$, $\ldots = 0.0$
- $\ldots = \text{Et}, \ldots = \text{tiBu}$, $\ldots = 1.0$
- $\ldots = \text{Et}, \ldots = \text{piBu}$, $\ldots = 1.0$
- $\ldots = \text{piBu}, \ldots = \text{tiBu}$, $\ldots = 1.0$
DISCUSSION.

(1) **Calculation of absolute rate constants.**

The relative A factors and activation energy differences obtained from the Arrhenius plots are listed in Table 15. The relative rate constants for methane and ethane were obtained by Knox in excellent agreement with the results of Pritchard, Pyke and Trotman-Dickenson. The value for $k_{Et}/k_{Me}$ quoted in Reference 60 is in error, the correct expression being

$$\frac{k_{Et}}{k_{Me}} = 3.85 \exp (2,810 \pm 45 \text{ cal/RT}).$$

The relative A factors are those for the chlorine atom attack on all equivalent positions in a molecule. The relative A factors per hydrogen atom (or C-H bond) are obtained by allowing for all equivalent positions in the molecule. Absolute rate constants have been derived from the absolute value for hydrogen.

$$k_H = 0.8 \times 10^{14} \exp (-5,500 \pm 200 \text{ cal.mole}^{-1} \text{ mole}^{-1} \text{ cc sec}^{-1})$$

and are found in Table 16. The errors quoted do not take into account the error in $k$. In all cases (including hydrogen) the absolute A factor per molecule for attack on a particular type of bond is equal to the absolute A factor per hydrogen atom times the number of hydrogen atoms (per molecule) involved in these equivalent bonds.

(2) **Systematic errors.**

While the errors quoted in Tables 15 and 16 represent the/
# TABLE 15

**RELATIVE RATE CONSTANTS.**

<table>
<thead>
<tr>
<th>Mixtures chlorinated.</th>
<th>$A_{Ra}/A_{Rb}$ per molecule</th>
<th>$A_{Ra}/A_{Rb}$ per H atom</th>
<th>$E_{Ra} - E_{Rb}$ cal.mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>0.30</td>
<td>0.15 ± 0.015</td>
<td>1,650 ± 60</td>
</tr>
<tr>
<td>CH₃-H</td>
<td>3.65</td>
<td>2.57 ± 0.16</td>
<td>2,010 ± 45</td>
</tr>
<tr>
<td>C₂H₅-H</td>
<td>1.11</td>
<td>1.11 ± 0.025</td>
<td>40 ± 10</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.78</td>
<td>2.34 ± 0.04</td>
<td>360 ± 10</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.89</td>
<td>0.89 ± 0.04</td>
<td>250 ± 30</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.94</td>
<td>1.41 ± 0.08</td>
<td>770 ± 35</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.30</td>
<td>0.87 ± 0.04</td>
<td>220 ± 25</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.18</td>
<td>1.08 ± 0.10</td>
<td>1,020 ± 45</td>
</tr>
<tr>
<td>pri. C₃H₇-H</td>
<td>1.65</td>
<td>0.62 ± 0.02</td>
<td>80 ± 20</td>
</tr>
<tr>
<td>C₂H₅-H</td>
<td>0.56</td>
<td>0.56 ± 0.02</td>
<td>-3,100 ± 50</td>
</tr>
<tr>
<td>pri. C₃H₇-H</td>
<td>2.54</td>
<td>1.90 ± 0.13</td>
<td>175 ± 40</td>
</tr>
</tbody>
</table>

The errors quoted in the above table are the 50% probability limits.
### Absolute Rate Constants

<table>
<thead>
<tr>
<th>Type of bond attacked</th>
<th>R—H</th>
<th>$10^{-13} A_R$ per H atom</th>
<th>$E_R$ cal.mole.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—H</td>
<td>4.0</td>
<td></td>
<td>5,500</td>
</tr>
<tr>
<td>CH₃—H</td>
<td>0.6 ± 0.1</td>
<td></td>
<td>3,850 ± 60</td>
</tr>
<tr>
<td>Primary.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₅—H</td>
<td>1.5 ± 0.2</td>
<td>1,040 ± 75</td>
<td></td>
</tr>
<tr>
<td>pri.C₂H₅—H</td>
<td>1.7 ± 0.2</td>
<td>1,000 ± 75</td>
<td></td>
</tr>
<tr>
<td>pri.nC₄H₉—H</td>
<td>1.4 ± 0.2</td>
<td>790 ± 80</td>
<td></td>
</tr>
<tr>
<td>pri.iC₄H₉—H</td>
<td>1.3 ± 0.2</td>
<td>820 ± 80</td>
<td></td>
</tr>
<tr>
<td>neo C₅H₁₁—H</td>
<td>1.4 ± 0.2</td>
<td>920 ± 80</td>
<td></td>
</tr>
<tr>
<td>Secondary.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sec.C₃H₇—H</td>
<td>3.6 ± 0.5</td>
<td>680 ± 75</td>
<td></td>
</tr>
<tr>
<td>sec.nC₄H₉—H</td>
<td>2.2 ± 0.3</td>
<td>270 ± 80</td>
<td></td>
</tr>
<tr>
<td>cyclo C₃H₅—H</td>
<td>0.9 ± 0.1</td>
<td>4,140 ± 80</td>
<td></td>
</tr>
<tr>
<td>cyclo C₄H₇—H</td>
<td>3.2 ± 0.4</td>
<td>825 ± 85</td>
<td></td>
</tr>
<tr>
<td>Tertiary.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert.iC₄H₉—H</td>
<td>1.7 ± 0.3</td>
<td>20 ± 90</td>
<td></td>
</tr>
</tbody>
</table>

The errors quoted in the above table are the 50% cumulative probability limits, without consideration of the errors in the $A_R$ and $E_R$ values.
the probability that the best straight lines obtained from the Arrhenius plots are correct, no allowance has been made for the possibility of systematic errors. These may arise from

(a) an error in the absolute $k_H$ value
(b) errors in the relative sensitivities of the detector towards the various chlorides and benzene.
(c) the solution of certain chlorides in tap-grease.

This is most likely in the chlorination of neopentane and the butanes and is reflected in the poorer reproducibility of the results in such cases.

(d) the existence of the back reaction ($-2$). This is unlikely in view of the absence of any regular variation of the relative rate constants, at any one temperature, with either the hydrocarbon/chlorine or hydrocarbon A/hydrocarbon B ratios.

Added hydrogen chloride did not affect the chlorination of iso butane at the temperatures at which no decomposition occurred.

No evidence for the back reaction ($-2$) was obtained by Pritchard, Pyke and Trotman-Dickenson.

(e) the thermal decomposition of one or more of the chloride products. All results from work at temperatures at which decomposition was observed were rejected.

(f) bad sampling of products.

The experimental technique was adapted to reduce the possibility of errors from (b), (c) and (f) to a minimum. Apart from (c) and (f) which were probably the greatest sources of error, other/
other ever present errors were due to the measurement of the initial pressures of hydrocarbons and concentrations of the chloride products. Both measurements were carried out with an accuracy of about 2%.

(3) Values of the Activation Energies.

An examination of the activation energies listed in Table 16 leads to the following generalisations.

1. The activation energies for the chlorine atom attack on the primary positions decrease on ascending the straight chain members of the paraffin series, i.e. methane, ethane, propane and n-butane.

2. While increasing chain length leads to lower activation energies, branching of the chains leads to higher values.

3. The activation energies for attack at the secondary positions in propane and n-butane are considerably lower than those for the primary positions, there being a difference of 320 cal. for propane and 520 cal. for n-butane. This suggests that the primary and secondary values diverge on ascending the paraffin series and is supported by the observation of Chambers & Ubbelohde that

\[ (E_{pri} - E_{sec}) \text{ in } n \text{ hexane is } \sim 900 \text{ cal.} \]

These workers found, however, that for the normal \( C_5 \) - \( C_8 \) paraffins the reactivity of the secondary positions relative to the primary positions decreased on ascent of the series. It is possible that while the

\[ (E_{pri} - E_{sec}) \text{ values increase on ascending the series, the} \]

\[ A/ \]
A\textsubscript{sec}/A\textsubscript{pri} ratios approach unity. These workers in fact quote results for n hexane from which a value for A\textsubscript{sec}/A\textsubscript{pri} per H atom of unity may be calculated and this trend is also indicated in our A\textsubscript{sec}/A\textsubscript{pri} ratios for propane and n butane of 3.6 and 2.2 respectively.

4. The activation energy for attack at the tertiary position in iso butane is lower than those for the secondary positions studied. The value of (E\textsubscript{pri.} - E\textsubscript{tert.}) in iso butane is 800 cal.

5. The activation energies for methane and cyclopropane are abnormal, that for attack at the so called primary bond in methane being much greater than the other primary attacks and that for the attack on the secondary position in cyclopropane much greater than the other secondary positions.

Recent work by Anson, Fredricks, and Tedder on the gas phase chlorination of n butane and iso butane leads to the values

\[
\frac{k_{\text{snBu}}}{k_{\text{pnBu}}} = 1.8 \exp (480 \pm 70 \text{ cal/RT})
\]

and

\[
\frac{k_{\text{tIBu}}}{k_{\text{pIBu}}} = 2.1 \exp (540 \pm 70 \text{ cal/RT})
\]

While the n butane results are in good agreement with those obtained in the present work, the iso butane results give an (E/
(E_{pri} - E_{tert}) difference of 540 cal, which is considerably lower than our value of 800 cal. It thus seems possible that 700 cal. is a more reliable value and is not far outside the 50% probability limits of either determination.

An attempt to correlate activation energy with the bond strength of the bond being broken in the course of the reaction was made by Butler & Polanyi for the reactions of sodium atoms with alkyl chlorides. It had been suggested previously \footnote{Butler & Polanyi} that 

E = \alpha \Delta H \quad \text{where} \quad E = \text{activation energy,} \quad \Delta H = \text{heat of the reaction}

and \( \alpha \) lies between 0 and 1, being constant for a series of similar reactions. Although Butler & Polanyi \footnote{Butler & Polanyi} found that \( \alpha \) was constant at about 0.26 where \( \Delta H \) values were obtained from the bond strengths of the corresponding iodides, the most recent values for the strengths of carbon-chlorine bonds do not lead to such constancy in \( \alpha \). \footnote{Steiner & Watson}

Steiner & Watson \footnote{Steiner & Watson} applied the same reasoning to the reactions of chlorine atoms with propane and iso butane. From the results of Hass, McBee \& Weber \footnote{Hass, McBee \& Weber} they showed that for propane

\[(E_{pri} - E_{sec}) = 0.225 (\Delta H_{pri} - \Delta H_{sec})\]

and for iso butane

\[(E_{pri} - E_{tert}) = 0.215 (\Delta H_{pri} - \Delta H_{tert}).\]

However, since grave doubts must be cast on any activation energies calculated from Hass, McBee \& Webers results, these conclusions are unjustified.\footnote{However, since grave doubts must be cast on any activation energies calculated from Hass, McBee \& Webers results, these conclusions are unjustified.}
## Table 17

**Activation Energies and Bond Strengths.**

<table>
<thead>
<tr>
<th>Bond in R—H</th>
<th>$E_R$ (cal/mole) for Cl attack</th>
<th>$E_R$ (k.cal/mole) for Br attack</th>
<th>$D(R-H)$ (k.cal/mole) at 0°C</th>
<th>$D(R-H)$ from electron impact work alone</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>5,500</td>
<td>17.2</td>
<td>103.2</td>
<td></td>
</tr>
<tr>
<td>CH$_3$-H</td>
<td>3,950</td>
<td>17.8</td>
<td>101.5</td>
<td>102</td>
</tr>
<tr>
<td>C$_2$H$_5$-H</td>
<td>1,040</td>
<td>13.3</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>pri.C$_2$H$_7$-H</td>
<td>1,000</td>
<td></td>
<td>98</td>
<td>99.5</td>
</tr>
<tr>
<td>pri.nC$_4$H$_9$-H</td>
<td>790</td>
<td></td>
<td>101</td>
<td>101</td>
</tr>
<tr>
<td>pri.iC$_4$H$_9$-H</td>
<td>820</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>neoC$<em>5$H$</em>{11}$-H</td>
<td>920</td>
<td>17.8</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>sec.C$_2$H$_7$-H</td>
<td>680</td>
<td></td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>sec.nC$_4$H$_9$-H</td>
<td>270</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cycloC$_3$H$_5$-H</td>
<td>4,140</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cycloC$_4$H$_7$-H</td>
<td>825</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert.iC$_4$H$_9$-H</td>
<td>20</td>
<td>11.4</td>
<td>89</td>
<td>89</td>
</tr>
</tbody>
</table>

The $D(R-H)$ values are taken from reference (9).

$E_R$ for Br attack are quoted in reference (79).
The most recent values for the bond dissociation energies $D(R-H)$ in Table 17 are taken from reference 9 and are based on electron impact and kinetic study evidence. Although the general trend of the activation energies for the attack on $H-H$, $\text{CH}_3-H$, $\text{C}_2\text{H}_5-H$, sec $\text{C}_3\text{H}_7-H$ and tert $\text{C}_4\text{H}_9-H$ is related to the corresponding bond strengths, this relationship is non-linear and breaks down in the cases of pri $\text{C}_3\text{H}_7-H$, pri n $\text{C}_4\text{H}_9-H$ and neo $\text{C}_5\text{H}_{11}-H$. Although the bond energies are only accurate to within $\pm 1$ or $2$ k. cal., it is unlikely that any errors in these values can account for the discrepancies.

Invoking the reasoning employed by Russell, an empirical explanation of these activation energies may be advanced. In the cases of hydrogen and methane where the activation energies are relatively high a chlorine atom is not allowed to approach too closely to the hydrogen atom being abstracted and the controlling factor in the formation of the activated complex is the bond energy. In the cases of low activation energies the chlorine atom is allowed a closer approach and the controlling factor is then the availability of electrons to the incipient $H-Cl$ bond from the rest of the hydrocarbon molecule. Hence the magnitude of the low activation energies should depend on the extent of the inductive effect of the remaining hydrocarbon group. From the results of the present work this would suggest that the following are/
are in order of their inductive effect:

\[
\begin{align*}
(CH_3)_3C & \rightarrow CH_3CH_2CHCH_3 \rightarrow (CH_3)_2CH \rightarrow \\
CH_3(CH_2)_2CH_2 & \rightarrow (CH_3)_2CHCH_2 \rightarrow (CH_3)_2CH_2 \rightarrow \\
CH_3CH_2CH_2 & \rightarrow CH_3CH_2 \rightarrow CH_3.
\end{align*}
\]

If methane is considered as the parent of the paraffin series and the formation of the activated complex dependent entirely on the inductive effect of the methyl group, then this effect increases with

1. increasing replacement of the hydrogen atoms in methane by methyl groups.
2. replacement of a methyl group by an ethyl group.
3. replacement of an ethyl group by a secondary propyl or tertiary butyl group.

Rule 1 is well established and can be shown to apply in the carboxylic acids homologous to acetic acid from a study of the pK values for these acids.

Rules 2 and 3 are not well established but in general it can be said that the inductive effect tends to increase as the complexity of R in \( R - H - Cl \) increases.

Russell has shown that the relative reactivities of primary, secondary and tertiary positions towards chlorine atoms depend not only on the differing inductive effects present but also on the differing bond strengths.

The magnitude of the activation energies \( E_{cPr} \) and \( E_{cBu} \) for/
for chlorine atom attack on the cycloalkanes, cyclopropane and cyclobutane will now be considered. Together with these values for $E_{\text{CPr}}$ of 4,140 cal. and for $E_{\text{CBr}}$ of 825 cal. may be taken the activation energy for attack on cyclopentane $E_{\text{CPe}}$ of 580 cal. obtained by Pritchard, Pyke & Trotman-Dickenson. In the formation of the $R-H-Cl$ activated complex with subsequent production of a free radical the coordination number of the carbon atom decreases from 4 to 3. Brown has suggested that in small rings the distortion of bond angle is the major source of internal ring strain or I strain. Reactions with a change in coordination number of one of the carbon atoms involved in the ring and which produce additional I strain will be unfavoured.

<table>
<thead>
<tr>
<th>Cycloalkane</th>
<th>Bond $\angle$ present</th>
<th>Theoretical bond $\angle$ for coord. No.4.</th>
<th>$\angle$ for coord. No.3.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$</td>
<td>60°</td>
<td>109.5°</td>
<td>120°</td>
</tr>
<tr>
<td>$\Box$</td>
<td>90°</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\Diamond$</td>
<td>108°</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

From the above table, a change in the coordination number of a ring carbon atom from 4 to 3 results in an increase of I strain in all three cases. Since the strain is originally greatest in cyclopropane the change in coordination number will occur with most difficulty, leading to a high activation energy. The corresponding changes in cyclobutane and cyclopentane will occur with increasing facility and this trend is reflected in the values of/
of $E_{cPr}$, $E_{cBu}$ and $E_{cPe}$. Studies of the hydrogen abstraction from a ring carbon atom by methyl radicals show a similar trend and give activation energies of 10.3, 9.3 and 8.5 k. cal. for cyclopropane, cyclobutane and cyclopentane.

The low value for $E_{tBu}$ is of considerable interest. While the temperature dependence of reaction rates are usually given in terms of activation energies ($E_{\text{exp}}$) the more fundamental concept is $\Delta u_0^\ddagger$, the internal energy of activation at absolute zero.

$$\Delta u_0^\ddagger = E_{\text{exp}} - RT$$

and

$$\Delta u_0^\ddagger = E_{\text{exp}} - RT - \int_0^T \Delta C_v^\ddagger \, dT$$

$\Delta C_v^\ddagger$ is the difference between the specific heat of the activated complex and those of the reactants, all at constant volume.

$$\Delta C_v^\ddagger = C_v(\text{AHCl}) - C_v(\text{RH}) - C_v(\text{Cl})$$

The total specific heat $C_v$ is composed of translation, rotation and vibration terms

$$C_v = C_{v,\text{trans}} + C_{v,\text{rot}} + C_{v,\text{vib}}.$$  

The $C_{v,\text{trans}}$ and $C_{v,\text{rot}}$ values for the RH Cl complex and RH molecule are identical, hence

$$\Delta C_v^\ddagger = C_{v,\text{vib}}(\text{RH Cl}) - C_{v,\text{vib}}(\text{RH}) - C_v(\text{Cl})$$

The specific heat of the chlorine atom is dependent only on translation and is $\frac{3}{2}R$. The difference in the vibrational specific heats/
heats of the complex and hydrocarbon is due mainly to the introduction of new vibrations and from reasoning which will be given later the maximum frequencies are of the order of \(200\ \text{cm}^{-1}\) for the doubly degenerate bending and \(500\ \text{cm}^{-1}\) for the stretching of the \(\text{R}...\text{H}...\text{Cl}\) complex. It has been calculated that these frequencies give rise to internal energy contributions at \(300^\circ\text{A}\) of \(2 \times 0.59\ \text{RT}\) and \(0.24\ \text{RT}\).

Hence

\[
\int_0^{300} \Delta C_v \frac{\Delta H}{T} \, dT = 2 \times 0.59\ \text{RT} + 0.24\ \text{RT} - 1.5\ \text{RT}
\]

\[
= -0.1\ \text{RT}.
\]

\[
\Delta u_o^\ddagger = E_{\text{exp}} - 0.9\ \text{RT}
\]

\[
= E_{\text{exp}} - 500\ \text{cal. mole}^{-1}\text{ at }300^\circ\text{A}.
\]

If lower bending and stretching frequencies for the complex had been employed, the value of \(\Delta u_o^\ddagger\) would be even lower.

The internal energy of activation at absolute zero for the chlorine attack on the tertiary position in iso-butane thus appears to be negative to the extent of \(500\ \text{cal}\). Similar reasoning for the attack on the secondary position in \(n\)-butane suggests an apparent \(\Delta u_o^\ddagger\) value of \(-200\ \text{cal}\). These surprising results may be explained in three ways:

(a) By postulating that \(\Delta u_o^\ddagger\) may in fact have negative values. Negative activation energies are not usually found in bimolecular processes but have been shown to occur in termolecular reactions.

(b) By an overall error in \(E_{\text{tibu}}\) of \(500\ \text{cal}\). assuming \(k_H^*\) to be correct.

(c) By an overall error in \(E_{\text{tibu}}\) of \(500\ \text{cal}\). assuming \(k_H^*\) to be inaccurate.

Of possibilities (b) and (c) the latter is much more likely and/
and leads to the conclusion that the $E_a$ value used is low. This view is supported by the fact that the results of the individual methods used in the evaluation of $k_H$ all give activation energies higher than 5,500 cal.

The activation energies for the chlorine atom attack on hydrocarbons lie between those for fluorine atom and bromine atom attack. Those for bromine attack are in the range 11 to 18 k. cal. for paraffins whereas fluorine requires little or no activation energy. This is expected since the electronegativity, and hence reactivity, of the chlorine atom is intermediate between those of the fluorine and bromine atoms. Although the activation energies for bromine atom attack are much higher than those for chlorine, the expected linear relationship between activation energies and bond strengths as quoted in Table 17 does not materialise.

(4) **Values of the A Factors.**

On first inspection the A factors for the attack on the primary positions are fairly constant apart from the cases of hydrogen and methane which cannot in any case be regarded as possessing true primary bonds. The secondary positions in the straight chained alkanes have A factors almost twice those of the corresponding primary positions and the A factor of the tertiary position in isobutane is similar to those of the primary positions. The secondary bond in cyclobutane gives an A factor of the same order as the other secondary positions whereas that for cyclopropane is similar to the case of methane.

As was indicated previously the A factor of a bimolecular reaction/
reaction is dependent on the entropy of activation $\Delta S^\ddagger$ which in turn is composed of translational, rotational and vibrational contributions. Whereas the translational and rotational entropies can be calculated with reasonable certainty from classical partition functions, the calculation of the vibrational entropy of activation presents formidable problems since the frequencies of the three additional vibrations in the activated complex are usually unknown.

81 Bigeleisen & Wolfsberg evaluated the 'symmetrical' stretching frequency of the H – H – Cl complex from the known relative rates of reaction of H₂ and HT with chlorine atoms at 0°C. Making a small correction for the bending frequency, their value of 1460 cm⁻¹ for the stretching frequency gave good agreement with experimental results. The longitudinal vibration of the central H atom is in the reaction path and has a zero (or imaginary) frequency.

Using this value of 1460 cm⁻¹ for the frequency of the stretching vibration and the known entropy of activation at 600°C (obtained from the $A_H$ factor) Pitzer has calculated that the frequency of the doubly degenerate bending of the H – H – Cl complex is 540 cm⁻¹. Although these frequencies lead to a $\Delta S^\ddagger$ value at 600°C in perfect harmony with the experimental $A_H$ factor the $\Delta S^\ddagger$ value for 300°C does not lead to the same measure of agreement (see Table 18). While 600°C is the mid temperature in the $k_H$ determinations, 300°C is nearer the mid temperature for the work on the hydrocarbons.

Pitzer also calculated a $\Delta S^\ddagger$ value for the chlorine attack/
attack on methane on the assumption that the potential energy function in the reaction area was the same for the CH₃ – H – Cl complex as for the H – H – Cl complex. Whereas 0.9Å and 1.5 Å were used for the H – H and H – Cl distances in H – H – Cl, the C – H length in CH₃ – H – Cl was assumed to be that present in CH₄ while the H – Cl distance was taken as 1.6 Å. This value leads to a theoretical A factor of 0.92 x 10⁻¹³ c.c. mole sec⁻¹ at 400°C which is near the experimental value of 0.6 x 10⁻¹³ c.c. mole sec⁻¹. Allowing for the increased mass and moment of inertia of CH₃ as compared to H, values of 440 cm⁻¹ and 160 cm⁻¹ were obtained for the frequencies of the stretching and bending vibrations of the CH₃ – H – Cl complex.

Wilson & Johnston have calculated theoretical A factors for reactions involving hydrogen abstraction by bromine and methyl radicals. From calculated stretching and bending force constants for the bonds of the activated complexes, the frequencies of the new vibrations have been obtained. These frequencies together with small changes in the original vibrations of the hydrocarbons give the ΔS^vib values quoted in Table 18. These values in combination with ΔS^trans, ΔS^rot and ΔS^vibr lead to the theoretical A factors which are in good agreement with experimental values except in the case of the iso-butane bromination.

Knox & Trotman-Dickenson attempted to correlate the known relative A factors for chlorine atom reactions with calculated values.
values using the equation

\[
\frac{A_{R_a}}{A_{R_b}} = \left( \frac{M_{R_a} \text{HCl} / M_{R_a} \text{H}}{M_{R_b} \text{HCl} / M_{R_b} \text{H}} \right)^{3/2} \times \left( \frac{(ABC)_{R_a} \text{HCl} / (ABC)_{R_a} \text{H}}{(ABC)_{R_b} \text{HCl} / (ABC)_{R_b} \text{H}} \right)^{1/2}
\]

where \( M_s \) are molecular weights and \((ABC)\) is the product of the moments of inertia about the three principal axes of the molecules. The vibration entropy terms were neglected in these calculations, being assumed to be relatively unimportant. The discrepancies between experimental and calculated \( A \) factors, however, were rather serious.

The \( A \) factors obtained from the present work form a more extended series than were formerly available and Knox & Nelson have attempted to calculate the vibrational contributions to the entropy of activation. The frequencies of the stretching and doubly degenerate bending vibrations have been calculated from Pitzer's values for the \( \text{H - H - Cl} \) complex, making due allowance for the changes in the reduced masses and moments of inertia. The vibrational entropy of activation \( \Delta S^\pm_{\text{vib}} \) for the chlorine atom attack on hydrocarbons has been assumed to be due solely to these two new vibrational modes and not to changes in the other vibrations of the hydrocarbon molecule. These calculated \( \Delta S^\pm_{\text{vib}} \) values are given in Table 18 together with experimental \( \Delta S^\pm_{\text{vib}} \) values obtained from the experimental absolute \( A \) factors in combination with calculated \( \Delta S^\pm_{\text{trans}} \) and \( \Delta S^\pm_{\text{rot}} \) values. Also included in this table are the \( \Delta S^\pm_{\text{vib}} \) values calculated by Wilson & Johnston for bromine/
<table>
<thead>
<tr>
<th>R—H</th>
<th>$\Delta S_{\text{trans}}$ e.u. calc. for Cl.</th>
<th>$\Delta S_{\text{rot}}$ e.u. calc. for Cl.</th>
<th>$\Delta S_{\text{vib}}$ e.u. calc. for Cl.</th>
<th>$\Delta S_{\text{vib}}$ e.u. exp. for Cl.</th>
<th>$\Delta S_{\text{vib}}$ e.u. calc. for CH₃</th>
<th>$\Delta S_{\text{vib}}$ e.u. calc. for Br.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>-7.87</td>
<td>5.51</td>
<td>1.0</td>
<td>2.1</td>
<td>1.3</td>
<td>3.6</td>
</tr>
<tr>
<td>CH₃-H</td>
<td>-13.12</td>
<td>6.25</td>
<td>5.9</td>
<td>2.8</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>C₂H₅-H</td>
<td>-14.28</td>
<td>4.96</td>
<td>7.5</td>
<td>7.1</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>pri.C₂H₇-H</td>
<td>-14.83</td>
<td>3.45</td>
<td>8.2</td>
<td>9.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pri.nC₄H₉-H</td>
<td>-15.18</td>
<td>3.15</td>
<td>8.7</td>
<td>9.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pri.iC₄H₉-H</td>
<td>-15.18</td>
<td>2.77</td>
<td>8.7</td>
<td>9.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>neo C₅H₁₁-H</td>
<td>-15.41</td>
<td>2.63</td>
<td>9.0</td>
<td>10.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sec.C₃H₇-H</td>
<td>-14.83</td>
<td>3.70</td>
<td>8.2</td>
<td>10.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sec.C₄H₉-H</td>
<td>-15.18</td>
<td>2.74</td>
<td>8.6</td>
<td>10.9</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>cyclo C₂H₅-H</td>
<td>-14.77</td>
<td>4.05</td>
<td>8.1</td>
<td>7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclo C₄H₇-H</td>
<td>-15.15</td>
<td>3.36</td>
<td>8.5</td>
<td>11.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert.iC₄H₉-H</td>
<td>-15.18</td>
<td>2.67</td>
<td>8.6</td>
<td>10.5</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>C∞</td>
<td></td>
<td></td>
<td></td>
<td>11.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
bromine and methyl radical attack on hydrocarbons.

**Detailed account of Knox & Nelson's calculations.**

In reactions of the type

\[ R - H + Cl \rightarrow R...H...Cl \]

\[ \Delta S^\ddagger = \Delta S^\ddagger_{\text{trans}} + \Delta S^\ddagger_{\text{rot}} + \Delta S^\ddagger_{\text{vib}} \]

Now

\[ \Delta S^\ddagger_{\text{trans}} = S_{\text{tr}, RHC} - S_{\text{tr}, RH} - S_{\text{tr}, Cl} \]

\[ = \frac{3}{2} R \ln \frac{M_{\text{RHC}}}{M_{\text{RH}}} - S_{\text{tr}, Cl} \]

From the Sackur-Tetrode equation:

\[ S_{\text{tr}, Cl} = \left( \frac{5}{2} \ln T + \frac{3}{2} \ln M - \ln \text{Patm} \right) - 1.164 \]

\[ = 16.60 \text{ e.u.} \]

where the standard state is 1 mole cm\(^{-1}\) at 298°C.

Also

\[ \Delta S^\ddagger_{\text{rot}} = \frac{1}{2} R \ln \frac{A^* B^* C^*}{ABC} \]

where \(A^* B^* C^*\) and \(ABC\) are the products of the moments of inertia of \(RHC\) and \(RH\) about the principal axes in these molecules. The bond lengths used in the molecular models were \(H - H = 0.96\ \text{Å}\) and \(C - H = 1.15\ \text{Å}\) in the normal molecules and \(H - H = 1.15\ \text{Å}\), \(C - H = 1.15\ \text{Å}\) and \(H - Cl = 1.45\ \text{Å}\) in the activated complexes. The value of 1.15 Å for the H - H bond in the activated complex corresponds to the length of a half bond using Pauling formula.

The bond length used for H - Cl is also that for a half bond but the length of the C - H bond in the activated complex has not been correspondingly/
### Table 19:

**Calculation of \( \Delta S_{\text{trans}} \) and \( \Delta S_{\text{rot}} \) Values.**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mol. Wt.</th>
<th>( \frac{\text{Mol. Wt.} - \text{HCl}}{\text{Mol. Wt.} - \text{RH}} )</th>
<th>( \text{(ABC)} )</th>
<th>( \frac{\text{H}_2}{\text{H}_2\text{Cl}} )</th>
<th>( \frac{1}{\text{H}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>2</td>
<td>1.00</td>
<td>( \text{I}_{\text{H}_2} = 0.48 )</td>
<td>( \text{I}_{\text{H}_2\text{Cl}} = 7.72 )</td>
<td>( \frac{1}{\text{H}_2} = 259 )</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>16</td>
<td>1.00</td>
<td>( 36.1 )</td>
<td>( 538 )</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_4\text{Cl} )</td>
<td>51.5</td>
<td>1.00</td>
<td>( 194.0 \times 10^2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>30</td>
<td>1.00</td>
<td>( 41.4 \times 10^2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6\text{Cl} )</td>
<td>65.5</td>
<td>1.00</td>
<td>( 5.96 \times 10^5 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_8 )</td>
<td>44</td>
<td>1.00</td>
<td>( 6.98 \times 10^4 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{pri.} \text{C}_3\text{H}_6\text{Cl} )</td>
<td>79.5</td>
<td>1.00</td>
<td>( 2.28 \times 10^6 )</td>
<td>( 2.94 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td>( \text{sec.} \text{C}_3\text{H}_6\text{Cl} )</td>
<td>79.5</td>
<td>1.00</td>
<td>( 2.28 \times 10^6 )</td>
<td>( 2.94 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td>( \text{nC}<em>4\text{H}</em>{10} )</td>
<td>58</td>
<td>1.00</td>
<td>( 4.22 \times 10^5 )</td>
<td>( 10.1 \times 10^6 )</td>
<td>( 24.0 )</td>
</tr>
<tr>
<td>( \text{pri.} \text{nC}<em>4\text{H}</em>{10}\text{Cl} )</td>
<td>93.5</td>
<td>1.00</td>
<td>( 6.8 \times 10^6 )</td>
<td>( 6.8 \times 10^6 )</td>
<td>( 16.1 )</td>
</tr>
<tr>
<td>( \text{sec.} \text{nC}<em>4\text{H}</em>{10}\text{Cl} )</td>
<td>93.5</td>
<td>1.00</td>
<td>( 5.8 \times 10^5 )</td>
<td>( 5.8 \times 10^5 )</td>
<td></td>
</tr>
<tr>
<td>( \text{iC}<em>4\text{H}</em>{10} )</td>
<td>58</td>
<td>1.00</td>
<td>( 9.45 \times 10^6 )</td>
<td>( 8.55 \times 10^6 )</td>
<td>( 14.7 )</td>
</tr>
<tr>
<td>( \text{pri.} \text{iC}<em>4\text{H}</em>{10}\text{Cl} )</td>
<td>93.5</td>
<td>1.00</td>
<td>( 1.5 \times 10^6 )</td>
<td>( 1.5 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td>( \text{tert.} \text{iC}<em>4\text{H}</em>{10}\text{Cl} )</td>
<td>93.5</td>
<td>1.00</td>
<td>( 21.3 \times 10^6 )</td>
<td>( 21.3 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td>( \text{neo} \text{C}<em>5\text{H}</em>{12} )</td>
<td>72</td>
<td>1.00</td>
<td>( 2.51 \times 10^4 )</td>
<td>( 2.51 \times 10^4 )</td>
<td></td>
</tr>
<tr>
<td>( \text{neo} \text{C}<em>5\text{H}</em>{12}\text{Cl} )</td>
<td>107.5</td>
<td>1.00</td>
<td>( 1.50 \times 10^6 )</td>
<td>( 1.50 \times 10^6 )</td>
<td>( 59.7 )</td>
</tr>
<tr>
<td>( \text{cyclo} \text{C}_3\text{H}_6 )</td>
<td>42</td>
<td>1.00</td>
<td>( 17.4 \times 10^4 )</td>
<td>( 17.4 \times 10^4 )</td>
<td></td>
</tr>
<tr>
<td>( \text{cyclo} \text{C}_3\text{H}_6\text{Cl} )</td>
<td>77.5</td>
<td>1.00</td>
<td>( 5.14 \times 10^6 )</td>
<td>( 5.14 \times 10^6 )</td>
<td>( 29.5 )</td>
</tr>
<tr>
<td>( \text{cyclo} \text{C}_4\text{H}_8 )</td>
<td>56</td>
<td>1.00</td>
<td>( 5.14 \times 10^6 )</td>
<td>( 5.14 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td>( \text{cyclo} \text{C}_4\text{H}_8\text{Cl} )</td>
<td>91.5</td>
<td>1.00</td>
<td>( 5.14 \times 10^6 )</td>
<td>( 5.14 \times 10^6 )</td>
<td></td>
</tr>
</tbody>
</table>

\*\* = average of expanded and contracted forms.
correspondingly lengthened. Any error introduced in using the wrong
H - H distance in the H - H - Cl complex alters A B C by ∼ 6% per 0.1 Å while in neopentane the error in the C - H distance used
in the complex affects A B C by ∼ 4% per 0.1 Å. The details
necessary for the calculation of Δ S trans and Δ S rot are
given in Table 19. In all molecular models the C - H - Cl in the
complex was assumed to be linear.

The frequencies of the vibrations present in the activated
complexes were derived from Pitzer's values for ν st.H2Cl of 1460 cm
-1 and ν bend.H2Cl of 540 cm by the following methods.

**Stretching vibrations.** The frequencies of the stretching
vibrations are decreased as the R groups in R - H - Cl increase in mass.

\[
\left( \frac{\nu_{\text{st}H2Cl}}{\nu_{\text{strHCl}}} \right)^2 = \left( \frac{\mu_{H\ldots Cl}}{\mu_{R\ldots Cl}} \right)^{-1}
\]

where \( \mu \) the reduced mass is given by

\[
\frac{1}{\mu_{R\ldots Cl}} = \frac{1}{M_R} + \frac{1}{M_{Cl}}
\]

where \( M \) are the molecular weights of the fragments.

**Bending vibrations.** The frequency of these vibrations is
given by

\[
\left( \frac{\nu_{\text{bend}H2Cl}}{\nu_{\text{bendRHCl}}} \right)^2 = \left( \frac{\lambda_{H\ldots Cl}}{\lambda_{R\ldots Cl}} \right)^{-1}
\]
Knox & Nelson used the reduced moments of inertia of the fragments about the central H atom as the λ values

\[ \frac{1}{\lambda_{\text{R...Cl}}} = \frac{1}{I_{\text{R}}} + \frac{1}{I_{\text{Cl}}} \]

where \( I_{\#} = I + M_r r^2 \) where \( r \) is the distance of the centre of gravity of the fragment from the central H atom in the complex.

Schlapp has shown that this is inaccurate and that

\[ \frac{1}{\lambda_{\text{R...Cl}}} = \frac{1}{J_{\text{R}}} + \frac{1}{J_{\text{Cl}}} \]

where

\[ J_{\text{R}} = I_{\text{R}} + \frac{M_{\text{Cl}} + M_{\text{H}}}{M_{\text{Cl}} + M_{\text{H}} + M_{\text{R}}} \cdot M_{\text{R}} \cdot a^2 \]

and

\[ J_{\text{Cl}} = I_{\text{Cl}} + \frac{M_{\text{R}} + M_{\text{H}}}{M_{\text{Cl}} + M_{\text{H}} + M_{\text{R}}} \cdot M_{\text{Cl}} \cdot b^2 \]

Since \( M_{\text{H}} \) is small compared with \( M_{\text{R}} \) and \( M_{\text{Cl}} \), except in the H - H - Cl complex, these equations reduce to

\[ J_{\text{R}} = I_{\text{R}} + \mu_{\text{R...Cl}} \cdot a^2 \]

\[ J_{\text{Cl}} = I_{\text{Cl}} + \mu_{\text{R...Cl}} \cdot b^2 \]

\( a \) and \( b \) are the R...H and H...Cl distances in the R...H...Cl complexes, measuring from the centre of gravity of R and Cl to the central H atom.

The entropy values corresponding to particular frequencies are derived from \( \left\{ \frac{E - E_0}{T} \right\} \) and \( \left\{ \frac{P - P_0}{T} \right\} \) values. All entropy calculations were made for 298°C and the details for \( \Delta S_{\text{vib}}^\# \) are given in Table 20. The differences between \( \Delta S_{\text{vib}}^\# \) values using/
### TABLE 20.

Calculation of \( S \) stretching and \( S \) bending for the new vibrational modes of the \( R-H-Cl \) complex.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( (ABG)^{1/2} ) or ( L_R )</th>
<th>( a ) ( \AA )</th>
<th>( \mu )</th>
<th>( J ) ( R )</th>
<th>( \lambda )</th>
<th>( \nu_{st} ) ( \text{cm}^{-1} )</th>
<th>( \nu_{be} ) ( \text{cm}^{-1} )</th>
<th>( S_{st} ) at 298 ( \text{K} )</th>
<th>( S_{be} ) at 298 ( \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{Cl} )</td>
<td>1.15</td>
<td>0.97</td>
<td>1.28</td>
<td>0.91</td>
<td>1460</td>
<td>560</td>
<td>0.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_4\text{Cl} )</td>
<td>3.3</td>
<td>1.15</td>
<td>10.5</td>
<td>23</td>
<td>440</td>
<td>160</td>
<td>0.8</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6\text{Cl} )</td>
<td>16.2</td>
<td>1.6</td>
<td>16.0</td>
<td>57</td>
<td>365</td>
<td>115</td>
<td>1.1</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>pri. ( \text{C}_2\text{H}_5\text{Cl} )</td>
<td>40.7</td>
<td>2.0</td>
<td>19.4</td>
<td>115</td>
<td>330</td>
<td>97</td>
<td>1.25</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>sec. ( \text{C}_2\text{H}_5\text{Cl} )</td>
<td>&quot;</td>
<td>1.6</td>
<td>&quot;</td>
<td>90</td>
<td>100</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>pri. ( \text{C}_4\text{H}_10\text{Cl} )</td>
<td>74</td>
<td>2.15</td>
<td>21.8</td>
<td>175</td>
<td>320</td>
<td>89</td>
<td>1.3</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>sec. ( \text{C}_4\text{H}_10\text{Cl} )</td>
<td>&quot;</td>
<td>1.6</td>
<td>&quot;</td>
<td>130</td>
<td>91</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3.65</td>
<td></td>
</tr>
<tr>
<td>pri. ( \text{C}_4\text{H}_10\text{Cl} )</td>
<td>83</td>
<td>2.3</td>
<td>&quot;</td>
<td>190</td>
<td>&quot;</td>
<td>88</td>
<td>&quot;</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>tert. ( \text{C}_4\text{H}_10\text{Cl} )</td>
<td>&quot;</td>
<td>1.7</td>
<td>&quot;</td>
<td>146</td>
<td>90</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3.65</td>
<td></td>
</tr>
<tr>
<td>neo ( \text{C}_5\text{H}_12\text{Cl} )</td>
<td>115</td>
<td>2.2</td>
<td>23.6</td>
<td>230</td>
<td>300</td>
<td>83</td>
<td>1.4</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>cyclo ( \text{C}_5\text{H}_6\text{Cl} )</td>
<td>29</td>
<td>1.7</td>
<td>19.0</td>
<td>85</td>
<td>335</td>
<td>102</td>
<td>1.2</td>
<td>3.45</td>
<td></td>
</tr>
<tr>
<td>cyclo ( \text{C}_4\text{H}_8\text{Cl} )</td>
<td>56</td>
<td>1.8</td>
<td>21.6</td>
<td>126</td>
<td>310</td>
<td>92</td>
<td>1.3</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>( \text{C}_\infty )</td>
<td>35.5</td>
<td>75</td>
<td>245</td>
<td>57</td>
<td>1.8</td>
<td>4.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N.B. \( \Delta S_{\text{vib}} \) (calculated) = \( S_{st} + S_{be} \times 2 \) since the bending mode is doubly degenerate.

\( ^* \)
using the two formulae for \( \text{R} \ldots \text{Cl} \) are small.

Comparison of the calculated and experimental \( \Delta S_{\text{vib}}^\dagger \) values given in Table 18 leads to the conclusion that although the introduction of two new vibrational modes in the activated complex accounts for most of the vibrational entropy of activation in reactions of the type

\[
\text{R} - \text{H} + \text{Cl} \rightarrow \text{R} + \text{H} - \text{Cl}
\]

in most cases the calculated values are lower than the experimental values suggesting that other contributions to \( \Delta S_{\text{vib}}^\dagger \) should be considered.

The calculated value for hydrogen is lower than the experimental value because these calculations were made for 298\(^\circ\)A, the mid-temperature of most Arrhenius plots in the present work whereas Pitzer obtained the vibrational frequencies from the \( \Delta S_{\text{vib}}^\dagger \) value at 600\(^\circ\)A. This discrepancy between calculated and experimental \( \Delta S_{\text{vib}}^\dagger \) values for hydrogen possibly explains the discrepancies for the hydrocarbons to a certain extent, but the fact that

\[
\Delta S_{\text{vib}}^\dagger(\text{exp}) - \Delta S_{\text{vib}}^\dagger(\text{calc})
\]

varies from compound to compound is of some significance.

The low experimental vibrational entropy of activation of methane is anomalous and cannot at present be explained. The best agreement between calculated and experimental values is found/
found with ethane and cyclopropane, both relatively simple molecules, while poorest agreement occurs with the secondary positions in propane and n butane and the tertiary position in iso butane.

These facts can be explained if it is assumed that the presence of a chlorine atom in the activated complex has a significant effect on the frequencies of the vibrations in the parent hydrocarbon. In the simple molecules ethane and cyclopropane the lowest vibrational frequencies are of the order of 800 cm$^{-1}$ and little contribution to $\Delta S_{vib}^\neq$ can be expected. In the higher paraffins low frequency chain deformation vibrations occur and the contribution to $\Delta S_{vib}^\neq$ from changes in those frequencies can be expected to be larger.

The greater effect of a chlorine atom in the activated complex on such frequencies when attack occurs at secondary positions as compared to primary positions is not unreasonable.
SUMMARY.

The free radical, long chain competitive chlorination of hydrocarbons has led to accurate relative rate constants for reactions of the type:

\[ R - H + Cl. \rightarrow R_1 + H - Cl \]

where \( k_R \) is the rate constant for the reaction. Gas chromatography was used to analyse the chloride products from the chlorinations of hydrogen, methane, ethane, propane, n butane, iso butane, neopentane, cyclopropane and cyclobutane. Using the established value for \( k_H \) obtained by three independent methods, absolute rate constants \( k_R \) for all positions in the hydrocarbons studied were determined.

An attempt has been made to correlate the activation energies for the chlorine atom attack on the straight chain alkanes with (a) the bond dissociation energies of the C-H bonds which break in the course of the reaction and (b) the inductive effect of the hydrocarbon molecule which makes available electrons for the incipient H-Cl bond. The former effect predominates in the higher activation energies and the latter in the lower values. The very low value of \( E_{tibu} \) leads to an apparent negative value for \( \Delta u_0 \). The high value of \( E_{cpr} \) is due to the I strain present in the cyclopropane ring.

Using the theory of absolute reaction rates theoretical \( A \) factors have been considered. It is found that the main contribution to the vibrational entropies of activation are from two new vibrational modes (one being doubly degenerate) of the activated complex \( R - H - Cl \). Additional contributions may arise from changes in the low frequency chain deformation vibrations of the more complicated molecules.
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