COMPETITIVE CHLORINATION OF SUBSTITUTED ETHYLENES
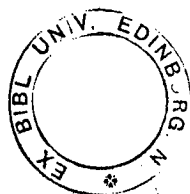
by

KENNETH C. WAUGH, B.Sc.

Thesis presented for the Degree of Doctor of Philosophy
of the University of Edinburgh

Edinburgh   August 1967

CONTENTS

ACKNOWLEDGEMENTS

ABBREVIATIONS

The following abbreviations have been used in the text.

PrH	Propane
iso PrCl	iso-Propyl chloride
n PrCl	n-Propyl chloride
TCE	1,1,2,2,-Tetrachloroethane
TrCE	1,1,2,- Trichloroethylene
PCE	Pentachloroethane
V. C.	Vinyl Chloride
HCE	Hexachloroethane
DCE	Dichloroethylene
P. V. C.	Polyvinyl Chloride
Tetra CE	Tetrachloroethylene

With respect to the 1,2-disubstituted ethylenes, the letters c and t refer to the cis and trans isomers, respectively, and the letter i is used when either cis and/or trans is intended.

The letter A is used to indicate an olefin, the meaning of ACl and ACl_2 is then obvious.

ABSTRACT OF THESIS.

The Arrhenius parameters of the rate constants of the reactions

$$Cl + A \longrightarrow ACl^* \qquad k_2''$$

$$and \quad ACl^* \longrightarrow A + Cl \qquad k_a$$
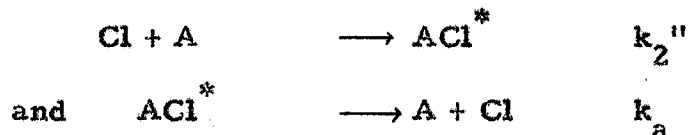
(where ACl^* is an active chloroalkyl radical and A an olefin)

have been determined by the competitive technique for trichloroethylene

and tetrachloroethylene. In the latter case, however, only a rough

estimate could be made of the rate of unimolecular decomposition of the

active pentrachloroethyl radical.

When A = trichloroethylene, the parameters are

$$k_2''(TrCE) = 2.68 \pm 1.36 \times 10^{10} \exp (+ 0.24 \pm 0.41/RT) mole^{-1}. l. sec^{-1}$$

and $k_a(TrCE) = 7.33 \pm 2.73 \times 10^{10} \exp (-3.26 \pm 0.38/RT) sec^{-1}$

where the activation energies are in k. cal. mole^{-1}.

The efficiency of various gases in deactivating the active

tetrachloroethyl radical by the reaction

$$ACl^* + Mi \longrightarrow ACl^0 + Mi \qquad (bi)$$

(where ACl^0 is an inactive chloroalkyl radical), has been found to be

Efficiency per collision relative to chlorine	Cl_2	PrH	TrCE	CO_2	Ar	SF_6
	1	0.85	1.46	0.83	1.23	1.17

The bimolecular A factor for trichloroethylene has been

calculated by absolute rate theory to be 1.37×10^9 mole^{-1}. l. sec^{-1}; this

value has to be compared with the experimental value of

$2.68 \times 10^{10} \text{mole}^{-1} . \text{l. sec}^{-1}$. The unimolecular rate constant has been calculated by the Marcus theory to be $0.92 \times 10^8 \text{sec}^{-1}$ which compares well with the experimental value of $7.0 \times 10^8 \text{sec}^{-1}$ at 79^0C. This reasonable agreement between the experimental and theoretical bimolecular A factors and unimolecular rate constants was achieved only after it was assumed that the activated complex and active radical rotate freely about the C-C bond.

When A = tetrachloroethylene a value of A_2" of $0.24 \times 10^{10} \text{mole}^{-1} . \text{l. sec}^{-1}$ at 79^0C was obtained experimentally which is to be compared with the value $0.87 \times 10^{10} \text{mole}^{-1} . \text{l. sec}^{-1}$, calculated from absolute theory of reaction rates. In this case, however, to achieve this degree of agreement between the theoretical and experimental bimolecular A factors it is necessary to assume that internal rotation, of the transition state complex, about the C-C bond is restricted; the assumption of free rotation in the transition state complex gives a theoretical value 30 times higher than the experimental one. Further, making the assumption of a rigid activated complex the lifetime of the pentrachloroethyl radical is calculated by the Marcus theory to be 5×10^{-7} seconds which compares well with the experimentally estimated lifetime of 2×10^{-7} seconds.

PREFACE

This work was undertaken with the aim of applying the hot radical mechanism of Knox and Riddick, (derived for dichloroethylene (53)), to the chlorination of trichloroethylene and, if possible, to extend it to the chlorination of the remaining chloroethylenes and ethylene. This was done to evaluate experimentally the rate constants k_2'' and k_a for the reactions.

$$A + Cl \rightarrow ACl^* \qquad k_2''$$

$$\text{and} \qquad ACl^* \rightarrow A + Cl \qquad k_a$$
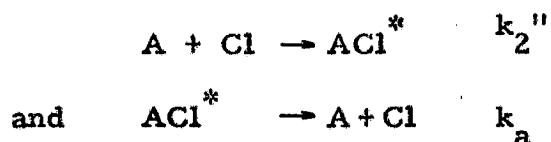
where ACl^* is an active chloroalkyl radical.

It would then be possible to test the theories of bimolecular and unimolecular reaction for a series of related compounds in which the structure of A was systematically varied in going from one member of the series to the next.

It was also intended to measure the deactivating efficiencies (relative to chlorine) of a number of varied compounds in the reaction

$$ACl^* + Mi \rightarrow ACl^o + Mi$$

(where ACl^o is an inactive radical), in an effort to observe a correlation if any, between molecular structure and deactivating efficiency.

CHAPTER I

INTRODUCTION

(a) Theoretical

The object of a considerable amount of experiment and thought in chemistry has been to try to obtain a clearer understanding of the nature of the processes which occur during chemical reaction. At present, no theory defines completely the many complexities of reaction, but it is hoped that, with increased sophistication of current ideas, some comprehensive theory may be evolved.

All of the theories which hold sway at the moment are a development of the first attempt, by Arrhenius (1), to interpret the large effect of temperature on the rate of chemical reaction. In an effort to explain the temperature dependence of the rate of inversion of sucrose, Arrhenius (1889) modified the Van't Hoff isochore to obtain an expression which relates the rate constant, k, for the inversion of sucrose to two parameters, A, and E. Thus

$$k = Ae^{-E/RT} \qquad\qquad I.a.1$$

A precise interpretation of the parameters has proved elusive. Arrhenius, himself, believed that an equilibrium existed between inert and active molecules and that the quantity E was the difference in heat content

between the inert and active molecules. The suggestion that only active molecules underwent reaction then explained, for the first time, the effect of temperature on the rate of chemical reaction. These ideas foreshadow those of modern transition state theory.

In 1928 Lewis (2) suggested that the parameter A be related to the frequency of collisions of the reacting molecules and thereby completed a useful, if rudimentary, picture of the nature of reaction.

Concern then centred on how the population of the active species was maintained. The idea that the parameter A might be related to a collisional frequency inferred that activation might occur as a result of collisions and, therefore, implied that the rate of reaction would show some dependence upon the pressure of an inert gas. However, in testing this theory by observing the dependence of the rate of decomposition of PH_4Cl upon argon pressure, Perrin (3) noticed no dependence of the rate of decomposition over the range of argon pressures then accessible and, therefore, concluded that activation resulted from the absorption of infra red radiation emitted by the walls of the containing vessel.

Evidence against the radiation hypothesis accumulated rapidly. Langmuir (4) showed that the density of radiation inside a black body was insufficient to account for the observed rate; this conclusion was later confirmed by calculations due to Lewis and Smith (5).

Later, Lindemann (6), in criticising the radiation hypothesis felt obliged

"to put forward a constructive suggestion to meet Professor Perrin's difficulty".
He proposed that activation occurred as a result of collision and that the active
species, once formed, had a sufficient lifetime that there was a high probability
of deactivation (also by collision). Lindemann's idea is expressed in the
equations

$$A + M \quad \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \quad A^* + M \qquad\qquad A$$

$$A^* \quad \xrightarrow{k_3} \quad products \qquad\qquad B$$
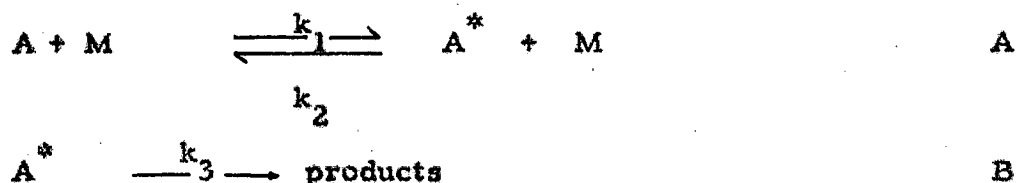
where M is any molecule or wall of the reaction vessel capable of transferring
energy to A. Further, it was believed that deactivation occurred at every
collision and hence $k_2 = Z^o$, the standard collision number. Assuming
steady state conditions for A^* an overall k_{uni} is obtained

$$k_{uni} = \frac{k_3 k_1 [M]}{k_2 [M] + k_3} \qquad\qquad I. a. 2$$

$$or \quad \frac{1}{k_{uni}} = \frac{k_2}{k_3 k_1} + \frac{1}{k_1 [M]} \qquad\qquad I. a. 3$$

$$or \quad k_{uni} = \frac{k_3 (k_1/k_2)}{1 + k_3/(k_2 [M])} \qquad\qquad I. a. 4$$

Thus at high pressures the theory predicts that k_{uni} should reach a
limiting value but should fall as the pressure is decreased. This was
verified by Hinshelwood and co-workers (7, 8, 9) who found that the
decompositions of proptional, diethyl and dimethyl ether, were all first
order at high pressures but deviated from first order kinetics at low
pressures, the rate constant becoming smaller with decreasing pressure in

accordance with equation 1a4. Ramsperger (10) observed the same type of decrease in the rate of decomposition of azomethane but to an even greater extent than in the reactions studied by Hinshelwood. It is of interest to note here that, although the theoretical interpretations of the rates of these supposed unimolecular reactions were sound, all the reactions which prompted early thinking were, in fact, chain reactions. (11) - (15).

About this time it was thought that the limiting high pressure unimolecular A factor, A∞, should be related directly to the number of collisions suffered per second by a single molecule; yet the experimental values were several powers of 10 greater than the collision frequency. To account for this discrepancy Hinshelwood (16) sketched a few calculations on an idea put to him by Lindemann that there might be enough collisions for the activation reaction if the total energy could be made up by any distribution among a considerable number of degrees of freedom, and not simply in the two degrees of freedom due to linear translation along the line of centres. Hinshelwood's calculations rested on the assumption that the rate constant for unimolecular decomposition, k_{uni}, could be calculated by the statistical mechanical evaluation of the equilibrium constant $K_1 = k_1/k_2$ (see eqn (1a4)) and he therefore proposed that the activated molecule contained energy in an indeterminate number of degrees of freedom or "square" terms, n, such that

$$q_1^2 + q_2^2 + q_3^2 + \ldots q_n^2 = \varepsilon \qquad \text{I. a. 5}$$

where ε refers to the total kinetic energy. According to Hinshelwood the vibrational degrees of freedom have an equal amount of potential energy which does not vary independently of kinetic energy and he therefore re-garded ε as the "effective" total energy.

Application of the Maxwell Boltzmann distribution law to obtain the most probable state of a system composed of numbers of identical elements give s

$$\frac{dN}{N} = \frac{e^{-\varepsilon/kT} \, dq_1 \, dq_2 \, dq_3 \cdots dq_n}{\int \cdots \int e^{-\varepsilon/kT} \, dq_1 \, dq_2 \cdots dq_n} \qquad \text{Ia, 6}$$

where N is the number of elements of some chosen kind whose momentary state might be completely defined by assigning values to the n parameters $q_1 \, q_2 \cdots q_n$; ε is the energy of an element defined by $q_1 \, q_2 \cdots q_n$ and dN is the number of elements whose energy lies between q_1 and $q_1 + dq_1$ q_2 and $q_2 + dq_2 \cdots q_n$ and $q_n + dq_n$. The integral in the denominator is taken over all values of $q_1 \, q_2 \cdots q_n$ which are physically allowed.

To find the chance that the total energy lay within the limits ε and $\varepsilon + d\varepsilon$ the numerator of equation (Ia, 6) was integrated over an (n-1) dimensional hyper sphere whose radii were $\sqrt{\varepsilon}$ and $\sqrt{\varepsilon} + \dfrac{d\varepsilon}{2\sqrt{\varepsilon}}$. Since $e^{-\varepsilon/kT}$ is constant the integral becomes

$$\int^{\varepsilon + d\varepsilon} dq_1 \, dq_2 \, dq_3 \cdots dq_n \qquad \text{Ia, 7}$$

$$q_1^2 + q_2^2 + q_3^2 \cdots + q_n^2 = \varepsilon$$

which is simply the volume of an (n-1) dimensional hyperspherical shell.

The volume of an n dimensional sphere is

$$V = \frac{\pi^{n/2} r^n}{\Gamma(n/2+1)} \qquad\qquad \text{Ia,8}$$

$$dV = \frac{\pi^{n/2} n r^{n-1} dr}{\Gamma(n/2+1)}$$

$$\text{Ia,9}$$

and hence the volume of the desired shell is

$$\frac{2\pi^{n/2} \varepsilon^{n/2-\frac{1}{2}}}{\Gamma(n/2)} \frac{d\varepsilon}{2\sqrt{\varepsilon}} \qquad\qquad \text{Ia,10}$$

i. e. $\qquad \dfrac{\pi^{n/2} \varepsilon^{n/2-1}}{\Gamma(n/2)} d\varepsilon \qquad\qquad$ Ia,11

The integral in the denominator of Ia,6 is taken throughout all space

i. e. $\qquad I = \displaystyle\int_0^\infty e^{-\varepsilon/kT} dq_1\, dq_2\, dq_3 \cdots dq_n \qquad$ Ia,12

$$= \int_0^\infty e^{-\varepsilon/kT} \frac{\pi^{n/2} \varepsilon^{n/2-1}}{\Gamma(n/2)} d\varepsilon \qquad\qquad \text{Ia,13}$$

$$= \frac{(\pi kT)^{n/2}}{\Gamma(n/2)} \int_0^\infty e^{-\varepsilon/kT} \left(\frac{\varepsilon}{kT}\right)^{n/2-1} d(\varepsilon/kT) \qquad \text{Ia,14}$$

$$= \frac{(\pi kT)^{n/2}}{\Gamma(n/2)} \Gamma(n/2) \qquad\qquad \text{Ia,15}$$

$$I = (\pi kT)^{n/2} \qquad \text{for n even} \qquad \text{Ia, 16}$$

The ratio of these two integrals gives the chance that the total energy of the

n oscillators will be within the limits ε and $\varepsilon + d\varepsilon$; this chance is

$$e^{-\varepsilon/kT} \frac{\varepsilon^{n/2-1} d\varepsilon}{\Gamma(n/2)(kT)^{n/2}} \qquad \text{Ia, 17}$$

The chance of possessing energy greater than some critical amount ε_0

is

$$\text{i.e.} \quad \frac{N\varepsilon_0}{N_0} = \frac{1}{\Gamma(n/2)(kT)^{n/2}} \int_{\varepsilon_0}^{\infty} e^{-\varepsilon/kT} \varepsilon^{(n/2-1)} d\varepsilon \qquad \text{Ia. 18}$$

This integral becomes

$$\frac{k_1}{k_2} = \frac{N\varepsilon_0}{N_0} = e^{-\varepsilon_0/kT} \left\{ \frac{1}{\Gamma(n/2)} \left(\frac{\varepsilon}{kT}\right)^{n/2-1} + \frac{1}{\Gamma(n/2-1)} \left(\frac{\varepsilon}{kT}\right)^{n/2-2} .. +1 \right\} \qquad \text{Ia. 19}$$

Hinshelwood stated that since ε was generally large compared to

$(n/2-1)kT$ it was permissible, for approximate calculations, to take only

the first term of the expansion. Thus the usual $e^{-\varepsilon/kT}$ in the Arrhenius

equation is replaced by

$$\frac{e^{-\varepsilon_0/kT} (\varepsilon_0/kT)^{n/2-1}}{\Gamma(n/2)} \qquad \text{Ia, 20}$$

Thus if n is large, the factor $(\varepsilon_0/kT)^{n/2-1} / (n/2-1)!$ might be

sufficiently great to account for the difference between the collisional

frequency and the abnormally high A factor for the activation processes in unimolecular reactions. Using a value of n equal to twelve Hinshelwood was able to account for the fact that the number of molecules of propional decomposing per second was 400 times greater than $Ze^{-E/RT}c^2$.

Hinshelwood assumed that all molecules with energy greater than a critical minimumamount decompose at the same rate, independent of the amount of energy they possess in excessof this critical amount i. e. k_3 was constant independent of the amount of energy possessed by A*. This would predict that a graph of $1/k_{uni}$ against $1/[M]$ would be linear (e. g. Ia, 4). This was verified within the limits of accuracy of the experimental results for propional, but the more accurate results for dimethyl and diethyl ether were in definite disagreement with the requirements of the theory. The plots of $1/k_{uni}$ against $1/[M]$ for these molecules were definitely curved. Here again, many of the reactions were not in fact elementary and the interpretations were therefore completely erroneous. They were, however, fortuitous since more recent data on reactions known to be elementary and unimolecular has amply confirmed the curved nature of the pressure dependence. (e. g. the decomposition of cyclopropane (17) and the isomerization of methyl isocyanide (18)). Thus it seems that, although the assumption of a reasonable number of degrees of freedom is capable of accounting for the order of magnitude of reaction rates of most unimolecular reactions, it is not able to account, quantitatively, for the variation of the rate constant with pressure.

Kassel (19) developed Hinshelwood's theory by arguing that, in order to decompose, it was not sufficient for a complex molecule simply to possess a large amount of excess energy: it was necessary for this energy - or some sufficient part of it - to be concentrated in a particular point of the molecule in order to cause its rupture. Therefore, on the assumption that some critical bond would break whenever it acquired energy in excess of some critical minimum amount, Kassel calculated a relation between the specific reaction rate of the activated molecules and their energy content.

The Kassel treatment implies an extension of the Lindemann scheme to include the rate of intra molecular energy transfer into the critical oscillator. A particular feature of this theory like that of Hinshelwood was the consideration of the active molecules in a particularly small range of energy, In terms of such a group of molecules the reaction may be written in detail as

$$A + M \xrightarrow{k_1(\varepsilon)d\varepsilon} A^*(\varepsilon \longrightarrow \varepsilon + d\varepsilon) + M$$

$$M + A^*(\varepsilon \longrightarrow \varepsilon + d\varepsilon) \xrightarrow{z^o} A + M$$

$$A^*(\varepsilon \longrightarrow \varepsilon + d\varepsilon) \xrightarrow{k_3(\varepsilon)} A^+ \xrightarrow{k^+} \text{products}$$
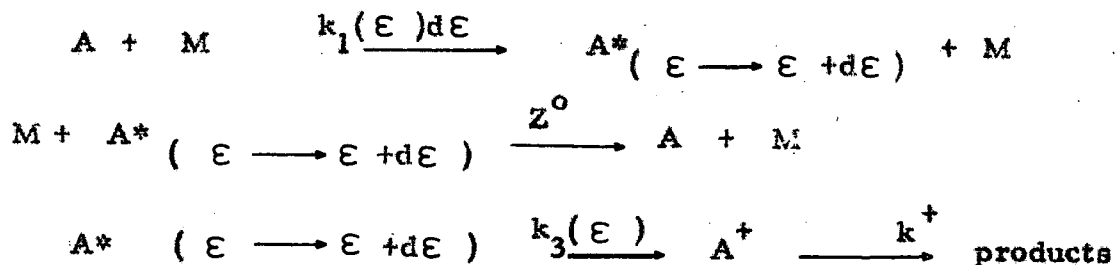
where A^* denotes a molecule where the excess energy is distributed throughout the oscillators - the active molecule; and A^+ is a molecule which has at least ε_o localised in one critical vibrator - in modern terminology the activated complex.

The contribution to the complete unimolecular rate constant for the group is then

$$dkuni = \frac{k_1(\epsilon) \; k_3(\epsilon) \; d\epsilon / Z^o}{1 + k_3(\epsilon)/Z^o \; [M]}$$
Ia, 21

and the overall unimolecular rate constant is obtained by integration from the minimum energy ϵ_o, to ∞

Thus

$$kuni = \int_{\epsilon_o}^{\infty} \frac{k_1(\epsilon) \; k_3(\epsilon) \; d\epsilon / Z^o}{1 + k_3(\epsilon)/ Z^o \; [M]}$$
Ia, 22

The problem of evaluation of kuni is therefore the evaluation of $k_1(\epsilon)$ and $k_3(\epsilon)$ as a function of ϵ.

Kassel's theory was similar to the second version of the theory of Rice and Ramsperger (20) who assumed that it was necessary for the energy ϵ_o to be concentrated in a single degree of freedom rather than in a chemical bond which Kassel considered as equivalent to a simple oscillator possessing two degrees of freedom. Thus a molecule was regarded by Kassel as a system of s weakly coupled harmonic oscillators, the weak coupling, inferring that the total energy could be regarded as the sum of the square term but the coupling being sufficiently strong to allow immigration of energy within the molecule. The expression for the total energy is then

$$\epsilon = p_1^2 + q_1^2 + p_2^2 + q_2^2 \; .... \; + p_s^2 + q_s^2$$
Ia, 23

where the p's are reduced momentum coordinates and the q's position coordinates.

Calculation of the chance that the total energy of the s oscillators lay within the limits ε and $\varepsilon + d\varepsilon$ was exactly analogous to Hinshelwood's development. The relevant equations can be obtained by replacing n by 2s in equations Ia. 8, Ia. 17, Ia. 19 etc. Thus the chance that the total energy of the s oscillators lies between ε and $\varepsilon + d\varepsilon$ is

$$\frac{\varepsilon^{s-1}}{(kT)^s (s-1)!} \quad e^{-\varepsilon/kT} \quad d\varepsilon \qquad \text{Ia. 23}$$

and the chance that the total energy of the s oscillators exceeds a limiting amount, ε_0, is

$$\sum_{r=1}^{s} \frac{e^{-\varepsilon_0/kT} (\varepsilon_0/kT)^{r-1}}{(r-1)!} \qquad \text{Ia. 24}$$

and the rate of activation into energies ε to $\varepsilon + d\varepsilon$ is

$$k_1(\varepsilon)d\varepsilon = Z^o \left(\frac{\varepsilon}{kT}\right)^{s-1} \frac{1}{(s-1)!} \quad e^{-\varepsilon/kT} \frac{d\varepsilon}{kT} \qquad \text{Ia. 25}$$

Kassel then extended Hinshelwood's theory by evaluating the chance that, when s oscillators had total energy in the range ε to $\varepsilon + d\varepsilon$, one of them would have energy at least ε_0. This chance is the ratio of the phase space volume corresponding to states which have total energy ε to $\varepsilon + d\varepsilon$ and for which some oscillator has energy at least ε_0, to the phase space volume corresponding to all states with total energy between ε and $\varepsilon + d\varepsilon$. This latter volume has been found by Hinshelwood (eqn. Ia. 11) the form of which was changed by Kassel to

$$\frac{\pi^s}{(s-1)!}\, \varepsilon^{s-1}\ d\varepsilon$$

Ia, 26

The former volume is

$$\iint\limits_{p_1^2 + q_1^2 = \varepsilon_0}^{\varepsilon} dp_1\, dq_1 \int\limits_{p_2^2 + q_2^2 + \cdots p_s^2 + q_s^2 = \varepsilon -(p_1^2+q_1^2)}^{\varepsilon -(p_1^2 + q_1^2)+ d\varepsilon} \int dp_2 \cdots dq_s$$

Ia, 27

$$= \iint\limits_{p_1^2 + q_1^2 = \varepsilon_0}^{\varepsilon} \frac{\pi^{s-1}}{(s-2)!}\ (\varepsilon -(p_1^2 + q_1^2))^{s-2}\, d\varepsilon\ dp_1\, dq_1$$

Ia, 28

$$= \frac{\pi^s}{(s-1)!}\ (\varepsilon - \varepsilon_0)^{s-1}\, d\varepsilon$$

Ia, 29

The last pair of integrations was effected by the substitution

$$p_1 = \sqrt{z}\ \cos \Theta$$

$$q_1 = \sqrt{z}\ \sin \Theta$$

The ratio of Ia, 26 to Ia, 29 is

$$\left(\frac{\varepsilon - \varepsilon_0}{\varepsilon}\right)^{s-1}$$

Ia, 30

which was the desired result.

Further , since the rate of decomposition of the active species is proportional to the probability of the energy ε_0 being located in the critical oscillator Kassel stated that

$$k_3 = A\left(\frac{\epsilon-\epsilon_0}{\epsilon}\right)^{s-1} \qquad \text{Ia, 31}$$

was effectively the rate of decomposition of the active molecule.

The constant A, defined by Kassel as a proportionality constant, has been variously identified with the experimental Arrhenius A factor at the high pressure limit (equation Ia, 39) and with a vibrational frequency.

Qualitatively, equation Ia, 31 may be interpreted as saying that unimolecular decomposition occurs at the first vibration of the critical oscillator when it contains at least energy ϵ_0, attenuated by the probability of the energy being localised in the bond.

The Kassel expression for the rate constant k_{uni} was derived from the differential expression for a small energy range $d\epsilon$

$$dkuni(\epsilon) = \frac{k_3(\epsilon)(k_1(\epsilon)/Z^0)d\epsilon}{1 + k_3(\epsilon)/k_2 Z^0[M]} \qquad \text{Ia, 32}$$

$$= \frac{Z^0\left(\frac{\epsilon}{kT}\right)^{s-1}\frac{1}{(s-1)!}e^{-\epsilon/kT}\frac{d\epsilon}{kT}A\left(\frac{\epsilon-\epsilon_0}{\epsilon}\right)^{s-1}}{1 + \frac{A}{Z^0_2[M]}\left(\frac{\epsilon-\epsilon_0}{\epsilon}\right)^{s-1}}$$

$$\text{Ia, 33}$$

giving an overall unimolecular rate constant

$$kuni = \frac{Ae^{-\epsilon_0/kT}}{(s-1)!(kT)^s}\int_{\epsilon_0}^{\infty}\frac{\epsilon^{s-1}((\epsilon-\epsilon_0)/\epsilon)^{s-1}e^{-(\epsilon-\epsilon_0)/kT}d\epsilon}{1 + \frac{A}{Z^0_2[M]}\left(\frac{\epsilon-\epsilon_0}{\epsilon}\right)^{s-1}} \qquad \text{Ia, 34}$$

$$k_{uni} = \frac{Ae^{-\varepsilon_o/kT}}{(s-1)!\,(kT)^s} \int_0^\infty \frac{\Delta\varepsilon^{s-1}\; e^{-\Delta\varepsilon/kT}d(\Delta\varepsilon)}{1 + \frac{A}{Z^c[M]}\,(\Delta\varepsilon/\varepsilon)^{s-1}} \qquad\text{Ia. 35}$$

The limiting high pressure unimolecular rate constant i.e. as

$[M] \to \infty$, k_∞ is

$$k_\infty = \frac{A}{(s-1)!} \int_{\varepsilon_o}^\infty \left(\frac{\varepsilon-\varepsilon_o}{kT}\right)^{s-1} e^{-\varepsilon/kT} d\left(\frac{\varepsilon}{kT}\right) \qquad\text{Ia. 36}$$

$$= \frac{A\, e^{-\varepsilon_o/kT}}{(s-1)!} \int_0^\infty \left(\frac{\Delta\varepsilon}{kT}\right)^{s-1} e^{-\Delta\varepsilon/kT} d\left(\frac{\Delta\varepsilon}{kT}\right) \qquad\text{Ia. 37}$$

$$= \frac{A\, e^{-\varepsilon_o/kT}}{(s-1)!} \;\Gamma(s) \qquad\text{Ia. 38}$$

$$= A\, e^{-\varepsilon_o/kT} \qquad\text{Ia. 39}$$

It now becomes obvious why the proportionality constant A of equation Ia. 31

should be identified with the experimental, high pressure, Arrherius A

factor.

Thus the ratio kp/k_∞ becomes

$$\frac{kp}{k_\infty} = \frac{1}{(s-1)!\,(kT)^s} \int_{\varepsilon_o}^\infty \frac{(\varepsilon-\varepsilon_o)^{s-1}\; e^{-(\varepsilon-\varepsilon_o)/kT}d\varepsilon}{1 + \frac{A}{Z^c[M]}\left(\frac{\varepsilon-\varepsilon_o}{\varepsilon}\right)^{s-1}} \qquad\text{Ia. 40}$$

$$\frac{k_p(w)}{k_\infty} = \frac{1}{(s-1)!} \int_0^\infty \frac{(\Delta\varepsilon/kT)^{s-1} e^{-\Delta\varepsilon/kT}}{1 + \frac{A}{Z^o[M]}(\Delta\varepsilon/(\varepsilon_o+\Delta\varepsilon))^{s-1}} d\,\Delta\varepsilon/kT \qquad \text{Ia, 41}$$

a form which is suitable for numerical calculation assuming values of the

adjustable parameter s, the experimental high pressure ε_o, and the A factor.

The main objection to the classical form of the Kassel theory is in the

use of the adjustable parameter s - the number of effective oscillators. In

the quantum form the assumption that all the oscillators have the same

frequency is also undesirable. Nevertheless, Kassel's expression for

the rate of decomposition of the active species, equation Ia, 31 is still widely

used; a reasonable fit to experimental data is generally obtained with s equal

to about half the number of vibrational modes in the molecule.

The Kassel theory provided chemists with a clear and qualitatively simple

picture of what happened during the course of reaction. The energy, acquired

as a result of collision, was distributed amongst the vibrators of the molecule

- a continuously changing distribution - with the result that one critical

oscillator, whose movement represented the stretching of a bond, had a

finite probability of acquiring sufficient energy for the rupture of the bond.

The possibility of the oscillator acquiring this amount of energy increased

with the total energy content of the molecule and depended inversely upon

the number of oscillators which could contribute to the energy in the critical

oscillator.

The proportionality constant A can be defined more precisely if one considers the complete equilibrium

$$A + M \xrightarrow{k_1(\varepsilon)} A* + M$$

$$A* + M \xrightarrow{k_2} A + M$$

$$A* \underset{k^+}{\overset{k_3(\varepsilon)}{\rightleftharpoons}} A^+_*$$

$$A^+_* \xrightarrow{k^+} products$$
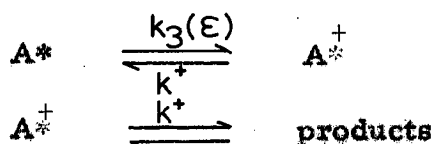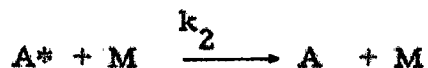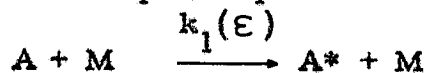
By the principle of microscopic reversibility, at equilibrium, the rate of decomposition of the activated complex is equal to its rate of redistribution of internal energy in changing to the active molecule. Therefore A can be regarded as the rate of migration of internal energy from a single oscillator into any other part of the molecule; it was believed that this could occur at every vibration and hence that $A \approx 10^{13-14}$ sec^{-1}.

Also, by the principle of detailed balancing, if the equilibrium

$$A* \underset{k^+}{\overset{k_3}{\rightleftharpoons}} A^+$$
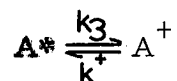
only, is considered, then

$$\frac{[A^+]}{[A*]} = \frac{k_3}{k^+} \qquad\qquad Ia, 42$$

and

$$k_3 = k^+ \frac{[A^+]}{[A*]} = k^+ \left(\frac{\varepsilon - \varepsilon_0}{\varepsilon}\right)^{s-1} \qquad\qquad Ia, 43$$

whence $\quad k^+ \equiv A \qquad\qquad Ia, 44$

and the proportionality constant A is equated directly with the rate constant

for decomposition of the activated complex.

However, the problem of the precise value and interpretation of A or, more generally, of the rate of decomposition, k^+, of what are now termed molecules in the transition state, was solved by Eyring (21) who was mainly responsible for the theory of absolute reaction rates. The theoretical evaluation of s is dealt with later.

The evaluation of the absolute rate of a reaction from purely theoretical ideas has two parts; (1) the evaluation of the activation energy; and (2) the evaluation of the pre-exponential or A factor. In its application to unimolecular reaction then, only the second type of calculation is relevant. However, it was from the ideas of the quantum calculation of activation energy by London (22), of a system of three atoms as a function of their internuclear separation, and reduced the concept of chemical reaction between three atoms

which

to their following the path of lowest energy along a potential energy surface, that Eyring derived his inspiration. The difference in energy between the lowest and highest points on such a path gives the activation energy for that particular reaction. Eyring concentrated his attention on that region of highest energy on the reaction path.

The activated state or transition state because of its definition is always to be found at the saddle point in the potential energy diagram (fig. I)

Potential Energy Diagram for the

Reaction $A + BC \rightleftharpoons AB + C$
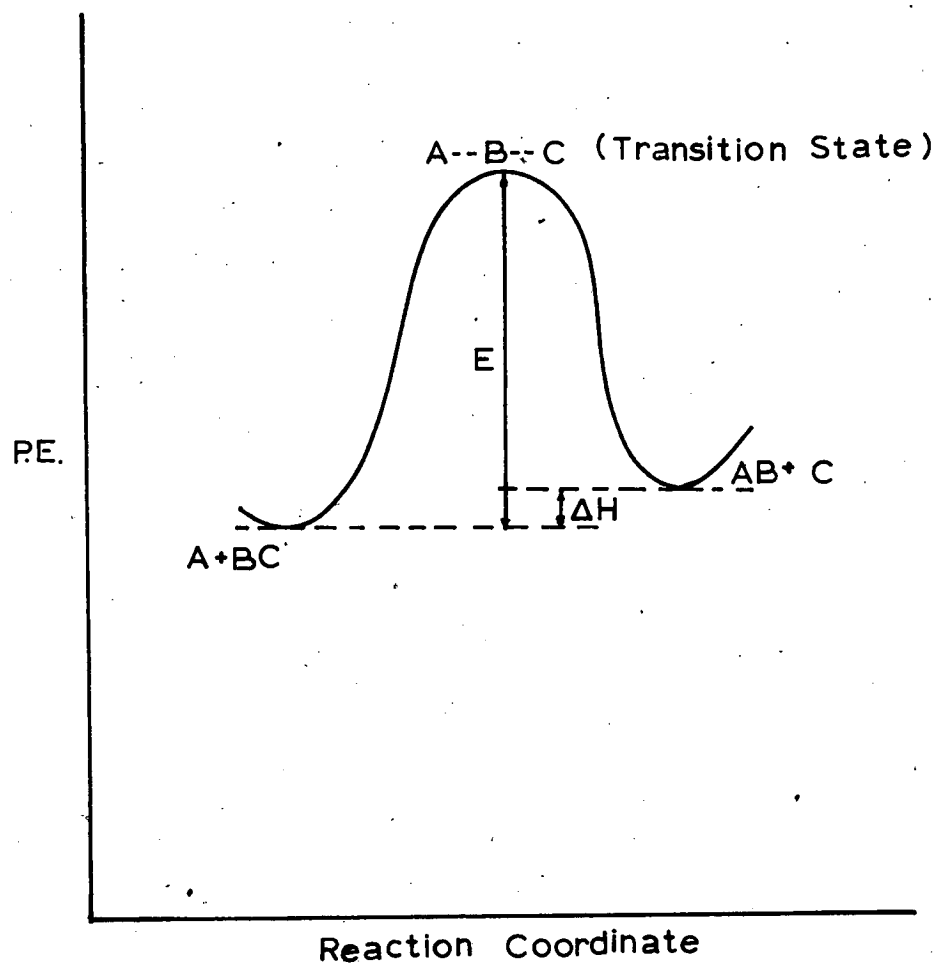
Figure 1

with a positive curvature of potential energy in all degrees of freedom except the one which corresponds to crossing the barrier, for which the curvature is negative. Thus at the saddle point

$$d\varepsilon/dZ \quad = \quad 0 \quad \text{and } \varepsilon \text{ is a maximum where } Z \text{ is measured}$$
$$\text{along the reaction coordinate}$$

and
$$d\varepsilon/dx_i \quad = \quad 0 \quad \text{and } \varepsilon \text{ is a minimum for all other normal}$$
$$\text{coordinates of the molecule, } x_i.$$

A configuration of atoms corresponding to the transition state thus has all the properties of a stable compound except in the normal mode corresponding to decomposition; this mode, because of the small curvature of the potential energy surface at the col, could, according to Eyring, be treated from the point of view of statistical mechanics as a translational degree of freedom.

The detailed mechanism derived from the theory can be represented as

$$A \quad + \quad B \underset{k^+}{\overset{k_1}{\rightleftharpoons}} X^+ \underset{k_2}{\overset{k^+}{\rightleftharpoons}} C + D$$
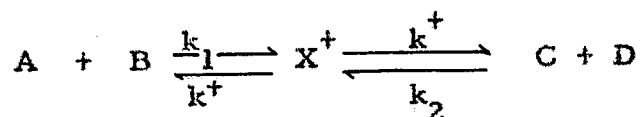
or, concentrating on a small energy range $d\varepsilon$, as

$$A \quad + \quad B \underset{k(\varepsilon)}{\overset{k_1(\varepsilon)d\varepsilon}{\rightleftharpoons}} X^+ \underset{(\varepsilon \text{ to } \varepsilon + d\varepsilon) \quad k_2(\varepsilon))d\varepsilon}{\overset{k^+(\varepsilon)}{\longrightarrow}} C + D$$
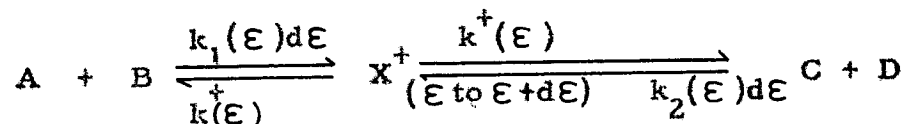
By the principle of microscopic reversibility the rate for decomposition of X^+ to $A + B$ must be the same as for decomposition to $C + D$ and at complete equilibrium

$$\frac{\frac{1}{2}\left[X^+\right]}{[A][B]} \quad = \quad \frac{k_1(\varepsilon)d\varepsilon}{k^+(\varepsilon)} \qquad \qquad \text{Ia. 45}$$

$$\text{and} \qquad \frac{\frac{1}{2} \left[X^+\right]}{[C]\,[D]} \;=\; \frac{k_2(\epsilon)\,d\epsilon}{k^+(\epsilon)} \qquad\qquad \text{Ia,46}$$

Since the motion of X^+ in the reaction coordinate is assumed to be translational, $k^+(\epsilon)$ is the velocity of translation in the reaction coordinate of those complexes with energy ϵ moving in one direction. Since only half the complexes move in any direction the factor $\frac{1}{2}$ is included.

With these assumptions the absolute theory of reaction rates was developed, through which, by being able to calculate the concentration of the transition state complex, $\left[X^+\right]$, and its rate of passage over the energy hump the rate of bimolecular reaction could be calculated.

Thus for molecules or radicals in the transition state, if one supposes that, instead of considering an energy range ϵ to $\epsilon + d\epsilon$, one considers an equivalent velocity range $\dot{x}$ to $\dot{x} + d\dot{x}$ in the reaction coordinate (where $\dot{x} = dx/dt$) and suppose that the concentration of complexes per unit volume per unit length of the reaction coordinate is $C_{\dot{x}}^+ d\dot{x}$ then, under equilibrium conditions

$$C_{\dot{x}}^+ = C_{-\dot{x}}^+ = \tfrac{1}{2} C_{|\dot{x}|}^+ = \tfrac{1}{2} \left[X^+\right] \qquad\qquad \text{Ia47}$$

where $C_{|\dot{x}|}$ is the concentration of the transition state complex per unit range in $\dot{x}$, irrespective of the direction of motion i.e. the equilibrium concentration of complexes, with $\epsilon = \tfrac{1}{2} m \dot{x}^{+2}$, which can be obtained by statistical mechanics. Thus

$$\frac{C_{|\dot{x}|}^+ \, d\dot{x}}{C_A C_B} \;=\; \frac{dq^+}{q_A q_B} \qquad\qquad \text{Ia,48}$$

and therefore $\qquad C_{\dot{x}}^{+} \, d\dot{x} \; = \; \frac{1}{2} \, C_A C_B \, \dfrac{dq^{+}}{q_A q_B}$

where dq^{+} is the partition function for a range $\dot{x}$ to $\dot{x} + d\dot{x}$ in the reaction coordinate irrespective of direction and q_A and q_B are the partition functions of A and B respectively. The partition function dq^{+} can be factorized into two parts: (1) for the reaction coordinate (dq_{rc}^{+}) and (II) for motion of the molecule (q^{+}). Thus

$$d_q^{+} \; = \; dq_{rc}^{+} \times q^{+}$$

where by definition $\qquad dq_{rc}^{+} \; = \; \displaystyle\sum g_i \; e^{-\,\mathcal{E} i(rc)/kT}$

where q_i is the degeneracy of the ith state and the $\mathcal{E} i$'s are the allowed energies in the reaction coordinate.

If an energy range $d\mathcal{E}$ is considered then only one term is required with $\mathcal{E} i = \frac{1}{2} m\dot{x}^2$, and g_i becomes the number of energy levels in the velocity range $\dot{x}$ to $\dot{x} + d\dot{x}$

Using de Broglie's equation

$$p \; = \; h/\lambda$$

and the condition for a stationary wave

$$\lambda = 2b/n$$

where b is the extension of the transition state in the reaction coordinate.
Thus

$$m\dot{x} \; = \; hn/2b$$

and the number of energy levels in the velocity range $\dot{x}$ to $\dot{x}+d\dot{x}$ is

$$dn = (2mb/h)\,d\dot{x} \qquad\qquad \text{Ia, 55}$$

and since we are considering a concentration per unit length of the reaction coordinate $b = 1$ and

$$dq_{rc}^{+} = (2m/h)\,e^{-\,\varepsilon(rc)/kT}\,d\dot{x} \qquad\qquad \text{Ia, 56}$$

Hence

$$C_{\dot{x}}^{+}\,d\dot{x} = \tfrac{1}{2}\frac{dq^{+}}{q_A q_B}\; C_A C_B \qquad\qquad \text{Ia, 57}$$

$$= (m/h)\,e^{-\,\varepsilon(rc)kT}\,d\dot{x}\,C_A C_B\,(q^{+}/q_A q_B) \qquad\qquad \text{Ia, 58}$$

The rate of passage over the energy barrier of molecules in the velocity range $\dot{x}$ to $\dot{x}+d\dot{x}$ is

$$\dot{x}\,C_{\dot{x}}^{+}\,d\dot{x} = \tfrac{1}{2}k^{+}(\varepsilon)\;[x^{+}] \qquad\qquad \text{Ia, 59}$$

and the total rate of passage for all molecules is

$$\text{rate} = k_{bim}\,C_A C_B = \int_0^{\infty}\dot{x}\,C_{\dot{x}}^{+}\,d\dot{x} \qquad\qquad \text{Ia, 60}$$

$$= 1/m\int_0^{\infty}C_{\dot{x}}^{+}\,d\,(m\dot{x}^2/2) \qquad\qquad \text{Ia, 61}$$

$$= 1/m\int_0^{\infty}C_{\dot{x}}^{+}\,d\varepsilon\,(rc) \qquad\qquad \text{Ia, 62}$$

Substituting the expression for C_X^+ from equation Ia,58 in equation Ia,62 gives

$$\text{rate} = k_{bim} C_A C_B = \frac{1}{h} \frac{q^+}{q_A q_B} C_A C_B \int_0^\infty e^{-\mathcal{E}(rc)/kT} d\mathcal{E}(rc) \qquad \text{Ia,63}$$

whence
$$k_{bim} = (kT/h)(q^+/q_A q_B) \qquad \text{Ia,64}$$

$$= (kT/h)(q^{+'}/q_A q_B) e^{-\Delta E_0^+/kT} \qquad \text{Ia,65}$$

Marcus & Rice (23) and Marcus (24) have combined the concepts of Kassel and of Eyring in the theory of unimolecular decomposition and obtained a more precise definition of the distribution of the excess energy of the activated complex and the active molecule. Whereas the Kassel theory had been concerned with the distribution of energy in the active species no account was taken of the energy distribution in the reaction coordinate; Eyring's theory, on the other hand, did not distinguish between the active molecule and activated complex. Thus, in retrospect, it seems obvious that a combination of the two theories should lead to a more comprehensive theory.

Marcus defined three degrees of freedom of the active molecule with respect to their role in intramolecular energy transfer as "active","adiabatic" and "inactive". Active degrees of freedom could contribute their energy to the breaking bond without restriction; adiabatic degrees of freedom were assumed to remain in the same quantum state during the course of decomposition of the molecule and so contribute no energy to the breaking bond, whereas

the transfer of energy between the inactive degrees of freedom and this bond

was assumed to occur with sufficient rapidity only when the molecule had

become essentially the activated complex.

The translation of the molecule as a whole which makes no contribution

to the reaction rate is a typical adiabatic degree of freedom; similarly

owing to restrictions of conservation of total angular momentum the molecule

must remain in the same rotational quantum state throughout the course of

decomposition. However, since unimolecular decomposition can be regarded

as a stretching of a critical bond, rotation of the molecule as a whole can

contribute energy to the breaking bond, since, if the molecule is rotating

with a constant angular velocity about an axis at right angles to the critical

oscillator, elongation of the bond will cause an increase in the moments of

inertia of the separating fragments - in a sense this is an inactive degree of

freedom. Thus the largest contribution of the angular momentum to the

breaking bond possesses the largest moments of inertia and contributes energy

$J(J+1)h_2/8\pi^2 I$ with J approximately constant. When averaged over all J's

the net contribution of these rotation to the reaction rate is a factor P_1^+/P_1

the ratio of the partition functions of these rotations for the activated complex

and active molecule respectively. In the 1951 paper a factor K was included,

rather indefinitely, to account for the contributions of rotation of the molecule

as a whole to the reaction rate.

The remaining energy of the activated complex, E^+, or the active

molecule, E^*, which is available for redistribution is termed the non-fixed

energy and is defined as that energy which the complex or molecule possesses in excess of their respective zero point energies. Since the activated complex contains energy Ea, the bond dissociation energy of the critical bond, localised in that bond then $E^{\ddagger} = E^* - Ea - Ei$ where Ei is the energy in the inactive degrees of freedom.

Both papers started from the premise of the Lindemann scheme as applied to a small energy range (eqns. 1a21 and 1a 22) to obtain an overall unimolecular rate constant which is the integral over all energies of the individual rate constants - which are themselves energy dependent.

Thus

$$k_{nni} = \int_0^\infty \frac{k_3(\epsilon) \dfrac{k_1(\epsilon)d\epsilon}{Z^o}}{1 + k_3(\epsilon)/Z^o[M]}$$

Ia. 22

The term $k_1(\epsilon)d\epsilon/Z^o$ here has the same significance as in the Kassel derivation and is equal to the equilibrium fraction of active molecules having energy in the range E^* to $E^* + dE^*$. If $N^*(E^* - Ei)$ is the number of states per unit energy of the active degrees of freedom and $D(Ei)$ the degeneracy of the inactive ones when their energies are $E^* - Ei$ and Ei, $k_1(\epsilon)d\epsilon/Z^o$ is given by

$$\frac{k_1(\epsilon)d\epsilon}{Z^o} = \frac{\displaystyle\sum_{Ei=o}^{E^*-Ea} N^*(E^*-Ei)\,D(Ei)\,\exp(-E^*/kT)dE^*}{\displaystyle\sum_{Ei=o}^{\infty} D(Ei) \int_{E^*=Ei}^{\infty} N^*(E^*-Ei)\exp(-E^*/kT)dE^*}$$

Ia. 66

Introduction of a new variable $x = E^* - Ei$ into the denominator enables the

latter to be factorized into a product of the partition functions of the active and inactive parts the latter of which is denoted by P_2.

If, as in the 1951 paper, no account is taken of the inactive degrees of freedom, $k_1(\varepsilon)d\varepsilon/Z^*$ becomes

$$\frac{k_1(\varepsilon)d\varepsilon}{Z^0} = \frac{N^*(E^*)\exp(-E^*/kT)dE^*}{f} \qquad \text{Ia 67}$$

where f is the partition function of the active degrees of freedom - in the 1951 paper these were taken to be purely vibrational and f is therefore given by

$$f = \prod_{i=1}^{s} (1-\exp(-h\nu_i/kT))^{-1} \qquad \text{Ia. 68}$$

Calculation of the rate of intramolecular energy transfer was accomplished by applying the principle of microscopic reversibility to the equilibrium

$$\underset{(\varepsilon \to \varepsilon + d\varepsilon)}{A^*} \underset{k^+(\varepsilon)}{\overset{k_3(\varepsilon)}{\rightleftharpoons}} \underset{(\varepsilon \to \varepsilon + d\varepsilon)}{A^+} \overset{k^+(\varepsilon)}{\underset{}{\rightleftharpoons}} \text{products}$$
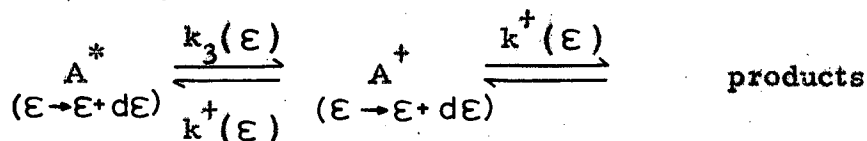
Since, at equilibrium, half the complexes A^* are going in the forward direction and half in the reverse direction

$$[A^*]k_{3(\varepsilon)}d\varepsilon = \tfrac{1}{2}[A^+]k^+_{(\varepsilon)}d\varepsilon \qquad \text{Ia 69}$$

Hence

$$\frac{2k_3(\varepsilon)d\varepsilon}{k^+(\varepsilon)d\varepsilon} = \frac{[A^+]_{(\varepsilon \to \varepsilon + d\varepsilon)}}{[A^*]_{(\varepsilon \to \varepsilon + d\varepsilon)}} \qquad \begin{array}{l}\text{Ia. 70}\\ \\ \text{(cf. equation Ia.43)}\end{array}$$

where $[A^+]$ and $[A^*]$ are the equilibrium concentrations of the activated

complex and active molecule per unit range in total energy $E^{\ddagger}$ and E^* respectively. Comparison of equation 1a70 and equation 1a43 shows the detailed extension of the Kassel theory by Marcus and it is also a useful point to reflect on how each theory grew out of the preceding one. Whereas Hinshelwood's theory assumed that all the active molecules decomposed at the same rate irrespective of energy content or distribution, Kassel extended this idea by assuming a specific energy distribution for decomposition and hence an energy dependence $\upsilon Of n$ the rate of decomposition of the active molecules. However, Kassel's theory stopped short in that it was assumed that the activated complex once formed, decomposed at a constant rate and Marcus's contribution was to apply Eyring's ideas on velocity distribution in the reaction coordinate, to the energy dependence of the rate of decomposition of the activated complex.

Since $A^{\ddagger}$ and A^* have the same total energy the concentration ratio $[A^{\ddagger}]/[A^*]$ is the number of quantum states accessible to the two forms of A.

Hence
$$\frac{[A^{\ddagger}]}{[A^*]} = \frac{N^{\ddagger}(E^{\ddagger})}{N^*(E^*)} \qquad \text{1a 71}$$

where $N^{\ddagger}(E^{\ddagger})$ is the number of quantum states of the activated complex per unit range of the non-fixed energy E^+ and $N^*(E^*)$ is the number of quantum states of the active molecule per unit range of the non-fixed energy E^*.

One of the degrees of freedom of $A^{\ddagger}$ according to transition state theory is a simple translation in the reaction co-ordinate. If $N_1(y)$ and $N_2(E^+ - y)$

denote the number of quantum states per unit energy of this translational

motion and in the remaining degrees of freedom A^+ when their energies are

y and E^+ - y respectively, then the number of energy states for a range ,

dE^+, of total energy and dy in the reaction coordinate is

$$N_2(E^+ - y) \; N_{(y)} \; dE^+ dy \qquad\qquad \text{1a 72}$$

and the number of quantum states per unit energy of the activated complex

which contains non-fixed energy E^+ is

$$N^+(E^+) \;=\; \int_{y=o}^{E^+} N_2(E^+ - y) \; N_1 y dy \qquad\qquad \text{Ia. 73}$$

Since $k^*_{(\varepsilon)}$ corresponds to the velocity of the activated complex along the

reaction coordinate when the translational energy is y it is possible to

replace $k^+(\varepsilon)$ by $(2y/m)^{\frac{1}{2}}.(1/b)$ where $(2y/m)^{\frac{1}{2}}$ is the

speed of passage of the activated complexes over the energy barrier (half

in each direction), m is the reduced mass of the complex and b is the

extension of the reaction coordinate.

From the usual expression for the energy levels of a particle in a box

$$y = \frac{n^2 h^2}{8mb^2} \qquad\qquad \text{1a 74}$$

and since the number of energy levels per unit energy range of the

translational motion $N1(y)$ is

$$N1(y) = \frac{dn}{dy} \qquad\qquad \text{1a 75}$$

then $\qquad\qquad N1(y) = \frac{b}{h} \left(\frac{2m}{y}\right)^{\frac{1}{2}} \qquad\qquad \text{1a 76}$

Equation 1a76 is analogous to the expression 1a 55 in the derivation of the

absolute theory of reaction rates in which the number of quantum states in the velocity range $\dot{x}$ to $\dot{x} + d\dot{x}$ is related to the reduced mass of the complex and the extension of the reaction coordinate.

Substituting $N_i(y)$ and $k^+(\epsilon)$ in equations la 70, la 71 and la 73 one obtains

$$N^*(E^*)k_3(\epsilon) = \int_{y=o}^{E^+} \tfrac{1}{2}(2y/m)^{\frac{1}{2}} 1/h \, (2m/y)^{\frac{1}{2}} N_2(E^+-y)dy$$

Ia. 77

Introducing a new variable $x = (E^+ - y)$ into la 77 and correcting by the factor P_1^+/P_1, $k_3(\epsilon)$ becomes

$$k_3(\epsilon) = \frac{P_1^+}{hP_1} \frac{\displaystyle\int_{x=o}^{E^+} N_2(x)dx}{\displaystyle\sum_{Ei=o}^{E^*-Ea} N^*(E^*-Ei)D(Ei)}$$

Ia. 78

where $\displaystyle\sum N^*(E^* - Ei)D(Ei)$ is the total number of quantum states per unit energy and available to the active molecules whose non-fixed energy is E*.

Again, if as in the 1951 paper, the inactive degrees of freedom are ignored and the remaining degrees of freedom are considered to be solely vibrational, $N_2(E^+ - y)$ becomes $P(Ev)$, the degeneracy of the vibrational modes. Substituting K for P_1^+/P_1 equation la 78 becomes

$$k_3(\epsilon) = \frac{K}{h \, N^*(E^*)} \times \sum_{E^+ \leq Ev} P(Ev)$$

Ia. 79

The beauty of the second paper lies in its generalisation to any decomposing molecule.

From equations 1a 22, 1a 66 and 1a 78

$$k_{uni} = \frac{P_1^+ \exp(-E_a/kT)}{P_1 P_2 h} \int_{E^+=o}^{\infty} \int_{x=o}^{E^+} \frac{N_2(x)dx \exp(-E^+/kT)dE^+}{1 + ka/Z^oM}$$

Ia. 80

To complete the derivation of k_{uni} it is necessary to obtain an expression for $N_2(x)$, the number of quantum states per unit energy of the degrees of freedom of A^+ (not involved in P_1^+ and excluding the translational motion along the reaction co-ordinate). These degrees of freedom are vibrations and internal rotations. It is assumed that the rotations can be treated as independent of each other and of those rotations involved in P_1^+ so that their energy is approximately equal to

$$\sum_{i=1}^{p} \frac{J_i^2 h^2}{8 \pi^2 I_i}$$

1a 81

where p is the number of rotations while J_i and I_i are the quantum number and the moment of inertia respectively of the ith rotational degree of freedom. The degeneracy of the J_i'th quantum state is 2 or $2J_i$ according as it is on one or two dimensional rotation. This number is written as $2(J_i)^{d_i - 1}$ where d_i is the degeneracy of the ith rotation.

The energy x is divided amongst its component degrees of freedom for which

the vibrational energy is Ev, the degeneracy of the vibrational states being

P(Ev). The number of rotational states per unit energy is equal to

$$(dx)^{-1} \int \cdots \iint_{\substack{\sum_i^p J_i^2 h^2/8\pi^2 I_i = x-Ev}}^{x+dx-Ev} \prod_i 2(J_i)^{d_i-1} dJ_i \qquad \text{1a 82}$$

and the number of rotational vibrational quantum states per unit energy is

$$N_2(x) = \sum_{Ev \leq E^+} \left\{ P_{(Ev)}(dx)^{-1} \int \cdots \iint \prod_i (2(J_i)^{d_i-1} dJ_i) \right\} \qquad \text{1a 83}$$

Putting $Z_i = J_i^2$, whence $dZ_i = 2J_i dJ_i$

$$N_2(x) = \sum_{Ev \leq E^+} \left\{ P_{(Ev)}(dx)^{-1} \int \cdots \iint_{\substack{\sum_i^p Z_i/I_i = (8\pi^2/h^2)(x-Ev)}}^{x+dx-Ev} \prod_i (Z_i)^{(d_i/2)-1} dZ_i \right\}$$

$$N_2(x) = \sum_{Ev \leq E^+} \left\{ P_{(Ev)}(dx)^{-1} \int \cdots \iint_{\substack{\sum_i^p Z_i/I_i = (8\pi^2/h^2)(x-Ev)}}^{x+dx-Ev} \prod_i I_i^{d_i/2} \left(\frac{Z_i}{I_i}\right)^{d_i/2} \frac{dZ_i}{I_i} \right\} \qquad \text{1a 84}$$

This multiple integral is a particular case of the Dirichlet integral (25).
Insertion of the appropriate solution gives

$$N_2(x) = \sum_{Ev \leq E^+} \left\{ \frac{P_{(Ev)}(dx)^{-1} \prod i(Ii \; \Gamma(di/2)) (8\pi^2/h^2)(x-Ev)^{r/2-1} dx}{\Gamma(\sum_i^p di/2)} \right\}$$

la 85

$$N_2(x) = \sum_{Ev \leq E^+} \left\{ \frac{P_{(Ev)}}{\Gamma(r/2)} (8\pi^2/h^2)^{r/2-1} (x-Ev)^{r/2-1} \prod i \left[Ii^{di/2} \Gamma(di/2) \right] \right\}$$

la 86

Since the partition functions for p internal rotations making in all

$$\sum_i^p di = r$$

degrees of freedom with individual moments of inertia Ii

is given by

$$P_r^+ = \left(\frac{8\pi^2 kT}{h^2} \right)^{r/2} \times \left\{ \prod i (Ii^{di/2} \; \Gamma(di/2)) \right\}$$

la 87

equation la 86 may be more simply expressed as

$$N_2(x) = \sum_{Ev \leq E^+} \frac{P_{(Ev)}}{\Gamma(r/2)} \left(\frac{x-Ev}{kT} \right)^{r/2-1} \frac{Pr^+}{kT}$$

la 88

Substitution of the expression for $N_2(x)$ given by equation la 88 into
the equation for $k_3(\epsilon)$ (equation la 78) gives

$$k_3(\epsilon) = \frac{P_1^+ P_r^+}{hP_1 \sum\limits_{Ei=o}^{E^*-Ea} N^*(E^*-Ei)D(Ei)} \times \int\limits_{x=o}^{E^+} \sum\limits_{Ev \leq E^+} \frac{P_{(Ev)}}{\Gamma(r/2)} \left(\frac{x-Ev}{kT}\right)^{r/2-1} \frac{dx}{kT}$$

<div align="right">Ia 89</div>

The integration is achieved by reversing the order of summation and integration such that

$$k_3(\epsilon) = \frac{P_1^+ P_r^+}{hP_1 \Gamma(r/2) \sum\limits_{Ei=o}^{E^*-Ea} N^*(E^*-Ei)D(Ei)} \times \sum\limits_{Ev \leq E^+} P_{(Ev)} \int\limits_{Ev}^{E^+} \left(\frac{x-Ev}{kT}\right)^{r/2-1} \frac{dx}{kT}$$

<div align="right">Ia 90</div>

$$= \frac{P_1^+ P_r^+}{hP_1 \Gamma(r/2+1) \sum\limits_{Ei \leq E^+} N^*(E^*-Ei)D(Ei)} \times \sum\limits_{Ev \leq E^+} P_{(Ev)} \left(\frac{E^+-Ev}{kT}\right)^{r/2}$$

<div align="right">Ia. 91</div>

$$= \frac{P_1^+ P_r^+ \sum\limits_{Ev \leq E^+} P_{(Ev)} \left(\frac{E^+-Ev}{kT}\right)^{r/2}}{hP_1 \Gamma(r/2+1) \sum\limits_{Ei \leq E^+} N^*(E^*-Ei)D(Ei)}$$

<div align="right">Ia 92</div>

Generally a precise statement about the amount of energy Ei, in the inactive modes is not possible, and for simplicity Ei is taken as zero.

To complete the derivation an expression for $N^*(Ea + E^+)$ is required. Marcus and Rice (23) showed that a good approximation to the average number of vibrational quantum states per unit energy is given by the following semiclassical expression

$$N_v^*(Ea + E^+) = \frac{(E^* + Eo)^{s-1}}{\Gamma(s) \prod\limits_{i=1}^{s}(h\nu_i)}$$

Ia 93

where Eo, the zero point energies of the active molecules is defined as

$$Eo = \sum_{i=1}^{s} h\nu_i / 2$$

Ia. 94

ν_i is the ith vibrational frequency and s is the number of active vibrational modes.

$N_r^*(z)$, the total number of quantum states per unit energy of the rotational degrees of freedom (other than those involved in F_i) of the active molecule when their energy is x, is given by an expression exactly analagous to that derived for $N_2(x)$.

Therefore

$$N_r^*(z) = \frac{P_a}{\Gamma(t/2)} \left(\frac{z}{kT}\right)^{t/2-1} \frac{1}{kT}$$

Ia 95

where P_a is the product of the partition functions for the t active rotations of the active molecule.

Therefore the total number of vibrational rotational quantum states of the active molecule per unit range of E* is

$$N^*(Ea + E^+) = \int_{z=o}^{Ea + E^+} N_v^*(Ea + E^+ - z) N_r^*(z)dz$$

Ia 96

$$N^*(E_a + E^+) = \frac{P_a}{kT\,\Gamma(s)\,\Gamma(t/2)\,\prod\limits_{i=1}^{s}(h\nu_i)} \int\limits_{z=0}^{E_a+E^+} (E_a+E^+ +E_0-z)^{s-1}\left(\frac{z}{kT}\right)^{t/2-1} dz$$

<div align="right">Ia, 97</div>

and therefore the final expression for $k_3(\epsilon)$, assuming that $E_i = 0$,

becomes

$$k_3(\epsilon) = \frac{kT}{h}\,\frac{P_1^+\,P_r^+}{P_1\,P_a}\,\frac{\Gamma(s)\,\Gamma(t/2)}{\Gamma(r/2+1)}\,\prod_i(h\nu_i)\,\frac{\sum\limits_{E_v\leq E^+}P(E_v)\left[\frac{E^+-E_v}{kT}\right]^{r/2}}{\int\limits_{z=0}^{E^*}(E^*+E_0-z)^{s-1}(z/kT)^{t/2-1}dz}$$

<div align="right">Ia, 98</div>

This is the generalized form of the Marcus expression for $k_3(\epsilon)$ which was

used by Knox (26) for the calculation of the rate of unimolecular decomposition

of the chemically activated trichlorethyl radical and which will be the basis of

calculations of the rate of unimolecular decomposition of the active tetra-

chloroethyl radical, given in this thesis.

(b) Experimental Review

No matter how self consistent the logic nor how elegant the development

of a theory, pursuit of theory alone would soon abstract thought out of all

physical meaning. Only by recourse to experiment can one obtain verification

of theoretical concepts. It is, therefore, necessary to establish the validity of

the experimental technique.

The experimental technique employed in this work was to chlorinate an

olefin in competition with a saturated hydrocarbon, the reference reaction

being the abstraction of the primary H atom in propane whose specific rate

constant is known.

The generally accepted mechanism for chain propagation in the chlorination

of a hydrocarbon is

<u>Scheme I</u>

Initiation

$$Cl_2 + M \quad = \quad 2Cl + M \qquad\qquad\qquad \text{Thermal (1)}$$

$$Cl_2 + h\nu \quad = \quad 2Cl \qquad\qquad\qquad\qquad \text{Photochemical(1)}$$

Propagation

$$Cl + RH = HCl + R \quad (2') \qquad A + Cl = ACl \qquad\qquad (2)$$

$$R + Cl_2 = RCl + Cl \quad (3') \qquad ACl + Cl_2 = ACl_2 + Cl \qquad (3)$$

Inhibition

$$R + HCl = RH + Cl \quad (4') \qquad ACl \quad\quad = A + Cl \qquad\qquad (4)$$

$$Cl + RCl = R + Cl_2 \quad (5') \qquad ACl_2 + Cl = ACl + Cl_2 \qquad (5)$$

Termination $\qquad\qquad Cl + Cl + M = Cl_2 + M \qquad\qquad\qquad (6)$

$$Cl + R \quad = \quad RCl \; (\text{or } A + HCl) \; (7') \; ACl + Cl = ACl_2(\text{or } A+Cl_2) \; (7)$$

$$R + R \quad = \quad R_2 \; (\text{or } RH + A) \quad (8') \; ACl + ACl = ClAACl$$
$$(\text{or } A+ACl_2) \qquad (8)$$

Molecular

$$RH + Cl_2 = RCl + HCl \;(9') \qquad A + Cl_2 = ACl_2 \qquad\qquad (9)$$

$$RCl + HCl = RH + Cl_2 \quad (10')$$
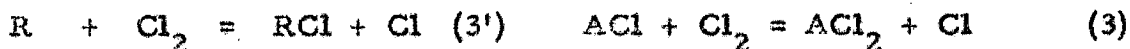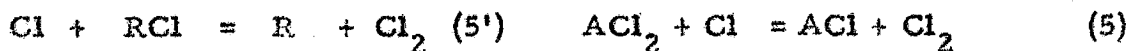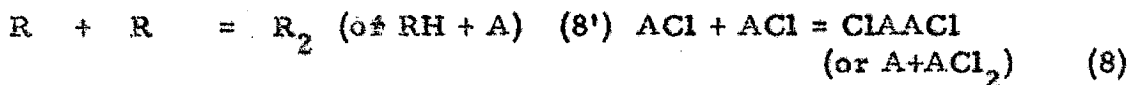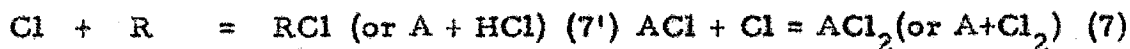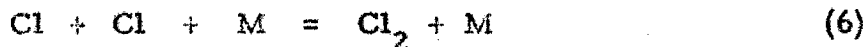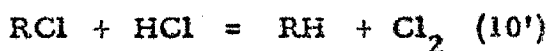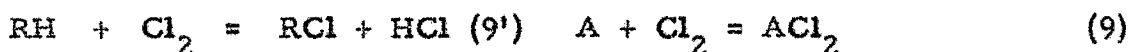
where A denotes an olefin and RH a hydrocarbon

The chief difficulty in determining the absolute rate constants or even the

activation energies of these reactions lies in the extraordinary length of the chains

and the consequent extreme sensitivity of the reaction rates to traces of inhibition. The overriding difficulty can, however, be overcome by the use of the competitive method if one is temporarily willing to sacrifice the determination of absolute rate constants. These can be found later if the absolute rate constant is known for one of the competing reactions. The accuracy of the results obtained in a competitive experiment is unaffected by the nature of the chain initiation or chain termination steps provided that the chains are not too short. Since the results always give the ratios of the rate constants, they should, in principle, enable highly accurate values to be obtained for activation energy differences and A factor ratios, since, when differences in reactivity are small, experiments can be carried out over a wide temperature range. The same proportional accuracy should be obtained whatever the actual magnitude of the activation energy differences.

When hydrogen and an olefin A, are chlorinated simultaneously, the rates of the two reactions removing the two substances are

$$- R_{HH} = k_2'[H_2][Cl] \quad \text{and} \quad -R_A = k_2[A][Cl] \qquad \text{I. b. 1}$$

and the relative rates are

$$\frac{R_A}{R_{HH}} = \frac{-d[A]/dt}{-d[H_2]/dt} = \frac{k_2[A]}{k_2'[H_2]} \qquad \text{I. b. 2}$$

giving on integration

$$\frac{k_2}{k_2'} = \frac{\ln ([A]_i/[A]_f)}{\ln ([H_2]_i/[H_2]_f)} = R \qquad \text{I. b. 3}$$

where $[A]_i$ and $[A]_f$ are the initial and final olefin concentrations.

Thus

$$\frac{k_2}{k_2'} = \frac{\ln \left(([A]_f + \Delta[A])/[A]_f\right)}{\ln \left(([H]_f + \Delta[H_2])/[H_2]_f\right)} \qquad (\Delta[A] = [A]_i - [A]_f)$$

I. b. 4

$$= \frac{\ln \left(1 + \Delta[A]/[A]_f\right)}{\ln \left(1 + \Delta[H_2]/[H_2]_f\right)}$$

I. b. 5

If the amount of reaction is assumed to be small, then the approximation

$$\ln (1+x) \approx x, \quad (x \longrightarrow 0)$$

I. b. 6

may be used giving

$$\frac{k_2}{k_2'} = \frac{\Delta[A][H_2]}{\Delta[H_2][A]}$$

I. b. 7

where $\Delta[A]$ is the change in olefin concentration and $[A]$ is taken as the initial olefin concentration. Therefore one does not require to know the concentration of free radicals.

The competitive technique was used by Pyke, Pritchard and Trotman-Dickenson (27) who measured by difference the quantities of various hydrocarbons consumed in competitive chlorinations. Mixtures of hydrocarbons were sealed up in small bulbs brought up to reaction temperature and then

illuminated. Analysis was carried out for the hydrocarbon content of the products using a controlled temperature still. The accuracy of their results was limited by the difficulty of measuring the relatively small changes in hydrocarbon concentrations. Their method also suffered from the serious disadvantage that it was impossible by measurement of the disappearance of the hydrocarbons alone to determine the relative rates of attack of Cl atoms at different positions in the same molecule. This could only have been achieved by analysis for the products characteristic of the initial point of attack. With the application of gas chromatography by Knox (28), by Anson, Fredricks and Tedder (29) (30) and by Knox and Nelson (31) it became possible to obtain accurate relative rates by analysing the reaction products. This method is particularly useful when the two competitors differ greatly in reactivity and also enables relative rates of attack of chlorine atoms at different points in the same molecule to be determined.

Hydrogen is, however, not always a convenient substance to use as a competitor with an olefin mainly because of its relative unreactivity and it is for this reason that propane was used as the competitive standard in this work. Thus replacing a hydrocarbon, RH, for hydrogen in equation I.b.7 one obtains,

$$\frac{k_2}{k_2{}'} = \frac{\Delta[A]\ [RH]}{\Delta[RH]\ [A]} \qquad\qquad \text{I.b.8}$$

and, provided the chains are long

$$\frac{k_2}{k_2{}'} = \frac{[ACl_2]\ [RH]}{[RCl]\ [A]} = R\frac{ACl_2}{RCl} \qquad \text{I.b.9}$$

where $[ACl_2]$ and $[RCl]$ are the concentrations of the chlorinated products. The independence on reactant pressure of this ratio at a given temperature (provided the ration $[RH]/[A]$ remains constant) should be a delicate test of the reaction mechanism, Scheme I. Equation I. b. 9 is the basis of the product method of calculation of relative fractional rates of chlorination in competitive systems. Comparison of the results of Knox and Nelson, of Pritchard, Pyke and Trotman-Dickenson, and of Anson Fredricks and Tedder show excellent agreement where they overlap and provide good evidence that the product method is reliable for hydrocarbons (See table I. b. I).

TABLE I. b. I   ABSOLUTE ARRHENIUS PARAMETERS FOR CHLORINATIONS

Standard Reaction: $Cl + H_2 = HCl + H$: $A = (4.1 \pm 0.3).10^{10}$ mole.$^{-1}$l. sec.$^{-1}$ $E = 5480 \pm 140$ cal. mole^{-1}

Secondary Standard: $Cl + CH_4 = CH_3 + HCl$: $A = (0.6 \pm 0.3) 10^{10}$ mole.$^{-1}$l. sec.$^{-1}$ $E = 3830 \pm 250$ cal. mole^{-1}

Compound	Competitors	10^{-10} A mole.$^{-1}$l.sec^{-1} per H Atom	E cal. mole^{-1}	Ref
H_2	Standard	4.1	5480	see text
CH_4	H_2	0.6 ± 0.2	3830 ± 180	27, 31
Primary C-H bonds				
CH_4	Secondary standard	0.6	3830	31, 27
C_2H_6	CH_4	1.5 ± 0.3	1020 ± 130	27, 28
C_3H_8	C_2H_6, CH_4	1.7 ± 0.3	980 ± 130	31
Secondary C-H bonds				
C_3H_8	C_2H_6, CH_4	3.6 ± 0.7	660 ± 130	31
nC_4H_{10}	C_2H_6,CH_4; pri C_4H_{10}*	2.4 ± 0.5	300 ± 140	29, 31
cyclo C_5H_{10}	C_2H_6, CH_4	2.3 ± 0.6	600 ± 200	27, 32
Tertiary C-H bond				
iso C_4H_{10}	C_2H_6, CH_4; pri-iso C_4H_{10}	2.1 ± 0.5	100 ± 160	29, 31
Chlorinated hydrocarbons				
CH_3Cl	$CHCl_3$, CH_4; C_3H_8	1.1 ± 0.3	3280 ± 200	27, 32
C_2H_5Cl	C_2H_6, CH_4	0.7 ± 0.25	1500 ± 250	27, 31
C_2HCl_5	C_2Cl_4, chloromethanes	0.5 ± 0.15	3400 ± 200	32, 46

* Commas are placed between competitors in a series, semicolons between different series of competitors.

Since the rate of chlorination of hydrogen is the competitor against which the parameters of methane chlorination were deterimined and therefore is indirectly responsible for the derivation of the parameters for propane, the validity of the absolute determination of the rate constant of the hydrogen molecule/chlorine atom reaction must be considered.

The chlorine atom/hydrogen molecule reaction has been the subject of three highly elegant, independent investigations, the results of which, when combined, lie on the same Arrhenius plot. (40). The earliest investigation was carried out by Rodebush and Klingelhoeffer (33) who generated chlorine atoms up to a maximum chlorine pressure of 1 mm. A stream of hydrogen was then added to the chlorine atom chlorine molecule mixture and passed at about room temperature through a 10 ml. reaction vessel which terminated in a silver gauze catalyst.

The chlorine atom pressure was measured directly by a Wrede gauge (34) the principle feature of which is a hole, small compared with the mean free path, in the wall of the reaction vessel containing the partly atomized gas. Behind the hole is an enclosed space containing a silver catalyst for combining the atoms to molecules. Atoms and molecules enter this space through the hole but because of the catalyst only molecules leave. If the hole is sufficiently small compared with the mean free path, the atoms and molecules pass through the hole purely by effusion. Atoms transport mass less efficiently than molecules by a factor of $1/\sqrt{2}$ (if the molecules are diatomic) because, though moving with an average velocity $\sqrt{2}$ times the molecular velocity, they are only

half the mass. Consequently a pressure difference develops across the orifice and if α is defined as the fraction of gas outside the orifice which is atomic, and the pressures outside and inside the orifice are p and p^i, then for a mass balance

$$\frac{\alpha p}{\sqrt{2}} + (1-\alpha)p = p'$$

I. b. 10

or

$$\alpha = \frac{3.41 \Delta p}{p} \quad \text{where } \Delta p = p-p'$$

I. b. 11

By measuring p and Δp Rodebush and Klingelhoeffer determined the chlorine atom concentration directly. Together with measurements of flow rate and of hydrogen chloride formed they could calculate the absolute rate constant for

$$Cl + H_2 = HCl + H.$$

Rodebush and Klingelhoeffer claim that the error in determining the degree of dissociation to be 5% the error in the flow rates to be about 2% and the titration errors to be about 5%, claiming a total error for all measurements of about 10%. This claim is probably optimistic. A reaction probability of 1.4×10^{-5} per collision at $0^\circ C$ and 3.3×10^{-5} at $25^\circ C$ was obtained and an activation energy of 6.1 ± 1 k. cal mole^{-1} was estimated.

In a particularly elegant experiment Steiner and Rideal (35) were able to obtain the rate constant for the reaction $Cl + H_2 = HCl + H$ in the temperature range $901^\circ K$ to $1071^\circ K$ by making use of the ortho-para hydrogen conversion. The elegance of the thinking behind this experiment lies in the fact that an apparently unrelated property was used to calculate the rate constant.

Normal hydrogen is a 3:1 mixture of ortho to para hydrogen at ordinary

temperatures due to the threefold degeneracy of the symmetrical nuclear spin wave function of ortho hydrogen. However, since the overall wave function must be anti-symmetric and since in its ground state the electronic and translational wave functions are symmetrical, the ortho hydrogen wave function is a linear combination of the symmetrical nuclear spin function and the anti-symmetrical rotational wave function for which the J states are 1, 3, 5 -- etc. Thus at low temperatures where the difference in energy between the rotational energy levels of hydrogen is large compared with kT, para hydrogen predominates since its rotational quantum levels are 0, 2, 4 --etc.

Steiner and Rideal therefore enriched normal hydrogen with para hydrogen by absorption of normal hydrogen on charcoal at - 194°C and pumping off the evaporating gas. Since the interconversion of the two forms is not thermally activated to any appreciable extent until temperatures high enough to cause dissociation and recombination are reached, Steiner and Rideal worked above 600°C where they assumed that the atomic reaction prevailed. By observing the rate of HCl catalysed conversion of para to ortho hydrogen by following the change in thermal conductivity of the gas mixture (the two forms of hydrogen differ appreciably in thermal conductivity) Steiner and Rideal were able to calculate the rate of reaction k_4 in

$$\text{H} + \text{HCl} \underset{k_2}{\overset{k_4}{\rightleftharpoons}} \text{H}_2 + \text{Cl}$$
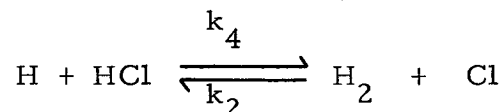
At temperatures above 600°C homogeneous ortho para hydrogen conversion occurs by the following reactions (36)

$$\text{H} + \text{H}_2\text{p} \rightarrow \text{H}_{20} + \text{H} \quad k_1'$$

$$\text{H} + \text{H}_{20} \rightarrow \text{H}_{2\text{p}} + \text{H} \quad k_1''$$
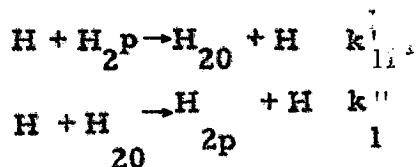
which in the presence of HCl competes with the following reactions,

$$H + HCl \longrightarrow H_{2o} + Cl \ k_4'$$

$$H + HCl \longrightarrow H_{2p} + Cl \ k_4''$$

$$\left.\begin{array}{l} Cl + H_{2o} \longrightarrow HCl + H \\ Cl + H_{2p} \longrightarrow HCl + H \end{array}\right\} \ k_2$$
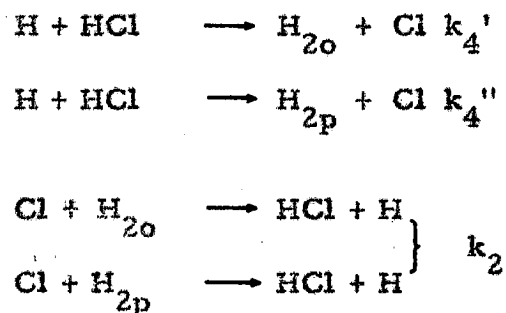
leading to the expression for the rate of conversåtion

$$\frac{d[H_{2o}]}{dt} = \frac{d[H_{2p}]}{dt} = k_1'[H][H_{2p}] + k_4'[H][HCl] - k_1''[H][H_{2o}] - k_2[Cl][H_{2o}]$$

$$= k_1'[H][H_{2p}] + k_2[Cl][H_{2p}] - k_1''[H][H_{2o}] - k_4''[H][HCl]$$

I. b. 12

On cancellation of equal terms one obtains

$$k_4'[H][HCl] - k_2[Cl][H_{2o}] = k_2[Cl][H_{2p}] - k_4''[H][HCl] \qquad \text{I. b. 13}$$

Using the equilibrium condition

$$\frac{[H_{2p}]}{[H_{2o}]} = \frac{1}{3} = \frac{k_1''}{k_1'} \qquad \text{I. b. 14}$$

and introducing

$$k_1 = k_1' + k_1'' \qquad \text{I. b. 15}$$

where k_1 gives all the interchanges between hydrogen atoms and molecules

one obtains

$$k_1' = \frac{3}{4} k_1 \qquad \text{I. b. 16}$$

$$k_1'' = \frac{1}{4} k_1 \qquad \text{I. b. 17}$$

Further, since at equilibrium, the condition I.b.14 holds and each side of equation I.b.13 may be equated to zero, then

$$\frac{k_2[Cl][H_{2p}]}{k_2[Cl][H_{2o}]} = \frac{k_4''[H][HCl]}{k_4'[H][HCl]}$$

I.b.18

and therefore $\quad \frac{k_4'}{k_4''} = 3$

I.b.19

Introducing $k_4 = k_4' + k_4''$, k_4 now representing all the interactions of hydrogen atoms and hydrogen chloride one obtains

$$k_4' = \tfrac{3}{4} k_4$$

I.b.20

and $\quad k_4'' = \tfrac{1}{4} k_4$

I.b.21

The concentration of hydrogen and chlorine atoms is given by the equilibrium

$$\bar{K}_1 = [H]^2 / [H_2]$$

I.b.22

$$\bar{K}_2 = \frac{[H][Cl]}{[HCl]}$$

I.b.23

which together with I.b.13 gives

$$k_3 = k_4 \frac{\bar{K}_1}{\bar{K}_2}$$

I.b.24

Introducing (I.b.16, 17), (I.b.20, 21), (I.b.22,23) and I.b. 24 into I.b.12 one obtains finally

$$\frac{d H_{2o}}{dt} = \sqrt{\bar{K}_1}\sqrt{[H_2]} \, (x-\tfrac{1}{4}) \, (k_1[H_2] + k_4[HCl])$$

I.b.25

where x is the para hydrogen content of the gas.

Integration of I. b. 25 gives

$$\log_{10} \frac{(x_o - \frac{1}{4})}{(x_t - \frac{1}{4})} = \sqrt{\overline{K}}_1 \; \frac{1}{2.303} \; \sqrt{[H_2]} \; (k_1 + k_4 \frac{[HCl]}{[H_2]}) \cdot t$$

<div align="right">I. b. 26</div>

which is the exponential law, previously determined experimentally to be

$$\log_{10} \frac{(x_o - \frac{1}{4})}{(x_t - \frac{1}{4})} = \frac{A}{2.303} \; t\sqrt{[H_2]}$$

<div align="right">I. b. 27</div>

The constant A therefore equals $\sqrt{\overline{K}}_1 \, (k_1 + k_4 [HCl] / [H_2])$ and was found to be a linear function of the ratio $[HCl] / [H_2]$

From the slope and intercept of graphs of A against $[HCl] / [H_2]$, $\sqrt{\overline{K}}_1$, k_4 and $\sqrt{\overline{K}}_1 \, k_1$ were determined and hence k_4 was obtained. In some experiments the reaction vessel was packed increasing the surface to volume ratio by a factor of 10 but the results obtained coincided with those for the un‑packed vessel. Steiner and Rideal concluded that the reaction was homogeneous.

The equilibrium constant k_4/k_2 was calculated from known thermodynamic data and so having found k_4 experimentally k_2 was obtained. The results obtained by Steiner and Rideal and the values recalculated by Fettis & Knox (37) are given in table I. b. II

Table I. b. II

Temperature $^{\circ}K$	$k_2 \, mole^{-1} \, 1 \, sec^{-1}$	Ref.
901	3.1×10^9	(35)
960	3.9×10^9	(35)
1013	4.5×10^9	(35)
1071	5.9×10^9	(35)
523	4.8×10^8	(40)
298	8.2×10^6	(33)
273	3.3×10^6	(33)
901	3.6×10^9	(37)
960	4.6×10^9	(37)
1013	5.2×10^9	(37)
1071	7.0×10^9	(37)

However, there remains one flaw in the Steiner, Rideal argument and that is in their insistence on the homogeniety of the hydrogen atom generation by the reaction

$$H_2 + M \underset{k_t}{\overset{k_i}{\rightleftharpoons}} 2H + M$$
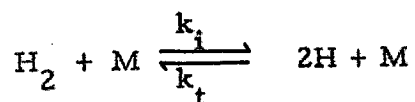
I. b. 28

Benson and Buss (38) have called to question the factors affecting the approach to a stationary state concentration of atoms which they suggest is not achieved instantaneously, but for which the time may be calculated from the kinetic mechanism if the individual rate constants for initiation k_i and termination k_t are known. For a homogeneous chain reaction Benson has

calculated the time, t_a , required to reach any fraction, a, of the stationary state concentration of H atoms to be

$$t_a \text{ (thermal)} = \frac{1}{4 [M] k_t K_{eq}^{\frac{1}{2}} [H_2]^{\frac{1}{2}}} \ln \frac{1+a}{1-a}$$

I. b. 29

where K_{eq} = ki/kt. In addition, with the aid of some simplifying assumptions Benson and Buss (38) have also calculated the "threshold temperatures" i.e. temperatures at which 90% of the stationary concentration of radicals will have been reached within a given time, t_a, with the startling results shown in table I. b. III.

Table I. b. III

Species = H_2	Time (sec)	Threshold Temperature
	0.1	2330
	1.0	1860
	10.0	1560
	100.0	1340

In all these calculations M = 1 atm H_2 = 2 mm. Hg and k_t = 3 x 10^{10} litres^2/ mole^2-sec.

Thus it seems obvious that, in the system studied by Steiner and Rideal, for the stationary state approximation to be valid, the hydrogen atom concentration must first have been achieved by a heterogeneous process, which, however, would not affect their equilibrium assumption for the hydrogen atom concentration.

Finally, Ashmore and Chanmugam (40) obtained a value of k_2 for hydrogen

at an intermediate temperature. The slow chlorination of hydrogen was carried out in the presence of small amounts of NO and NOCl. The had found that NOCl alone in the presence of chlorine and hydrogen brought about a short induction period of about 20 seconds during which no HCl was formed, and concluded that, since the atomic reaction showed no induction period any possible molecular reaction between hydrogen and chlorine had a rate which was negligible compared with that of the chain process. Further, since inert gases produced no effect on the rate of production of HCl, Ashmore and Chanmugam were able to state that termination by the removal of centres by combination of atoms whether by Cl + Cl + M or H + H + M or Cl + H + M was unlikely. The main terminating reaction was thought to be k_{11}

$$NOCl \ + \ Cl \ \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} \ NO + Cl_2$$
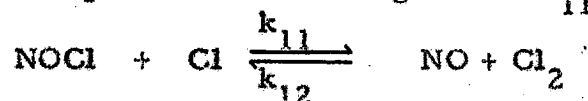
whilst the initiation step in the chlorination in the presence of NO and NOCl was thought to be the fast reaction k_{12} - k_{12} is fast in comparison to the $Cl + H_2$ reaction at the temperatures studied by Ashmore and Chanmugam.

Thus knowing the equilibrium constant k_{11}/k_{12} (41) and hence the chlorine atom concentration and by measuring the amounts of HCl formed as a function of time, Ashmore and Chanmugam calculated k_2 ($Cl + H_2$) to be 4. 8 x 10^6 $mole^{-1}$ 1 sec^{-1} at $523^{\circ}K$. Combining this result with the results of Steiner and Rideal and Rodebush and Klingelhoeffer one obtains the Arrhenius parameters for the reaction k_2 ($Cl + H_2$) to be

$$k_2 \ (Cl + H_2) \ = \ 8. \ 3 \pm 0. \ 6). \ 10^{10} \ exp \ (-(5480 \pm 140)/RT)$$

the un its of E being in cals. mole^{-1} and of A in mole^{-1}.1.sec^{-1}.

The extremely small error limits for the Arrhenius parameters from three independent and completely different sets of experiments argues favourably for the validity of the parameters.

Therefore, having justified the competitive technique and with the Arrhenius parameters of the hydrogen molecule/chlorine atom reaction on such a firm footing, one can attach considerable confidence to the parameters for the rate of abstraction of a primary hydrogen atom from propane. (31).

i. e. $\qquad k_2(Cl + pri\ C_3H_8) = (1.7 \pm 0.3).10^{10} \exp(-(980 \pm 130/RT))$

$$\text{per primary H atom}$$

It is now possible to assess other experimental methods for the determination of the elementary rate constants for the reaction of chlorine with an olefin. Early experimentation was concerned with evaluating these rate constants absolutely and, in particular, with overcoming the problem of the determination of the chlorine atom concentration in a static system.

One method which circumvented the direct calculation of chlorine atom concentration but which afforded an opportunity of measuring radical lifetime in a photolytic system was by interposing between the light source and the reaction vessel a rotating disc from which a sector of known dimensions had been cut. The attractiveness of this rotating sector technique lay not only in the chance of accurate measurements of radical lifetimes but also in the possibility of a complete analysis of the mechanism of all reactions in which termination was by the mutual destruction of chain centres. (42)

Qualitatively the effect can be seen from the following considerations. Since termination is by mutual destruction of chain centres the rate of reaction is proportional to the intensity of the illumination, raised to the power $\frac{1}{2}$. Also, if a number of radicals are generated during a period of illumination then, on cessation of illumination, their concentration falls to zero and, when the light is switched on again this cycle of events is repeated. However, if the second period of illumination occurs before the radical concentration has fallen to zero, a second crop of radicals interferes with the concentration of the first lot. Therefore, the rate of reaction varies fairly rapidlyy with the speed of rotation of the disc when the time between flashes is comparable with lifetime of the radicals. Below and above this value the rate is independent of flash time. If the disc is cut in such a way that periods of light to dark times are 1:3 then at fast sector speeds when the period of illumination is short compared with the radical lifetime the rate of reaction is reduced by a factor of $(\frac{1}{4})^{\frac{1}{2}}$; at slow sector speeds when the period between illuminations is long compared with the radical lifetime the rate is reduced by a factor of $\frac{1}{4}$. Thus the ratio of maximum to minimum rates is 2:1. The procedure for applying this technique to systems in which the generation of chain centres is not uniform throughout the reaction cell, i. e., when the reactant absorbs a considerable proportion of the incident light, has been described by Burns and Dainton (43).

In the normal case, with small absorption, experimental values of ρ , where

$$\rho = \underline{\frac{2 \text{ x rate with sector running}}{\text{rate in continuous light with same Io}}} \qquad \text{I. b. 30}$$

are plotted against $\log_{10} (t_I \ Io)^{\frac{1}{2}}$, where t_1 is the light period. This is

compared with a theoretical curve of ρ against $\log_{10}(M)$, where M is a

dimensionless parameter including a term corresponding to the lifetime of the

chain centres.

$$\text{viz} \qquad M = (I \ k_8)^{\frac{1}{2}}/t_1 \qquad \text{I. b. 31}$$

The mean lifetime of a radical under stationary state conditions is

$$\tau_S = \underline{\frac{\text{stationary state concentration of radicals}}{\text{rate of removal of radicals}}} \qquad \text{I. b. 32}$$

and if termination is entirely by (8)

$$\text{then} \qquad \tau_S = \frac{[R]}{k_8 [R]^2} \qquad \text{I. b. 33}$$

In photochemical experiments

$$[R] \qquad = \left(\frac{2Ia}{k_8}\right)^{\frac{1}{2}} \qquad \text{I. b. 34}$$

and therefore

$$\tau_S = \frac{1}{(2k_8 Ia)^{\frac{1}{2}}} \qquad \text{I. b. 35}$$

When non-uniform absorption is taken into account the theoretical curve

has an ordinate $\log_{10} M'$, where $\underline{\frac{M'}{M}} = \frac{(\alpha \ Io \ [Cl_2])^{\frac{1}{2}}}{Ia}$

At the position of best fit of the theoretical curve to the experimental

values, the value of $\log (t_1 \ Io)^{\frac{1}{2}}$ is read off corresponding to the point at

which $\log(M) = 0$ i. e. $M = 1$ and $t_1 = \tau_s$, the lifetime of the chain centre. Since $\tau_s = (2k_8 Ia)^{-\frac{1}{2}}$ values of k_8 can be obtained and since the overall rate of reaction, above a characteristic limiting concentration is given by $k_3 \frac{(2Ia)^{\frac{1}{2}}}{(k_8)} [Cl_2]$ values of k_3 can also be obtained.

In validating the technique Dainton, who has applied the method exhaustively (47), (52), (55), (56), addends the additional precaution that before each set of experiments it was established that half the ratio of the rate in continuous light to that in intermittant light was equal to $1.00 \overset{+}{-} 0.015$ for fast sector speeds, which, according to Dainton, indicates that termination was entirely be mutual interation of chain centres. However, this statement has been questioned by Benson (38) who points out that the dependence of the reaction rate on the half power of intensity is no criterion for homogeneity, as wall termination might well be second order with respect to chain centres.

Fired with the idea of obtaining a complete analysis of a system and with the possibility of testing the transition state theory for the addition of a chlorine atom to a family of related compounds, CGoldfinger et al and Dainton et al applied the rotating sector technique to the chlorination of the chloroethylenes. Early work of Adam, CGoldfinger and CGosselain (44) evaluated the rate constants k_3 and k_8 for the tetrachloroethylene system, but this work was later repeated by Dusoleil, CGoldfinger, Mahiew-Van der Auwera, Martens and Van der Auwera (45) who obtained values of k_3 and k_8 to be $\log k_3 = 8.31 - 1186/T$ and $\log k_8 = 8.66 - 18/T$, the units of A and E being $mole^{-1}sec^{-1}$ and cal mole^{-1} respectively.

In order to obtain a value of k_2 for the tetrachloroethylene system Gold-finger, Huybrechts and Martens (46) photochlorinated mixtures of tetra-chloroethylene and methane, methyl chloride, methylene chloride, chloroform and pentachloroethane in a static system following the reaction rates mano-metrically and potentiometrically. Values of the rate constant, k_2', of the competitors methane, methyl chloride, methylene chloride etc. were those determined by Knox (32) having been communicated to Goldfinger et al privately. The value obtained for the rate constant $k_{2 (Cl + C_2 Cl_4)}$ was then 0.24×10^{10} moles^{-1} 1. sec^{-1}.

A similar determination of the rate constants k_3 and k_8 for the trichloro-ethylene system was carried out by Dainton, Lomax and Weston (47) who ob-tained the same overall rate expression as Muller and Schumacher (48)

i.e. rate of reaction $= k_o \, Ia^{\frac{1}{2}} \, [Cl_2]$

and hence obtained values of $k_8 = (3.6 \pm 2.0) \times 10^9 \exp - (0.5 \pm 0.2/RT)$ mole^{-1} 1. sec^{-1} and $k_3 = (3.0 \pm 1.0) \times 10^8 \exp - (5.1 \pm 0.2/RT)$ moles^{-1} 1. sec^{-1}, the values of the activation energies being in k. cal mole^{-1}. The rate of reaction was followed manometrically which assumed that in a long chain system the overall reaction could be represented as

$$A + Cl_2 \longrightarrow ACl_2$$
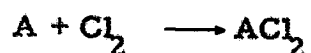
and hence, when proceeding in the gas phase at constant temperature and volume, is accompanied by a decrease in volume, allowance first having had to be made for a small Draper effect.

Dainton reasoned that reaction (2) was in principle, reversible and on

general grounds it would be expected that the rate constant for the reverse reaction would have Arrhenius parameters $A_{-2} = 10^{13}$ sec^{-1} and E_{-2} close to D_{A---Cl}. The bond dissociation energy, $D_{A...Cl}$, was thought to be about 25k cal mole^{-1} for C_2H_4Cl and was believed to diminish as n decreased along the series $C_2H_nCl_{5-n}$, some support for this statement being found in Goldfinger's work (49), which showed that, when $A = C_2Cl_4$ the parameters for k_{-2} (or k_4) were $A_4 = 10^{12.8}$ sec^{-1} and $E_4 = 16.8$ k cal mole^{-1} and also in the work of Huybrechts, Meyers and Verbeke (56) in which, for $A = C_2HCl_3$, the parameters of k_4 were quoted as $A_4 = 10^{13.7}$ sec^{-1} and $E_4 = 20.4$ k cal mole^{-1}.

In an effort to observe reaction (4) directly Ayscough, Cocker and Dainton (51) photochlorinated cis-dichloroethylene in the normal chlorine concentration range, ca 2 mM, in which it was considered that the ACl radicals formed in reaction (2) would have a lifetime of about 10^{-5} seconds before reacting with chlorine. This would allow sufficient time for many free rotations about the C-C bond. Therefore a 1,1,2-trichloroethyl radical formed in the photochlorination of 1,2-dichloroethylene would have a probablity, x, of forming trans-dichloroethylene and a probablity of 1-x of forming the cis isomer. Geometrical isomerization accompanying the photochlorination of 1,2-dichloroethylene would thus provide direct evidence for reaction (4) and by comparing the initial rate Ri of isomerization of the pure isomers with their rates of chlorination x and k_4/k_3 could be determined, since

$$Ri/R_p \text{ for pure cis } = x\,k_4/k_3\,[Cl_2]$$
I. b. 36

$$Ri/R_p \text{ for pure trans } = (1-x)\,k_4/k_3\,[Cl_2]$$
I. b. 37

where R_i is the rate of isomerization and R_p the rate of photochlorination.

Experiments were therefore undertaken originally with the aim of applying equation I. b. 36 and 37, not anticipating any isomerization to be detectable below $200^\circ C$, but finding considerable amounts of the geometrical isomer at temperatures as low as $30^\circ C$. Ayscough et al therefore undertook a detailed investigation of the reaction in the temperature range $30-65^\circ C$.

Their results showed (1) no pressure dependence of R_i/R_p on $[A]$ but a linear one on $1/[Cl_2]$ as predicted; (2) R_i/R_p values were much greater than $(10^{13} \exp -20/RT)/(10^{8.7} \exp -2.74/RT) [Cl_2]$, the values of parameters of k_3 being obtained from Ayscough, Cocker, Dainton and Hirst (52); (3) R_i/R_p values were not inversely proportional to $[Cl_2]$. Instead plots of R_i/R_p against $[Cl_2]^{-1}$ though linear, all had a positive intercept. Purely phenomenologically these intercepts were accounted for by the incorporation into the reaction Scheme I, of an additional isomerization reaction which increased in rate proportionately with an increase in chlorine concentration.

Dainton was therefore forced to propose a "hot radical" mechanism in which the reaction

$$A + Cl \longrightarrow ACl^* \qquad (2'')$$
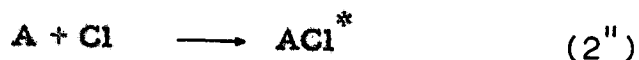
where the ACl^* entity was considered to retain the C-Cl bond dissociation energy and be capable of four different reactions.

viz.

$$A + Cl \longrightarrow ACl* \begin{cases} \xrightarrow{\alpha} x\ trans - A + (1-x)cis - A + Cl \\ +Cl_2 \xrightarrow{\beta} y\ trans - A + (1-y)cis - A + Cl_3 \\ +Cl_2 \xrightarrow{\gamma} ACl^\circ + Cl_2 \ (\text{deactivation}) \\ + A \xrightarrow{\delta} A + ClA* \ (\text{Cl atom exchange}). \end{cases}$$
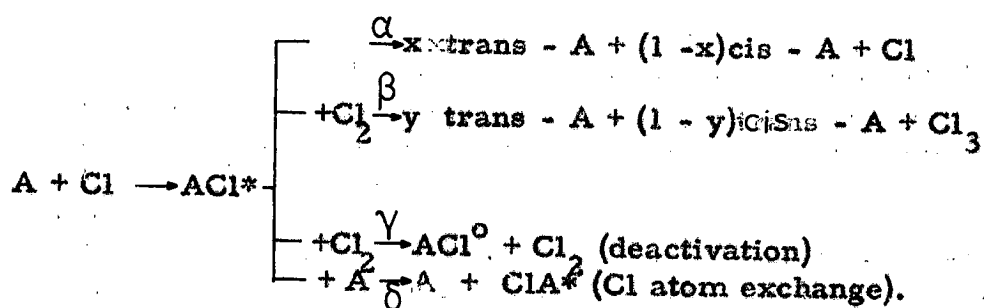
The expressions for the isomerization rates of initially pure cis and trans $(CHCl)_2$ were then given by

cis
$$\frac{R_i}{R_p} = \frac{xk_\alpha + yk_\beta}{k_\gamma [Cl_2]} = \frac{xk_\alpha}{k_\gamma [Cl_2]} + y\frac{k_\beta}{k_\gamma} \qquad \text{Ib 38}$$

trans
$$\frac{R_i}{R_p} = (1-y)\frac{k_\beta}{k_\gamma} + \frac{(1-x)k_\alpha}{k_\gamma [Cl_2]} \qquad \text{Ib 39}$$

Following the overall rate of reaction manometrically and using gas chromatography to follow the rate of isomerization enabled x and y and the relative rates of k_α, k_β, and k_γ to be obtained. (see table I. b. IV)

Table I. b. IV.

Temp. °C	x	y	k_α/k_β	k_γ/k_β
30	0.74	0.55	2.84×10^{-3}	2.56
40	0.77	0.57	3.19×10^{-3}	2.38
55	0.77	0.56	3.16×10^{-3}	2.29
65	0.74	0.60	3.29×10^{-3}	2.10

The results show no temperature dependence of x and would therefore seem to verify the hot radical mechanism.

ACl* must then have a lifetime greater than the rotational period; further

one could consider x to be the chance of spontaneous loss of a chlorine atom
from the internally rotating

$$\begin{array}{c} Cl \\ | \\ Cl\diagdown \qquad\qquad C \\ \diagdown C - C - H \\ H\diagup \qquad | \\ Cl \end{array}$$
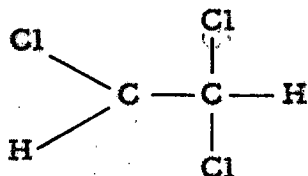
excited radical when it is in a configuration to form trans $(CHCl)_2$, and y the
corresponding chance of loss to a chlorine molecule.

An estimate of the lifetime of the hot radical could be made by assuming
that every time a chlorine molecule collided with ACl* either deactivation or
reaction β occurs, so that $k_\gamma + k_\beta = Z^o$, where Z^o is the standard collisioi
number. k_α then has a value of about $10^8 secs^{-1}$ and the lifetime of ACl*
before decomposition would be about 10^{-8} secs. which was considered likel
to exceed the period of one internal rotation. (This was later calculated by
Knox (53) to be 1.25×10^{-12} seconds.) The addition of the hot radical
mechanism to the chlorination of olefins was a considerable advance in
thinking on the mechanism of this reaction, bringing halogenation reactions
into line with similar atom reactions which formed "hot" adducts with olefins
viz oxygen or CH_2 radicals (54).

To obtain the individual rate contstants k_2, k_3, k_6, and k_8 for the chlor
ination of 1,2 - dichloroethylene Ayscough et al (52) applied the rotating
sector technique to the problem. However, in applying the technique many
corrections had to be made to the original equations, Ib 30 - Ib 35, due to

non-uniform absorption of light by chlorine along the reaction call. Burns and Dainton (43) had shown that if the local rate per unit volume Rp^j in a lamina of thickness dL was given by $Rp^i = k(I^1)^{\frac{1}{2}}$ where I^1 is the absorbe light intensity, assumed constant across the lamina, then the mean rate per unit volume Rp of an element of thickness L (i. e. the depth of the reaction call) was obtained by integration and was given by

$$Rp = kg \, I_0^{\frac{1}{2}} \qquad\qquad \text{Ib 4}$$

where
$$g = \frac{2}{L} \quad \frac{1 - \exp(-\alpha' \, [Cl_2] \, L)}{(\alpha' \, [Cl_2])^{\frac{1}{2}}} \qquad\qquad \text{Ib 4}$$

and $\alpha' = 2.303$ times the decadic extinction coefficient α.

Evaluation of the rate constants k_6 and k_2 presented further difficultie in that allowance had to be made for a considerable amount (in some cases up to 70%) of termination due to heterogeneous processes. Ayscough et al argued that wall termination would be diffusion controlled by the rate of diffusion, ζ, of the chlorine atoms through the gas to the wall and since, under the experimental conditions, $[Cl_2] > [A]$ it was possible to equate reactions 6a

where $Cl + wall \longrightarrow$ termination (6a)
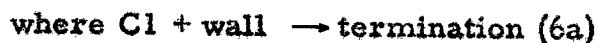
with $\zeta / [Cl_2]$.

At a given chlorine pressure the rate of chlorination was given by equations Ib 42, and Ib 43

$$R_p = \frac{k_2 c [A] \, k_\gamma [Cl_2]}{k_\alpha + (k_\beta + k_\gamma)[Cl_2]} \left\{ \frac{2Ia [Cl_2]}{\zeta} + (1 - x)\left(\frac{2Ia}{k_6 [Cl_2]}\right)^{\frac{1}{2}} \right\} \qquad \text{Ib 4}$$

i.e. $$R_p = \frac{k_2{}^c [A] \, k_\gamma [Cl_2]}{k_\alpha + (k_\beta + k_\gamma)[Cl_2]} \left\{ \tau_1 x + (1 - x)\, \tau_2 \right\} \qquad \text{Ib 4}$$

where τ_1 and τ_2 are the kinetic lifetimes of the linearly and mutually terminated chains and x is the fraction of chains terminated on the wall.

Therefore, the rotating sector technique, suitably modified, was used to measure $\tau_2 = (2Ia \, k_6 [Cl_2])^{\frac{1}{2}}$ and hence k_6 could be evaluated. From the average lifetime, τ, of the chlorine atoms, their stationary state concentration ($[Cl] = 2Ia\tau$) could be derived, and, since the rate constant $k_2{}^c$ could be expressed in the form

$$k_2{}^c = R_p \, \frac{(1 + k_\beta / k_\gamma)}{2Ia\tau \, [A]} \qquad \text{Ib 4}$$

the following values of $k_2{}^c$ were obtained;

$$k_2{}^c = (2.73 \pm 0.10) \times 10^9 \text{ mole}^{-1} \, 1 \, \text{sec}^{-1} \text{ at } 39.5^\circ C$$

$$k_2{}^c = (3.11 \pm 0.10) \times 10^9 \text{ mole}^{-1} \, 1 \, \text{sec}^{-1} \text{ at } 62.1^\circ C$$

from which the Arrhenius parameters were $\log_{10} A = 10.27 \pm 0.4$ and $E_2{}^c = 1.18 \pm 0.7$ cal mole^{-1}.

Finally Ayscough et al observed chlorine to be a highly efficient third body in promoting recombination of chlorine atoms by stabilizing $Cl_2{}^*$; CO_2, on the other hand, was found to be relatively inefficient as a third

body as the rate of photochlorination increased by only 15% upon the addition

of 280 mm of CO_2 to 400 mm Cl_2 and 2mm DCE.

In completing the chloroethylene series in an effort to observe the

effect of a small variation in structure, i.e. the systematic change of a C - H

bond to a C - Cl bond, upon the rates of the elementary reactions in chlorination

of olefins Dainton, Lomax, and Weston (55) obtained the parameters k_3 and k_8

for vinyl chloride and attempted the determination of those for ethylene. In

both cases some surface reaction was noticed which amounted in the case of

the ethylene chlorination to 2% of the photorate. k_α was estimated for ethylene

at 3 times the rate of cis D.C.E. causing Dainton to speculate, inconclusively ,

about a possible structure dependence of the rate of unimolecular decomposition.

The remaining elementary rate constants k_2, k_6, k_α for the vinyl

chloride and trichloro-ethylene chlorination were estimated by Ayscough,

Cocker, Dainton and Hirst (57) by carrying out the chlorination of vinyl

chloride and trichloroethylene, separately, in competition with the chlorination of

cis D.C.E. for which the elementary rate constants were known.

As outlined previously, the relative rates of formation of chloroethones in

the competitive techniques are independent of the nature of the chain termination

steps and are

$$R = \frac{d[ACl_2]/dt[A]}{d[A^i Cl_2]/dt[A^i]} \left\{ 1 + \frac{k_\alpha + k_\beta[Cl_2]}{k_\gamma[Cl_2]} \right\} = \frac{k_2}{k_2^i} \left\{ 1 + \frac{k_\beta^i}{k_\gamma^i} + \frac{k_\alpha^i}{k_\gamma^i[Cl_2]} \right\}$$

Ib 45

It was possible to calculate the ratio $k_\alpha/(k_\beta + k_\gamma)$ from the ratio of the slope to the intercept relating R to $(Cl_2)^{-1}$. Inclusion of the corresponding value for ethylene (55) in table Ib V shows that this ratio decreases progressively as the chlorine content of the ACl radical is increased

Table Ib V

Olefin	T°C	$10^3 \times k_\alpha/k_\beta + k_\gamma$	$10^3 k_\alpha/k_\beta$
C_2H_4	25	5.4	15
C_2H_3Cl	30	1.50	5.4
	45	1.60	5.5
	55	1.64	5.3
	65	1.70	5.25
cis $C_2H_2Cl_2$	30	0.8	2.84
	45	0.94	3.19
	55	0.97	3.16
	65	1.06	3.29
C_2HCl_3	81.3	0.95	2.85

From the observed values of R in the two competitive photochlorination systems studied, it was found that the ratios $k_2/k_2' > 0.75$ and $k_2/k_2'' < 1.25$ and were substantially independent of temperature between 30°C and 80°C. Thus the addition reactions of a chlorine atom to vinyl chloride, cis dichloroethylene and trichloroethylene were all assigned the same Arrhenius

parameters; $E_2 = 1.5 \pm 1.0$ k cal mole^{-1} and $\log_{10}A_2 = 10.3 \pm 0.6$ (mole.$^{-1}$ l. sec.$^{-1}$). Dainton then generalises that, since k_2 is virtually constant and temperature independent, this verifies his postulate that reactions involved in the formation and decomposition of the excited species are not markedly structure dependent. Whereas a chlorine atom adds on to olefins with nearly equal ease Dainton's assumption about the equity of the rates of decomposition of the various excited species seems to be at odds with his results (k_α seems to show a distinct structural dependence) and is most certainly at odds with unimolecular reaction rate theory.

A summary of the Arrhenius parameters derived by Dainton et al for the chlorination of chloroethylenes is given in table Ib VI.

Table Ib VI

Olefin	$\log A_2$ (l mole^{-1} sec^{-1}) E_2 (k cal mole^{-1})	$\log A_3$ (l mole^{-1} sec^{-1}) E_3 (k cal mole^{-1})	$\log A_8$ (l mole^{-1} sec^{-1}) E_8 (k cal mol^{-1})	Ref
ethylene	no parameters	obtained.		
Vinyl Chloride C_2H_3Cl	10.3 ± 0.6 1.5 ± 1.0	8.75 ± 0.2 0.92 ± 0.5	9.92 ± 0.2 0.3 ± 0.10	57, 55
cis - DCE. E. cis $C_2H_2Cl_2$	10.3 ± 0.4 1.2 ± 0.7	8.7 ± 0.3 2.73 ± 0.6	10.5 ± 0.3 $).5 \pm 0.5$	51, 52
Trichloro- ethylene C_2HCl_3	10.3 ± 0.6 1.5 ± 1.0	8.48 ± 0.2 5.1 ± 0.2	9.56 ± 0.3 0.5 ± 0.2	47, 57
Tetrachloro- ethylene C_2Cl_4	9.38 0.0	8.31 5.40	8.66 0.8	45 46

However, this formidable volume of data compiled by Dainton et al is open to criticism. Basically it would appear that, although the hot radical mechanism was conceived in Leeds, many of its implications were not realised by the authors, and therefore, in many cases, experiments were devised to confirm preconceived and limited assumptions. Their failure to observe any dependence of R_i/R_p upon olefin pressure is such a case. Having found a linear dependence of R_i/R_p on the reciprocal of chlorine press the experiments designed to measure the dependence on olefin pressure were carried out with a background pressure of 100 mm of chlorine, varying the olefin pressure from about 5mm to 30 mm. Their failure to observe any no-ticeable dependence on olefin pressure is hardly surprising, since the major deactivating species remains chlorine, the total deactivating pressure having been increased by only 20%, even although the olefin pressure was increased by a factor of 6. Also, the occurrance of an intercept in the graphs of R_i/R_j against $\left[Cl_2\right]^{-1}$ and the necessary incorporations into the reaction mechanism reaction (β) might have been more thoroughly investigated by working at extremely high chlorine concentrations.

However, these criticisms might well ~~be~~ arise from disadvantages inherent in the rotating sector technique, in that working with very high chlorine concentatio would lead to greater uncertainty about the uniformity of chlorine atom con-centration. Also, if the olefin concentration is increased above a limiting amount, the intensity exponent would no longer obey the simple $\frac{1}{2}$ rule and

would vary as the chain termination processes become more complex.
The concurrence of heterogeneous and homogeneous termination and the
subsequent allowance for this, places considerable doubt on the value of
k_2^c later used as the reference rate constant in competitive chlorinations (57).

Uncertainty about the value of k_2^c prompted Knox (53) to reinvestigate
the chlorination of 1,2- dichloroethylene using the competitive technique in
which the abstraction of the primary hydrogen atom in propane was the
absolute standard. Since the propagation steps in the chlorination of propane
are (2'') and (3'') and, if the only propagation reactions in the chlorination of
D.C.E. are (2) and (3) (scheme I), the ratio of the fractional rates of
formation of tetrachloroethane (ACl_2) and n propyl chloride would be
approximately k_2/k_2'

$$\text{i.e. } \frac{k_2}{k_2'} = \frac{[ACl_2][PrH]}{[nPrCl][A]} = R_{nPrCl}^{ACl_2} \qquad \text{Ib 46}$$

where $[ACl_2]$ and $[nPrCl]$ are the final concentrations of products and $[PrH]$
and $[A]$ are the initial concentrations of reactants. The error in writing
$R_{nPrCl}^{ACl_2} = k_2/k_2'$ becomes unimportant in comparison with experimental errors
if the consumption of propane and D.C.E. are less than 5%.

On the other hand, if reactions of the activated chloroalkyl radical ($ACl*$)
are important, the expression for $R_{nPrCl}^{ACl_2}$ becomes more complex. A
generalized scheme for the incorporation of reactions of the activated chloro-
alkyl radical in the chlorination of olefins modifies scheme I by including

$$A + Cl \longrightarrow ACl^* \qquad (2'')$$

$$ACl^* \longrightarrow x \text{ cis} A + (1 - x) \text{ trans } A + Cl \qquad (a)$$

$$ACl^* + M_i \longrightarrow ACl^\circ + M_i \qquad (b_i)$$

$$ACl^* + Cl_2 \longrightarrow y \text{ cis } A + (1 - y)\text{trans } A + Cl_3 \qquad (c1)$$

$$ACl^* + A \longrightarrow z \text{ cis } A + (1 - z) \text{ trans } A + ACl^\circ \qquad (c2)$$

$$ACl^* + A \longrightarrow z'' \text{ cis } A + (1 - z') \text{trans } A + ACl^* \qquad (c2')$$
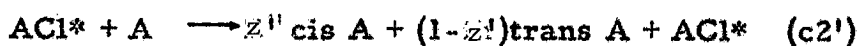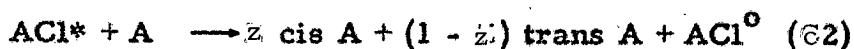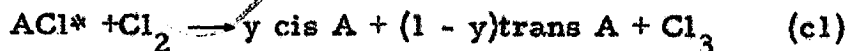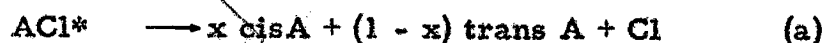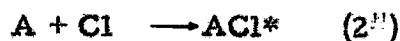
where ACl^* denotes the active radical and ACl° denotes the deactivated
radical

This scheme, used by Knox, is a generalization of Dainton's hot
radical mechanism in that any species, M_i, is considered capable of de-
activating the active radical; subscript $i = 1$ is used for chlorine, 2 for PrH,
3 for olefin (in this case D.C.EE.) and 4 for CO_2.

The selectivity ratios therefore take the form

$$R^{ACl_2}_{nPrCl} = \frac{k_2''\text{cis}}{k_2'} \times \frac{\sum_i kbi[M_i] + k_{c2}[A]}{ka + \sum kb_i[M_i] + k_{c1}[Cl_2] + (k_{c2} = k_{c2}')[A]} \qquad \text{Ib } 47$$

$$R^{tA}_{nPrCl} = \frac{k_2''\text{cis}}{k_2'} \times \frac{(1 - x)ka + (1 - y)k_{c1}[Cl_2] + \left\{(1 - z)k_{c2} + (1 - z')k_{c2}'\right\}[A]}{ka + \sum kb_i[M_i] + k_{c1}[Cl_2] + (k_{c2} = k_{c2}')[A]}$$

$$\text{Ib } 48$$

$$R^{tA}_{ACl_2} = \frac{(1 - x)ka + (1 - y)k_{c1}[Cl_2] + \left\{(1 - z)k_{c2} + (1 - z')k_{c2}'\right\}[A]}{\sum kb_i[M_i] + k_{c2}[A]}$$

$$\text{Ib } 49$$

where k_2'' cis is the rate constant for reaction (2'') starting with cis DCE,

and

$$R_{nPrCl}^{tA} \equiv [\text{trans A}] \quad [\text{PrH}] \; / \; [\text{PrCl}] \; [\text{A}]$$ I. b. 50

and $$R_{ACl_2}^{tA} \equiv [\text{trans A}] \quad / \; [ACl_2]$$ I. b. 51

The importance of reactions (c1), (c2) and (c2') were assessed by extrapolating the ratio $R_{ACl_2}^{\text{isomer A}}$ to infinite pressure of chlorine or (olefin + propane) when equation I. b. 49 reduces to

$$R_{ACl_2}^{tA} \; (\; [Cl_2] \longrightarrow \infty) \; = \; (1 - y) \, kc1/kb1 = \text{constant}$$ I. b. 52

$$R_{ACl_2}^{ta} \; ([A] + [PrH] \rightarrow \infty) = \frac{(1 - \bar{z})kc2 + (1 - \bar{z}')\, kc2'}{kb_3 + kb_2 \, [RH] \; / \; [A]}$$ I. b. 53

$$= \text{constant for a given } [RH] \; / \; [A] \text{ratio}$$

These ratios were plotted against the reciprocals of the chlorine and (olefin and propane) pressures; the curves, calculated on the assumption that all k_c's were zero fitted the experimental points exactly. Quantitatively this means that the overall rate of the exchange reactions is less than 5% of the deactivation rate. Expression I. b. 47 - 49 can therefore be simplified by setting all k_c equal to zero.

Thus for cis C. C. E. + propane mixtures:

$$R_{nPrCl}^{ACl_2} = \frac{k_2'' \text{ cis}}{k_2'} \times \frac{\sum kb_i \, [M_i]}{ka + \sum kb_i \, [M_i]}$$ I. b. 54c

$$R_{nPrCl}^{tA} = \frac{k_2 \text{''cis}}{k_2 \text{'}} \times \frac{(1 - x) \, ka}{ka + \sum kbi \, [M_i]} \qquad \text{I. b. 55c}$$

$$R_{tA}^{ACl_2} = \frac{\sum_i kbi \, [Mi]}{(1 - x) \, ka} \qquad \text{I. b. 56c}$$

and for trans D. C. E. + propane mixtures:

$$R_{nPrCl}^{ACl_2} = \frac{k_2 \text{'' trans}}{k_2 \text{'}} \times \frac{\sum_i kbi \, [Mi]}{ka + \sum kbi \, [Mi]} \qquad \text{I. b. 54}_t$$

$$R_{nPrCl}^{cA} = \frac{k_2 \text{''}}{k_2 \text{'}} \text{ trans} \quad \frac{x \, ka}{ka + \sum kbi \, [Mi]} \qquad \text{I. b. 55}_t$$

$$R_{cA}^{ACl_2} = \frac{\sum_i kbi \, [Mi]}{x ka} \qquad \text{I. b. 56}_t$$

Plots of $R_{tA}^{ACl_2}$ and of $R_{cA}^{ACl_2}$ against the pressure of any component in the mixture for a series of experiments in which the pressures of the remaining components were kept constant, were straight lines. Provided that x and ka were independent of the source of ACl* the gradients of these lines were kbi/ (1 - x) ka or kbi/xka. The ratio of the gradients of pairs of lines in such plots is x/(1 - x) and must be independent of Mi. A value of x/(1 - x) = 3. 6 was obtained leading to x = 0.78.

An independent determination of x (cis) and x (trans) was possible, since equations I. b. 54 and 55 gave

$$R_{nPrCl}^{ACl_2} = \frac{k_2 \text{'' cis}}{k_2 \text{'}} - \frac{1}{(1 - xc)} R_{ACl_2}^{tA} \qquad \text{I. b. 57}$$

$$R^{ACl_2}_{nPrH} = \frac{k_2'' \, tr}{k_2'} - \frac{1}{xt} \quad R^{cA}_{ACl_2} \qquad \text{I. b. 58}$$

Plots of $R^{ACl_2}_{nPrH}$ against $R^{isomer A}_{ACl_2}$ gave straight lines with negative

gradients, $1/(1 - xc)$ and $1/xt$, and intercepts on the ordinate of k_2'' cis$/k_2'$

respectively. Values of $1 - xc = 0.21 \pm 0.01$ and $x_t = 0.77 \pm 0.04$ were obtained,

and therefore within experimental error, $x_c = x_t = 0.78$; x was also found to be

independent of temperature.

This value of $x = 0.78$ contrasts sharply with $x = 0.25$ obtained by

Ayscough et al (51) and, even though the latter authors had confused cis for trans

D.C.E., there remains still an inexplicable discrepancy. However, the value

obtained by Knox is particularly pleasing since, from it, it is possible to

calculate the equilibrium constant for the following equilibrium.

$$Cl + cis \; A \underset{xka}{\overset{k_2'' \, cis}{\rightleftarrows}} ACl* \underset{k_2'' \, trans}{\overset{(1 - x) \, ka}{\rightleftarrows}} Cl + tr - A$$
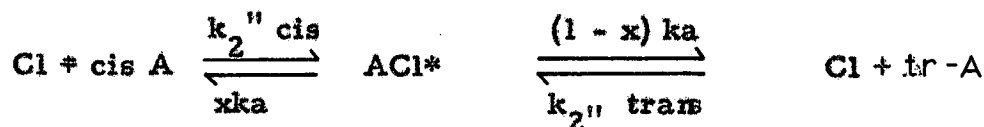
By the principle of microscopic reversibility

$$K_{eq} = \frac{[tr \; A] \, eq.}{[cis \; A] \, eq.}$$

and so

$$K_{eq} = \frac{k_2'' \, cis \, (1 - x)}{k_2'' \, tr. \, x} = \frac{(k_2'' \, cis/k_2') \, x \, (1 - x)}{k_2'' \, tr/k_2') \, x(x)}$$

$$= 0.42$$

which compares well with the thermodynamic value given by Pitzer and

Hollenberg (58), $Keq = 0.5$.

Numerical values of k_{bi}/k_a and hence k_{bi}/k_{b_1} were obtained from the gradients of the graphs of $R^{ACl_2}_{\text{isomer A}}$ against the pressure of any variable component of the mixture. The collisional deactivating efficiencies relative to chlorine (i = 1) were evaluated from the k_{bi} and the standard collision numbers, $Z^O (ACl^*, M_i)$. Whereas Ayscough et al (51) had found that only chlorine was an efficient deactivator, the results of Knox and Riddick show that other molecules are almost equally effective. (See Table I. b. VII)

Table I. b. VII

i	Molecule M_i	Temp. $^{\circ}C$	$10^3 \times k_{bi}/k_a$ mmHg	k_{b_i}/k_{b_1}	$10^8 \times \sigma_i$	$\dfrac{Z_i}{Z_1}$	Collisional efficiency relative to chlorine
1	Cl_2	35	4.9	1.0	4.5	1.0	
1	Cl_2	79	3.4	1.0	4.5	1.0	1.0
2	PrH	79	3.0	0.88	5.0	1.31	0.67
3	DCE	79	3.0	0.88	5.0	1.01	0.87
4	Co_2	79	1.75	0.51	4.2	1.12	0.45
1	Cl_2	133	2.7	1.00	4.5	1.0	

where σ_i is the collision diameter and Z_i the standard collision number for collision between ACl^* and M_i. Although it appears that chlorine is a slightly more efficient deactivator, the fact that four species of widely differing structure had such similar efficiencies suggested that deactivation must be efficient and that specific chemical reactions such as

$$ACl^* + Cl_2 \longrightarrow ACl_2 + Cl$$
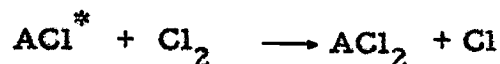
were unlikely.

Assuming that deactivation by chlorine occurs at every collision and using the collision diameters in table I.b. VII Knox calculated

$$kb_1 = Z^0 (ACl^*, Cl_2) = 8.6 \times 10^6 \text{ (mm Hg) sec}^{-1} \text{ at } 79^\circ C$$

$$= 1.9 \times 10^{11} \text{ mole}^{-1} \text{ sec}^{-1}$$

and hence

$$ka = 2.5 \times 10^9 \text{ sec}^{-1} \text{ at } 79^\circ C$$

Table I.B. VIII gives the rate constants derived by Knox

Table I.b. VIII

Temp.	k_2''/k_2		$10^{-6}kb_i$	$10^{-9}ka$	x
$^\circ C$	cis	trans	torr^{-1} sec^{-1}	sec^{-1}	
35	2.72 ± 0.1	1.94 ± 0.1	9.3	1.9	0.77 ± 0.04
79	2.18 ± 0.1	1.55 ± 0.1	8.6	2.5	0.78 ± 0.02
133	2.06 ± 0.1	1.23 ± 0.1	8.1	3.0	0.77 ± 0.04

from which the Arrhenius parameters for ka, k_2'' cis and k_2'' trans were obtained. These are

$$k_a = (1.8 \pm 0.5). \ 10^{10} \exp(-1330 \pm 200/RT) \text{ sec}^{-1}$$

$$k_2'' \text{ cis} = (8.0 \pm 2). \ 10^{10} \exp(-190 \pm 120/RT) \text{ mole}^{-1}.1. \text{ sec}^{-1}$$

$$k_2'' \text{ trans} = (3.0 \pm 0.7). \ 10^{10} \exp(+170 \pm 150/RT) \text{ mole}^{-1}.1. \text{ sec}^{-1}$$

where the activation energies are in cals mole^{-1}.

The internal consistency of Knox's results together with their freedom from correction factors and pragmatic postulates gives this work more credence than might be attached to the results of Dainton et al.

In an effort to reconcile the disparity between their results and those of Knox for the dichloroethylene system, Ayscough et al (59) reinvestigated the chlorination of cis dichloroethylene and have revised their ideas about the efficiency of gases other than chlorine in deactivating the active radical. They obtained the following deactivating efficiencies.

	DCE	Cl_2	He	Ar	CO_2	SF_6
k/k_δ	1	1.13	0.85	4.5	7.5	9.1

where k/k_δ is the relative rate of deactivation compared with reaction (δ)

$$ACl^* + A \longrightarrow ACl^o + A \qquad \qquad \delta$$

These results appear somewhat anomalous. The high deactivating efficiency of Argon relative to chlorine and DCE. is not easily understood. Graphs designed to show the relative collisional deactivating efficiencies by plotting the ratio of the rate of reaction in the presence of inert gas to the rate in its absence as a function of the inert gas pressure show nearly the same curve for Argon and CO_2. This causes the authors to comment that "the effects of Argon and CO_2 are virtually identical" and yet from their table of results CO_2 is nearly twice as efficient as Argon. Finally, the value of x has been re-calculated from 0.25 to 0.36.

It would therefore appear that the competitive technique was the better mode of investigation of the chlorination of olefins. This thesis is therefore concerned with the investigation of the chlorination of trichloroethylene and other cloro-olefins with a view to evaluating rate constants k_2'' and ka. The

rate, ka, of unimolecular decomposition is of particular theoretical importance since it affords an experimental test of Marcus's theory of unimolecular decomposition (24). It was further decided to investigate the collisional deactivating efficiency of various inert gases in an effort to correlate if possible deactivating efficiency with structure.

CHAPTER II

EXPERIMENTAL

1. Materials

Chlorine was obtained from an I. C. I. cylinder. The middle fraction was collected and freed from water by several trap to trap distillation from -80°C to -194°C. It was then exhaustively degassed and stored in a 2 litre bulb.

Propane was obtained from Cambrian Chemicals and was purified as above. Gas chromatographic analysis showed less than 0.1% C_2's, C_3H_6 and C_4' s.

Trans - 1, 2 - dichloroethylene was prepared from B. D. H. technical grade 1,2-dichloroethylene. The crude material was dried by standing over P_2O_5 and was distilled, the fraction boiling in the range 47.2°C to 47.8°C being collected. It was then re-distilled on a 6 foot column packed with glass helices using a reflux ratio of about 20:1. The trans-dichloroethylene which was collected boiled in the range 46.6°C to 47.0°C the only detectable impurity on gas chromatographic analysis being cis dichloroethylene present in less than 0.001%.

Trichloroethylene (B. D. H. Laboratory Reagent) was dried by standing over P_2O_5 and then fractionally distilled in a 6 foot column packed with glass helices. The fraction boiling between 86.2°C and 86.3°C at 750.3 mm. atmospheric pressure was that taken. Gas chromatographic analysis showed no detectable impurities.

Tetrachloroethylene (B.D.H. Technical Grade) was dried over P_2O_5 and purified by fractional distillation as before the faction boiling between $120.9^{\circ}C$ and $121.2^{\circ}C$ being that taken. No impurities were detected by gas chromatography.

Ethylene was obtained from an I.C.I. cylinder and dried by trap to trap distillation in the apparatus.

Vinyl Chloride was obtained from Cambrian Chemicals, freed from condensable impurities, degassed and stored in the same way as chlorine.

1,1,2,2 - Tetrachloroethane (B.D.H. Technical Grade) was purified by fractional distillation on the 6 foot packed column. No impurities were detected by gas chromatography.

1,12 - Trichloroethane was obtained from Eastman Chemicals and purified in the same way as trichloroethylene.

1,1,1,2, 2-Pentachloroethane (B.D.H. Technical Grade) was purified in the same way as trichloroethylene.

Hexachloroethane (B.D.H. Technical Grade) was purified by sublimation.

1,2-Dichloroethane (B.D.H. Technical Grade) was purified by fractional distillation in the same way as trichloroethylene.

n-Propyl Chloride. B.D.H. Laboratory Reagent.

1,2 - Dichloropropane B.D.H. Laboratory Reagent.

Carbon Dioxide. Commercial "Drikold" was used. It was freed from condensable impurities, degassed and stored in the same way as chlorine. Mass spectrometric analysis showed less than 0.1% impurities, i.e. H_2O etc. and less than 0.06% oxygen impurity.

Argon was obtained from a Matheson cylinder supplied by Cambrian Chemicals. It was introduced into the apparatus via removable trap 1 by passage over a column of manganous oxide (to remove any oxygen) and then through a U-tube packed with silica gel cooled to $-120^{\circ}C$ to remove any condensables. The resulting gas which was stored in a 2 litre bulb on mass spectrometric analysis showed less than 0.1% air impurity.

Sulphur Hexafluoride was supplied by I.C.I. It was freed from condensable impurities, degassed and stored in the same way as chlorine. Mass spectrometric analysis showed negligible impurities.

The mass spectrometer used in the analyses was an A.E.I. Ltd. M.S. 10.

Nitrosyl Chloride was prepared by passing nitrogen dioxide up a tower of moist potassium chloride (60) (NO_2 was obtained from a Matheson cylinder supplied by Cambrian Chemicals). The NOCl was fractionally distilled in the vacuum system to remove HCl, degassed in the usual manner and stored in a 2 litre bulb.

Hydrogen was obtained from a B.O.C. cylinder and was purified by passing over activated charcoal.

Celite: 60 - 80 mesh (G - Cel Plain supplied by (Gas Chromatography Limited.

Tween 60: supplied by L Light and Company Limited.

Silicone Oil: M & B Embaphase Grade.

2. Apparatus.

The experimental work was carried out in a conventional high vacuum apparatus and the reaction products were analysed by temperature programmed gas chromatography. The apparatus may be described under two headings: (a) kinetic system, (b) analysis system.

(a) <u>Kinetic System</u> (see Fig. II. 1). The apparatus was constructed from pyrex glass and was evacuated by means of two separate vacuum lines. The mercury diffusion pumps on the two lines were both backed by the same "Speedivac" rotary oil pump and a vacuum of about 10^{-6} mm. Hg was obtained as measured on a simple mercury vacuostat. Greased high vacuum taps were used on the vacuum lines but were replaced by metal valves with teflon seats and glands (manufactured by F. J. Hone Limited, 19 Eldon Park, London S. E. 25) in the rest of the apparatus. These valves had the advantage of a small dead volume and they also avoided problems arising from the solubility of high chlorinated reaction products in tap grease. The glass/metal seals were made by tightening a coupling nut on a polythene sleeve.

<u>Storage of Materials</u> . The reactants and oxygen were introduced into the system via removable trap 1 and stored in the bulbs and traps on manifold 1. The storage bulbs were equipped with attached pump-down traps and the reactants were exhaustively degassed each morning. Nitrosyl chloride was introduced via removable trap 3 and was stored in the 2 litre bulb on manifold 3. Care was taken to exclude the NOCl from the reactant and reaction part of the system (manifolds 1 and 2) and manifold 3 was evacuated by a separate vacuum line.

Kinetic System

Figure II 1

SG Spiral Gauge
RV Reaction Vessel
VB Vapour Bath
DB Dark Box
Z   Wire Gauze
W   Window
•   Hone Valve
◯   High Vac. Tap
LS Light Source
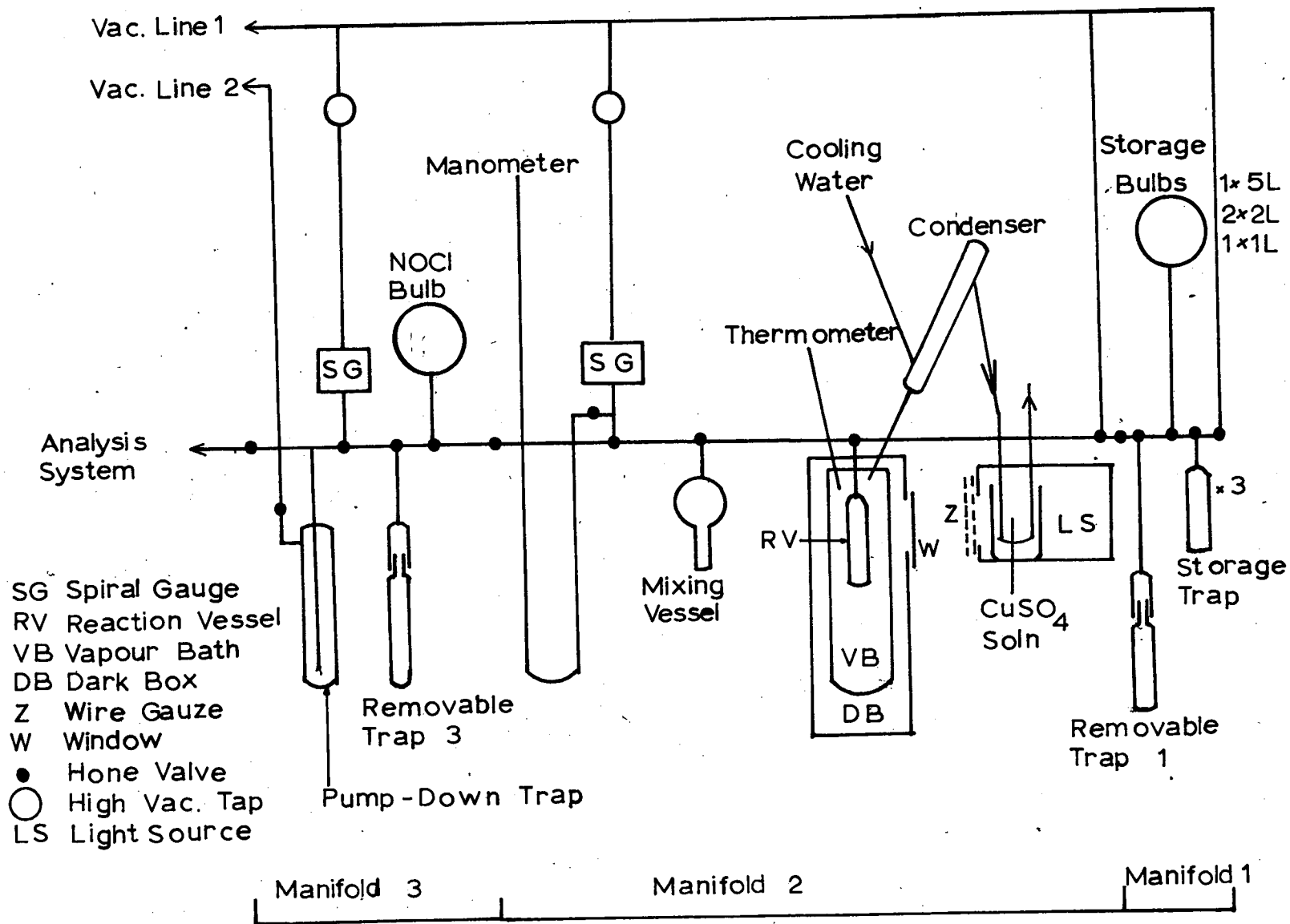
Pressure Measurement. The pressure of the reactant gases was measured with a pyrex spiral gauge. The gauge was stabilised to vibration by being immersed in liquid paraffin and by the use of a fine glass taught suspension. It had a mirror attached to it which reflected light from a projector lamp back to a centimetre scale, and was calibrated against a mercury manometer, a good straight line relationship being obtained.

$$2.34 \text{ scale cm.} = 1 \text{ cm. Hg.}$$

A second gauge, used for measuring pressures of NOCl, was found to have a calibration factor of 2 scale cm/cmHg.

Mixing Vessel. The darkened mixing vessel had a volume of 300 ml. and was equipped with a side arm which could be used for condensing gases, or, alternatively, heated to promote thermal mixing.

Reaction Vessel. The pyrex reaction vessel had a volume of 85 ml. and was entirely immersed in a thermostatting vapour bath apart from a short capillary lead of negligibly small volume (< 0.02 ml) attaching it to the apparatus. The vapour bath was provided by the following boiling liquids, the temperatures being read on thermometers placed in a thermometer well which protruded into the vapour.

methylene chloride	$40.1 \pm 0.5\,^0C$
Acetone	$56 \pm 0.5\,^oC$
Benzene	$79.5 \pm 1.0\,^oC$
Chlorobenzene	$132.5 \pm 0.5\,^oC$

The thermometers used to read the three lower temperatures were checked against National Physical Laboratory calibrated thermometers and

that used to read the upper temperature was calibrated by means of a standard thermocouple. The reaction vessel was kept in a light-proof box and the thermometer well and vapour bath condenser were blackened to prevent stray light entering the system. Illumination of the reaction vessel was achieved via a removable window in the box.

Illumination. The photochemical reaction was initiated by means of a 250 W Mazda projector lamp. The light passed through a 10% solution of copper sulphate in a 600 ml. beaker, which acted as a heat filter, and the intensity of the radiation incident on the reaction vessel could be adjusted by interspersing layers of wire gauge.

(b) Analysis System. The reaction products (see next section) had boiling points ranging from $30.8^{\circ}C$ to $163^{\circ}C$ and in order to achieve a good separation in a reasonable time and to obtain chromatographic peaks suitable for accurate measurement it was necessary to use temperature programmed gas chromatography and, in this section, attention will be drawn to the modifications that this entailed in the otherwise conventional system.

Carrier Gas: Hydrogen was used as the carrier gas and it was purified by passing it over activated charcoal (60 - 80 mesh). In order to maintain a constant flow rate as the temperature and hence the carrier gas viscosity and column back pressure increased, a constant-differential type flow controller (model 63 BU - L manufactured by Moor Products Company, H. and Lycoming Sts., Philadelphia) was used in conjunction with a needle valve (Edwards High Vacuum). This arrangement maintained the flow rate constant to within $\pm$ 2% over the temperature range $20^{\circ}C$ to $130^{\circ}C$. The flow

rate through the column was measured continuously with a capillary flow meter which had a response of 1 cm. for a flow rate of 20.2 ml H_2/min.

Columns. The columns were made of glass of 4 mm. internal diameter and were housed in an oven, the temperature of which could either be maintained constant or increased at a predetermined rate, as required. (Details of column packings used will be given in Section II 3).

Column Oven & Temperature Programmer. The column oven is shown diagramatically in figure II 2. The oven was of low heat capacity and was constructed from 1/32 in. aluminium sheet. The heating coils were wound on the interior wall and a uniform temperature was maintained throughout the oven by forced circulation of air. The filament of a 40 watt 250 volt bulb which had a linear resistance/temperature characteristic and a fast response, was used as the sensory element and was incorporated in a bridge circuit. The temperature controller was a D. C. amplifier which sensed out-of-balance signals from the bridge circuit and operated relays to control the heating circuit.

A timer operated a relay at predetermined intervals in the range of 1 pulse every 5 seconds to 1 pulse every 55 seconds, and a uniselector provided an increment in resistance equivalent to a change of $1C^o$ for each step, its drive magnet being so controlled that the uniselector was stopped each time the relay was released after a timing pulse. The selectors could also be stepped by a manual pulse button and this could be used to set the controller to a predetermined temperature or to zero it after use.

These facilities allowed the column oven to be thermostatted at $5C^o$

intervals in the range ambient - 200°C and provided for programming at a rate of $1\ C^{\circ}$/min to $12C^{\circ}$ /min in this range. Under the conditions used the programme was linear and reproducible to $\pm 2^{\circ}$C.

In the ethylene and vinyl chloride work, a commercial Pye series 104 temperature programmed chromatograph was used.

Detector. A hydrogen flame detector was used and was made from brass following a design given by Desty (61) (See Fig. II 3). Originally the jet was made of brass with a platinum tip inse rt. However, amounts of chlorine injected into the column with the products of a run attacked the brass causing sporadic ionisation and over a number of runs increased the background noise. The brass jet was therefore replaced with one made of a glass capillary with a platinum wire protruding into the flame. The platinum wire was main- tained at 270 v. by three 90 volt dry batteries connected in series, the detector current being measured by use of high value resistors (accurate to $\pm$ /%) in conjunction with an electrometer. The air flow to the detector was maintained at 1 l. /minute.

Amplifier. A Vibron Electrometer 33B (Electronic Instruments Ltd.) was used in conjunction with shunt unit type A49A. This contained resistors with the following values 10^5, 10^6, 10^7, 10^8, 10^9, 10^{11}, 10^{12} ohms. It was possible then to measure currents from 10^{-5} to 10^{-13} amps.

Recording. The elctrometer output was recorded on a 1 M. V. recorder (Honeywell Brown "Electronik") and the peak areas were measured as they were recorded by an electronic integrator (Gas Chromatography Ltd. , Model 1E165). A diagram of the detection and recording d rcuit is given in figure II 4.

Column Oven

Column Outlet
to Detector

Column Inlet

Temperature Sensor

Heating Coils

Support

1/32 in. Aluminium

Fan
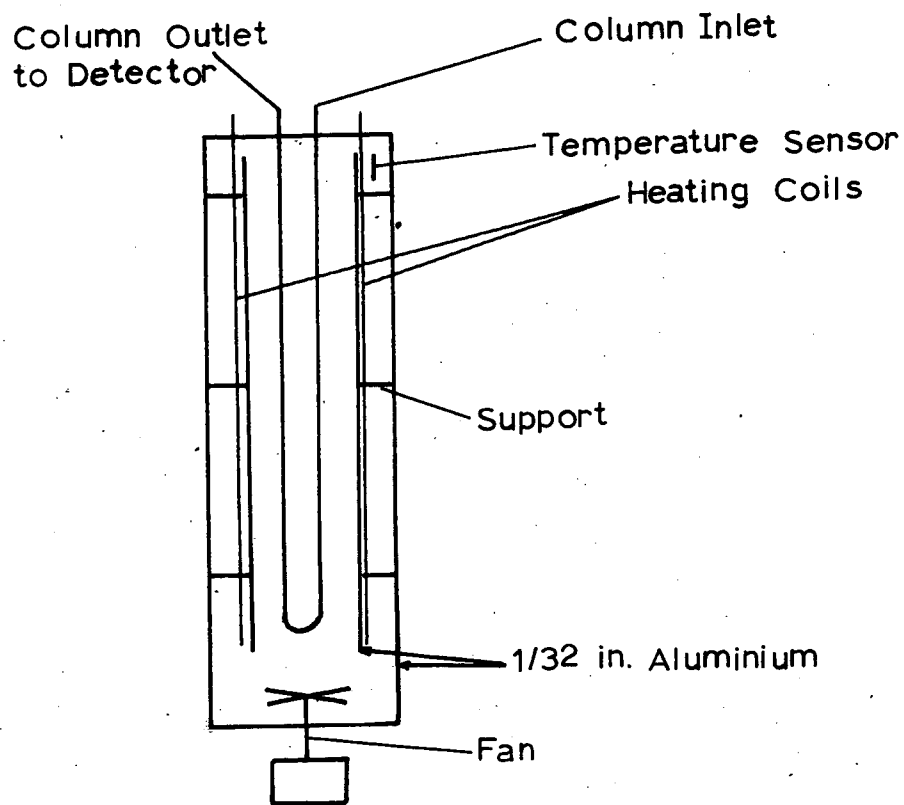
Figure II 2

Flame Ionisation Detector
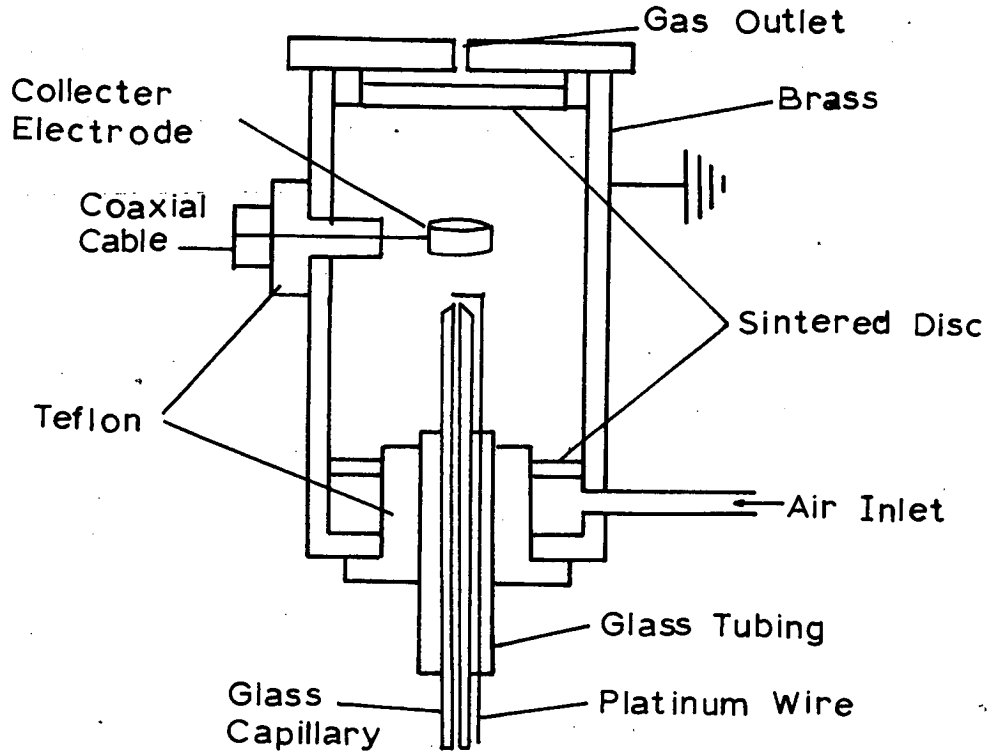
Figure II 3

Detector Circuit
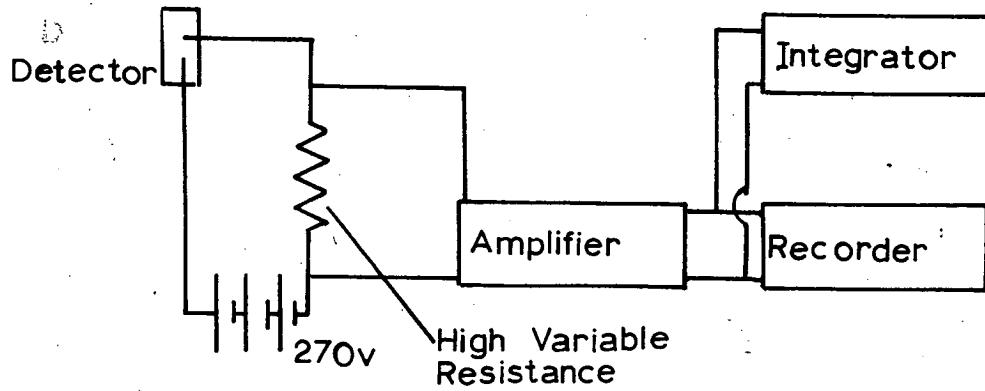
Figure II 4

Injection. The reaction products were condensed into the injection
U-tube cooled in liquid nitrogen; the column carrier gas was diverted through
the U-tube and the sample was injected on to the column by rapidly replacing the
liquid nitrogen flask with one of boiling water. Sharp injections were effected
by heating the Hone valves of the injection system and the pre-column leads to
a temperature of about 60°C. z

3.   Identification and Quantitative Analysis of Products.

Identification of reaction products was accomplished by matching their
retention times with those of authentic samples. In this way it was demonstrated
that the only products from the chlorination of trans-dichloroethylene was the
isomeric olefin and 1, 1, 2, 2 - tetrachloroethane and that the only products of the
chlorination of ethylene, vinyl chloride, trichloroethylene and tetrachloroethylene
were the corresponding addition products. (up to 30% conversion). For small
conversions (<10%) the only products from the chlorination of propane were
isopropyl chloride and n-propyl chloride. For higher percentage reaction four
other products were formed in small amounts and were assumed to be 1, 1 -
dichloropropane, 1, 3 -dichloropropane, 2, 2 dichloropropane and 1, 2-dichloropro-
pane. The last product was authenticated by comparison of its retention time with
that of B.D.H. reagent grade 1, 2-dichloropropane, but, although pure samples
were not available to check the retention times of the other products, the retention
times did match those of the products of chlorination of iso-propyl chloride and
n-propyl chloride.

For the quantitative study of the competitive chlorination of trans-

dichloroethylene or trichloroethylene or tetrachloroethylene with propane the reactions were stopped before a maximum of 10% of any of the reactants had been consumed. Gas chromatographic analysis of the reaction products was carried out on a column of 4 ft. 25% W/W silicone oil on celete and 2 ft. 15% W/W Tween 60 on celite. A carrier gas flow rate of 35 ml H_2/min was used and the column was maintained at 25°C for 15 minutes after the injection and then temperature programmed at $6C^{\circ}$/min to a maximum temperature of 130°C Under these conditions the retention times of the products (including minor and secondary products) were as follows:-

Compound	Retention Time		Boiling point $^{\circ}$C.
	mins.	secs.	
iso Propyl Chloride	6	30	30.8
n Propyl Chloride	9		47.2
trans Dichloroethylene	13	30	47.7
2,2 Dichloropropane	17	40	70.5
cis-Dichloroethylene	20		60.2
1,2-Dichloroethane	20	40	84
1,1,2--Trichloroethylene	22	35	87
1,1 Dichloropropane	22	20	88.6
1,2-Dichloropropane	23	20	95.6
1,1,3-Trichlor ethane	24	20	113
1,3 Dichloropropane	27	50	120.5
1,1,2,2-Tetrachloroethane	33	30	146.2
Pentachloroethane	34		162.5
Hexachloroethane	34	10	163

The sensitivity of the detector to the various products relative to dichloroethylene whose "effective carbon number" was taken as 2 was determined by analysing standard mixtures of two or three of them and comparing the peak areas. The peak areas were measured with the integrator and were converted to areas measured on the 100 mv x 10^{-9} amp range ~~at a flow rate of 35 ml. H_2/min~~ by the following relationship.

area(100 mv 10^{-9} amp, 35 ml. H_2 min) = (measured area) x (attenuation factor) ~~x (measured flow rate/35).~~

The "effective carbon numbers" of the various compounds were found to be:

	Effective Carbon Number
cis-Dichloroethylene	2
trans-Dichloroethylene	2
iso Propyl chloride	3
n Propyl chloride	3
Tetrachloroethane	1.359
Pentachloroethane	1.247
Hexachloroethane	0.1134
1,2-dichloroethane	1.346
1,1,2 Trichloroethane	1.214
1,1,2 Trichloroethylene	2

It was unnecessary to know the absolute sensitivities to calculate the results of the competitive experiments but desirable in order that the total amount of reaction could be estimated. By using samples of known volume and

pressure the absolute sensitivity for trans-dichloroethylene was found to be:

$$3750 \times 100 \ mv \times 10^{-9} \ = 1 \ \mu \ mole \ (trans \ DCE)$$

integrator units.

4.   Experimental Procedure

The kinetic apparatus was thoroughly evacuated and each of the reactants in turn was thoroughly degassed. This latter operation was done by pumping on the reactant at $-194^{\circ}C$ for about 20 minutes, ceasing pumping, allowing the reactant to warm to room temperature to free any occluded air, and then freezing down again and pumping for a further 10 minutes.

A pressure of olefin was then measured into the reaction vessel the excess frozen into the removable trap 1 and manifolds 1 and 2 re-evacuated before being filled with a pressure of propane of a magnitude calculated to give the desired pressure in the reaction vessel. The valve to the reaction vessel was opened, the pressure allowed to equilibrate, the valve reclosed and the excess propane condensed into removable trap 1. This procedure was repeated for the addition of chlorine and any of the inert diluents which were added to the reaction mixture. When the last component of the mixture was introduced into the reaction vessel two minutes were allowed to pass to allow for complete mixing of the components. The reaction mixture was then illuminated for a time and with an intensity of light sufficient to give the desired amount of reaction (< 10% consumption of any component). The required conditions were obtained by trial and error and were so adjusted that the illumination time was between 1 minute and 4 minutes.

1 mm. oxygen was measured into manifold 2 and 1 mm nitrosyl chloride

into manifold 3. When sufficient reaction had occurred illumination was discontinued and the reaction inhibited by opening the taps to manifolds 2 and 3 in rapid succession. After 30 seconds the reaction products were condensed into the pump down trap on manifold 3, complete transference of the products being ensured by pumping through for 10 minutes. The excess propane, chlorine and inert diluent were then distilled off at - 120°C (melting alcohol slush bath). In the set of runs in which argon was the inert diluent, since it was a non condensable and might tend to carry over the more volatile reaction products in the argon stream, as complete transference as possible of the reaction products to the analysis system was effected by pumping through the pump down trap on manifold 3 and also through the U-tube of the injection system which had been cooled to -194°C. In this way it was hoped that no n-propyl chloride might be carried over in the stream of uncondensed argon but at high argon pressure this could not be certain.

As can be seen the exact procedure adopted, and particularly the times involved, depended on the composition of the reaction mixture, but the general method was as follows: the pump down trap was heated up to -120°C by immersing in melting alcohol after the valve to manifold 3 had been closed, the valve to the vacuum was then opened and pumping continued for about 20 minutes. The reaction products, freed from the greater proportion of propane, chlorine, etc., were then transferred to the injection U-tube in preparation for analysis.

Inhibition Procedure and Removal of Chlorine.

The chlorination of the olefin/propane mixture had an appreciable rate

in room light and it was necessary, therefore, to inhibit the process to ensure that further reaction did not occur during the transference of the reaction products and the removal of excess chlorine by distillation. Oxygen and nitrosyl chloride are both well established inhibitors of chlorination reactions (62) and nitrosyl chloride has already been used as an inhibitor by Dainton (51) and Knox (53). In this work oxygen was used as inhibitor in manifold 2 to avoid introduction of NOCl into the kinetic part of the system and NOCl was used in manifold 3 and during distillation because of the low solubility of oxygen at -120°C.

In order to check that the reaction products were not lost during the removal of the excess propane, chlorine and inert diluent, a mixture was prepared in which the components were present in approximately the proportions expected from a reaction and submitted to the usual distillation procedure, the distillate being condensed out at -194°C and analysed. Apart from propane only traces of iso propyl chloride were obtained together with a small amount of the excess olefin. The excess olefin did not enter into the calculations and chlorine atom attack at the primary position in propane was used as the competitive standard so that it was unnecessary to know the amounts of iso propyl chloride produced and the procedure was regarded as satisfactory. The reproducibility of the kinetic results using the procedures outlined above was of the order of $\pm$ 7%.

5.   <u>Calculation of Results</u>.   The product peak areas on the chromatographs were measured and converted to the areas on the standard 100 mv $\times 10^{-9}$ amp and 35 ml H_2/min as indicated in section II 3.   The following functions were then calculated

(a)   Trans Dichloroethylene/Propane System

$$R_{nPrCl}^{TCE} = \frac{TCE_{formed.}}{nPrCl_{formed.}} \cdot \frac{PrH_{initial}}{t\text{-}DCE_{initial}} \qquad \text{II. 1}$$

$$R_{nPrCl}^{cisDCE} = \frac{c\text{-}DCE_{formed.}}{nPrCl_{formed.}} \cdot \frac{PrH_{initial}}{t\text{-}DCE_{initial}} \qquad \text{II. 2}$$

$$R_{TCE}^{c\text{-}DCE} = \frac{c\text{-}DCE_{formed.}}{TCE_{formed}} \qquad \text{II. 3}$$

Taking account of the effective carbon number given in section II 3 we have

$$R_{nPrCl}^{TCE} = \frac{(\text{Area TCE/effective carbon number})}{\text{Area}nPrCl \ /\text{effective carbon number}} \times \frac{P_{PrH}}{P_{t\text{-}DCE}} \qquad \text{II. 4}$$

$$= \frac{\text{Area TCE/1.359}}{\text{Area}nPrCl \ / \ 3} \times \frac{P_{PrH}}{P_{t\text{-}DCE}} \qquad \text{II. 5}$$

$$R_{nPrCl}^{c-DCE} = \frac{\text{Area c-DCE}/2}{\text{Area nPrCl}/3} \times \frac{P_{PrH}}{P_{t-DCE}} \qquad \text{II. 6}$$

$$R_{TCE}^{c-DCE} = \frac{\text{Area c DCE}/2}{\text{Area TCE}/1.359} \qquad \text{II.7}$$

(b) <u>Trichloroethylene/Propane System</u>

$$R_{nPrCl}^{PCE} = \frac{\text{Area PCE}/1.247}{\text{Area nPrCl}/3} \times \frac{P_{PrH}}{P_{TrCE}} \qquad \text{II. 8}$$

(c) <u>Tetrachloroethylene/Propane system</u>

$$R_{nPrCl}^{HCE} = \frac{\text{Area HCE}/0.1134}{\text{Area nPrCl}/3} \times \frac{P_{PrH}}{P_{tetra\ CE}} \qquad \text{II. 9}$$

(d) <u>Ethylene/Propane System</u>

$$R_{nPrCl}^{Dichloroethane} = \frac{\text{Area Dichloroethane}/1.346}{\text{Area nPrCl}/3} \times \frac{P_{PrH}}{P_{C_2H_4}} \qquad \text{II. 10}$$

(e) <u>Vinyl Chloride/Propane System</u>

$$R_{nPrCl}^{Trichloroethane} = \frac{\text{Area Trichloroethane}/1.214}{\text{Area nPrCl}/3} \times \frac{P_{PrH}}{P_{VC}} \qquad \text{II. 11}$$

where P_{PrH} and P_{olefin} are the initial pressures of propane and olefin.

CHAPTER III

RESULTS

Early experiments were undertaken with the aim of trying to resolve some of the differences between the sets of data of Knox and Riddick (53) and of Ayscough et al (51, 52, 59). It was also hoped to meet some of the objections of Ayscough et al (59) to the competitive technique as applied to the chlorination of dichloroethylene and to try to clarify what appeared to be an anomaly in Riddick's data.[*] Trans-dichloroethylene, therefore, was chlorinated in competition with propane at temperatures of $79^{o}C$ and $133^{o}C$ (The results are shown in Tables III. 1 and III. 2)

Notes: Corresponding tables and figures are given the same number. When a particular figure refers to more than one table, the additional tables are given a coding letter.

o

TABLE III 1 (DCE) .)   DEPENDENCE OF R ON CHLORINE PRESSURE TEMPERATURE 79.5°C

Run No.	trDCE Pressure	PrH Pressure	Cl$_2$ Pressure	Total Pressure	Area nPrCl	Area trDCE	Area cDCE	Area TCE	TCE R_{nPrCl}	cDCE R_{nPrCl}	cDCE R_{TCE}	TCE $R_{c\rightarrow DCE}$	nPrCl $R_{c\rightarrow DCE}$
	mm., Hg					100 mv	10^{-9} amp						
4	21.35	21.35	58.16	100.8	1338	-	812	314	0.52	0.91	1.76	0.57	1.1
5	21.35	21.35	68.25	110.9	1826	25810	960	387	0.47	0.79	1.69	0.59	1.27
6	21.35	21.35	105.2	148.0	3963	25860	1728	876	0.49	0.65	1.34	0.75	1.54
7	21.35	21.35	178.9	221.8	1536	29080	477	405	0.58	0.47	0.80	1.25	2.14
8	21.35	21.35	47.95	90.8	972	28630	503	125	0.28	0.78	2.74	0.37	1.31
9	21.35	21.35	58.12	100.8	2100	28790	1044	376	0.42	0.75	1.79	0.56	1.33
10	21.35	21.35	185.2	227.8	8640	22060	4257	2784	0.71	0.74	1.04	0.96	1.35
11	21.35	21.35	234.8	277.8	6750	22180	2979	2375	0.76	0.67	0.87	1.15	1.50
12	21.35	21.35	23.84	66.5	393	27700	291	85	0.68	1.11	2.33	0.47	0.90
13	21.35	21.35	180.9	224.0	1470	22400	579	325	0.49	0.59	1.21	0.83	1.70
14	21.35	21.35	153.6	196.1	2880	19520	1344	849	0.65	0.700	1.08	0.93	1.43
15	21.35	21.35	136.2	179.2	4230	22380	2025	1239	0.65	0.72	1.11	0.90	1.39
16	42.70	-	104.4	147.10	-	-	327	326	.	-	1.12	0.89	.
17	42.70	-	106.2	149.0	-	-	2183	1014			1.47	0.68	
18	42.70	-	104.3	147.0	-	-	2094	1305			1.09	0.92	
19	10.73	10.73	6.07	27.58	129.3	793	72.2	15.6	0.27	0.84	3.14	0.32	1.20
20	3.7	3.7	7.8	15.18	77	-	42.1	7.8	0.22	0.82	3.70	0.27	1.20
21	0.69	0.69	2.14	3.50	12.2	-	6.6	1.05	0.19	0.81	2.84	0.35	1.24
22	3.57	3.57	16.11	23.24	678	2000	411	61	0.20	0.91	4.59	0.218	1.10
23	6.52	6.52	34.02	47.10	756	6340	437	89	0.26	0.87	3.32	0.30	1.15
24	8.76	8.76	20.51	38.0	326.7	5080	115	27.9	0.19	0.53	2.86	0.36	1.90
25	5.6	5.6	13.33	26.52	275.4	3660	169.2	9.6	0.08	0.92	12.50	0.08	1.09
26	9.61	9.61	45.42	44.70	596	5940	242	60	0.22	0.61	2.71	0.37	1.45

TABLE III   2 (DCE)

DEPENDENCE OF R ON CHLORINE PRESSURE   TEMPERATURE 133°C

Run No.	tr.DCE Pressure	PrH Pressure	Cl_2 Pressure	Total Pressure	Area nPrCl	Area trDCE	Area c-DCE	Area TCE	TCE R_{nPrCl}	cDCE R_{nPrCl}	cDCE R_{TCE}	TCE R_{cDCE}	nPrCl R_{cDCE}
		mm. Hg			100 mv		10^{-9} amps						
27	21.35	21.35	10.00	52.7	549.3	–	302	12.3	0.05	0.82	16.7	0.06	1.22
28	21.35	21.35	24.66	67.4	1037	9950	504	39.3	0.08	0.73	8.71	0.12	1.37
29	21.35	21.35	7.65	50.3	472	–	55	1.5	0.03	0.84	25.0	0.04	1.19
30	21.35	21.35	(25.6 ?)	68.3	306.3	–	106.3	13.9	0.01	0.52	9.8	0.102	1.92
31	21.35	21.35	4.0	46.7	157.5	–	82.5	3.9	0.005	0.79	14.3	0.07	1.27
32	21.35	21.35	111.6	150.0	4840	–	3726	1599	0.73	1.15	1.59	0.63	0.87
33	21.35	21.35	112.1	130.8	4803	–	2952	1311	0.60	0.92	1.53	0.65	1.09
34	21.35	21.35	112.3	151.0	5425	–	5497	2061	1.03	1.86	1.47	0.68	0.97
35	21.35	21.35	62.3	105.0	3339	–	1758	336	0.22	0.79	3.56	0.28	1.28
36	21.35	21.35	63.1	105.1	3231	–	179.7	320	0.22	0.83	3.84	0.26	1.21
37	21.35	21.35	86.7	130.3	4131	–	2295	387	0.21	0.83	4.0	0.25	1.21
38	21.35	21.35	18.74	230.1	3984	–	2199	727	0.41	0.85	2.04	0.49	1.18
39	21.35	21.35	150.8	193.5	2164	–	801	248	0.25	0.56	2.18	0.46	1.8
40	21.35	21.35	111.2	153.9	2883	–	1329	278	0.21	0.69	3.22	0.31	1.45
41*	21.35	21.35	88.0	130.7	4110	–	3147	849	0.46	1.15	2.50	0.40	0.87
42*	21.35	21.35	62.1	104.8	2649	–	1272	282	0.24	0.72	3.00	0.33	1.39
43*	21.35	21.35	191.3	234.0	3393	–	3632	2040	1.32	1.52	1.14	0.88	0.66
44*	21.35	21.35	114.2	156.9	3381	–	2004	626	0.28	0.89	3.22	0.31	1.12
45*	21.35	21.35	25.6	68.3	2201	–	1194	95	0.10	0.81	8.55	0.12	1.24
46*	21.35	21.35	132.9	175.6	2291	–	1533	674	0.35	1.17	1.65	0.61	0.86
47*	21.35	21.35	62.7	105.4	3282	–	1836	504	0.34	0.84	2.50	0.40	1.19

Run 47   Dark time 35 minutes;   no illumination

* Packed Reaction Vessel ; S/V ratio x 10

Figure III 1

Dependence of R_{nPrCl}^{TCE} on Pressure

Chlorine Pressure = Variable

Temp. 79°C

Temp. 133°C

Total Pressure (mm. Hg)

R_{nPrCl}^{TCE}

1.0

0.6

0.2

0

100

200

300
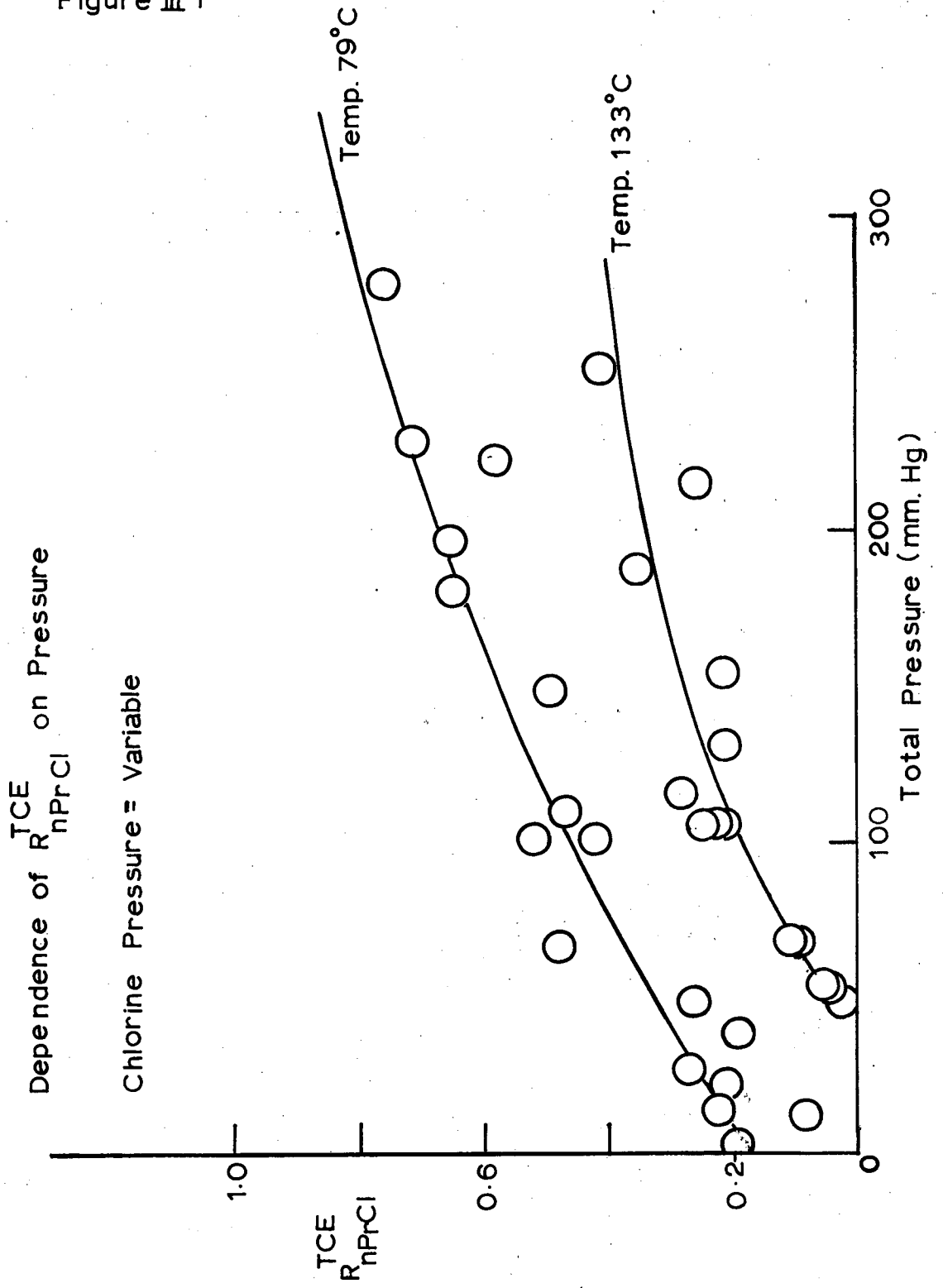
Figure III 2
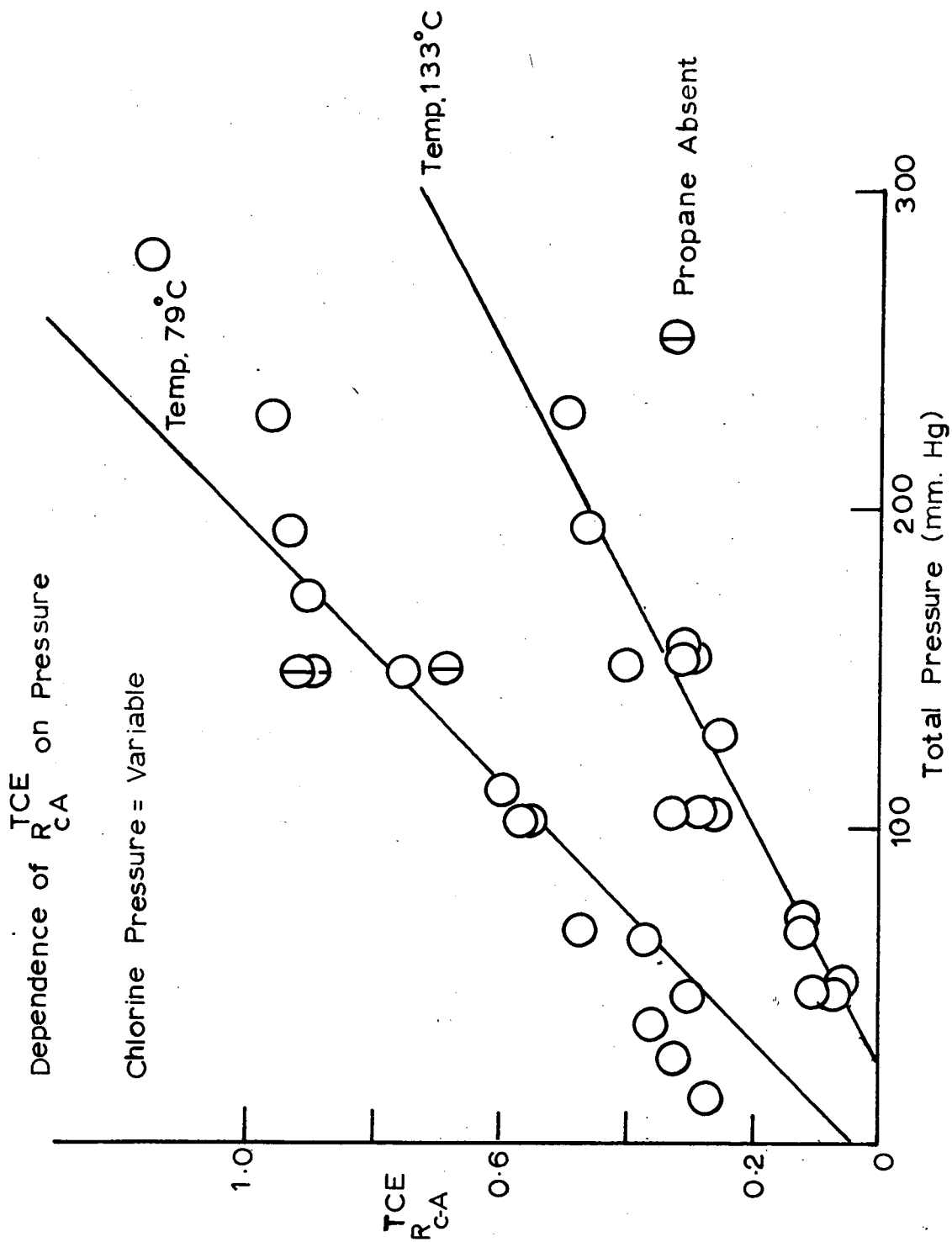
The apparent anomaly in the results of Knox and Riddick was their

necessity of including a reaction (d)

$$viz \quad ACl^* = AC_1 \tag{d}$$

where reaction (d) is unimolecular deactivation to give and inactive form,

in their reaction scheme

$$Cl_2 + h = 2 Cl \tag{1}$$

$$Cl + trA = ACl^* \tag{2}$$

$$ACl^* = x \, cis\text{-}A + (1\text{-}x) \, tr\text{-}A + Cl \tag{a}$$

$$ACl^* + Mi = ACl + Mi \tag{bi}$$

$$ACl^* + Cl_2 = y \, cis\text{-}A + (1\text{-}y) \, tr\text{-}A + Cl_3 \tag{c1}$$

$$ACl^* + A = z \, cis\text{-}A + (1\text{-}z) \, tr\text{-}A + ACl \tag{c2}$$

$$ACl^* + A = z' \, cis\text{-}A + (1\text{-}z') \, tr\text{-}A + ACl^* \tag{c3}$$
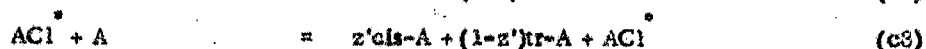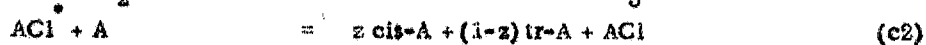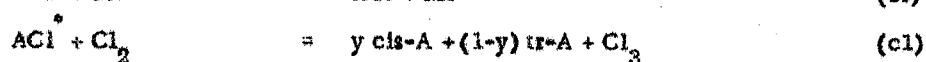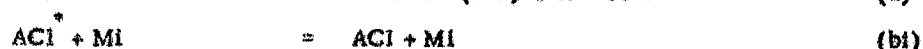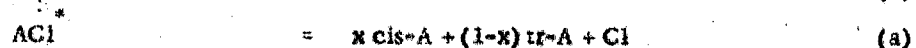
Where reaction (a) is unimolecular decomposition of the active radical;

(b) is bimolecular deactivation of the active radical; and (c) is bimolecular

atom transfer to a suitable acceptor.

The need of inclusion of reaction (d) into the scheme derived from the

fact that plots of $R_{iA}^{ACl_2}$ against chlorine pressure, when extrapolated back

to zero deactivant pressures, showed an intercept whose value depended

not only on temperature (being positive at $79^\circ C$ and $35^\circ C$ and negative at

$133^\circ C$) but also on the structure of the starting isomer.

Runs 20 to 26 at $79^\circ C$ and 27 to 31 at $133^\circ C$ were therefore conducted

at low total deactivant pressures. The values of $R_{cis\text{-}A}^{ACl_2}$ when plotted as a

function of total pressure fall on the extrapolated lines at $79^\circ C$ and $133^\circ C$.

These lines had been calculated by Knox and Riddick from their final set of

rate constants (Tables I. b VII and VIII) assuming reactions c1, c2 and c3

to have a negligible rate.

The expression for $R_{cis\text{-}A}^{ACl_2}$ is

$$R_{cis\text{-}A}^{ACl_2} = \frac{\sum kbi \, [Mi] + k_d}{(1\text{-}x) \, k_a} \tag{III. 1}$$

which at zero pressure becomes

$$R_{cis-A}^{ACl_2} = \frac{k_d}{(1-x)\,k_a} \qquad\qquad \text{III. 2.}$$

Therefore values of kd/ka and hence values of kd can be obtained from the intercept of the pressure dependence of $R_{cis-A}^{ACl_2}$ on the ordinate. Thus kd has a finite value at $79^{\circ}C$ and a negative one at $133^{\circ}C$ (Figure III. 2)

The finite value of kd at $79^{\circ}C$ implies the existence of a proportion of ACl° radicals which decompose so slowly that they are always deactivated by collision at pressures above 4 mm Hg (the minimum measurable pressure). These radicals are denoted by ACl' and it is suggested that they are formed from ACl° by a direct unimolecular process (d). This process can hardly be radiational which, in general, is much too slow. A unimolecular transformation into a different form of activated radical is at first sight attractive, tempting one to postulate the existence of normal and bridged forms of ACl*.

$$\text{CHCl}.\ \text{CHCl}_2^{\circ} \quad \text{and} \quad \text{CHCl} - - - - \text{Cl} - - - - \text{CHCl}$$

However the high rate of decomposition and of internal rotation of the form which can decompose demands that the normal structure be assigned to ACl*. Since the bridged form would have a lower entropy than the normal structure and since both ACl° and ACl must have the same energy, the bridged form will readily revert to the normal form. In the limit of low pressure all activated molecules therefore decompose via the normal form and kd should be zero.

Knox therefore suggests that a more reasonable explanation is that kd is an artefact and results from the pressure dependence of ka. ka will decrease as the pressure is decreased, according to unimolecular reaction theory and the gradients of lines in figure III 2 will accordingly increase as the deactivant pressure approaches zero. A value of kd/ka of 0.1 at $79^{o}C$ is obtained implying that about 10% of ACl* from trans-DCE decomposes at least 50 times slower than the average.

The apparently negative value of kd at $133^{o}C$ has no obvious explanation and it is suggested that it may result from two factors (1) the fall off in ka and (ii) the gradual onset of reaction (4) which is expected to become important about this temperature.

One of the objections raised by Ayscough et al (59) to the results of Riddick was that the propyl radicals formed in reaction (2') might catalyse isomerization of the olefin. However, experiments carried out in the absence of propane (Figure III 2) show the same rate of addition to isomerization as those in the presence of propane at the same total pressure.

It was concluded, therefore, that the results obtained by Knox and Riddick were sound, further verification of this being found in the fact that the lines drawn in figures III 1 and 2 were calculated from the values of the rate constants derived from these results. It has since been discovered that the cis and trans-DCE of Ayscough et al (51) had in fact been wrongly

labelled, resolving many of the differences in the results of cis-DCE but leaving still considerable discrepancies in those of trans-DCE.

It was decided to chlorinate trichloroethylene in competition with propane in an effort to observe experimentally the theoretical prediction that the rate of unimolecular decomposition of the active tetrachloroethyl radical would be less than the rate of decomposition of the active trichloroethyl radical. Qualitatively the theoretical prediction can be understood from the following considerations. Since the radical formed by the addition of a chlorine atom to trichloroethylene will have a greater number of low energy oscillators than that formed by the addition of a chlorine atom to dichloroethylene (the C-Cl bond vibrational frequency is lower than the C-h bond frequency), for a given energy the active tetrachloroethyl radical will have a greater number of accessible configurations than the active trichloroethyl radical. However, since the zero point energies of the activated complexes of each of these radicals is nearly the same, for the same given energy, each activated complex will have nearly the same non-fixed energy; this non-fixed energy is small in comparison with the mobile energy of the active radical and so, although the activated tetrachloroethyl complex will have a greater number of accessible configurations than the activated trichloroethyl complex, the increase will not be nearly so marked as in the case of the radicals. Therefore, since the rate of unimolecular decomposition is proportional to the ratio of the number of quantum states

of the activated complex to the number of quantum states of the active radical, the tetrachloroethyl radical should decompose slower than the trichloro-ethyl radical. Experimental verification of this prediction would be in the observation that $R_{nPrCl}^{ACl_2}$ would reach a limiting high pressure value at a lower total pressure for trichloroethylene than for dichloroethylene.

The dependence of R_{nPrCl}^{PCE} on chlorine and propane pressures at $79^{\circ}C$ (boiling benzene) is shown in figures III. 3 and 4. Comparison of these with figure III. 1 shows a steeper curvature of R_{nPrCl}^{PCE} than of R_{nPrCl}^{TCE} with pressure and a flattening off at lower total pressure, as predicted by the theory.

Whereas in the chlorination of dichloroethylene it was possible to obtain the rate of unimolecular decomposition of the active trichloroethyl radical directly by observing the rate of production of the addition compound relative to the rate of production of the geometrical isomer, as a function of pressure (i. e. the pressure dependence of $R_{isomerA}^{ACl_2}$) no direct measure of the rate of unimolecular decomposition of the tetrachloroethyl radical was possible.

The mechanism of the chlorination of trichloroethylene is exactly analogous to that for the chlorination of dichloroethylene and is

$$Cl_2 \quad + \quad h\nu \quad = \quad 2Cl \tag{1}$$

$$Cl \quad + \quad A \quad = \quad ACl^* \tag{2''}$$

$$ACl^* \quad \quad \quad = \quad A + Cl \tag{a}$$

$$\text{ACl}^* + \text{Mi} = \text{ACl} + \text{Mi} \qquad \text{(bi)}$$

$$\text{ACl} + \text{Cl}_2 = \text{ACl}_2 + \text{Cl} \qquad (3)$$
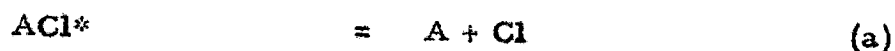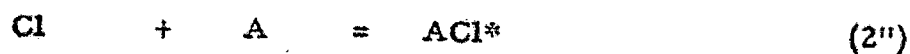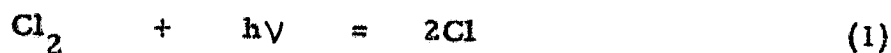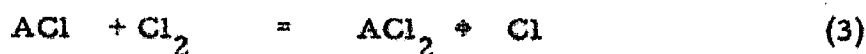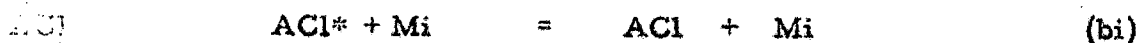
(Where A = TrCE)

which, in the presence of propane competes with the following reactions

$$\text{PrH} + \text{Cl} = \text{Pr} + \text{HCl} \qquad (2^i)$$

$$\text{Pr}^{\cdot} + \text{Cl}_2 = \text{PrCl} + \text{Cl} \qquad (3)$$
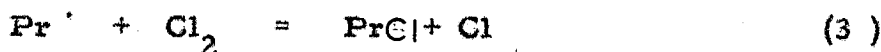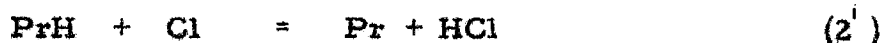
Thus, although the active radical undergoes unimolecular decomposition the product of the decomposition is indistinguishable from the reactant olefin, the only observable products of the chlorination being the addition product, pentachloroethane, and the propyl chlorides. The only observable selectivity ratio is, therefore, R^{PCE}_{nPrCl} which takes the form

$$R^{PCE}_{nPrCl} = \frac{k_2{}''}{k_2{}'} \times \frac{kb_1\left[\text{Cl}_2\right] + kb_2\left[\text{PrH}\right] + kb_3\left[\text{TrCE}\right] + kb_i\left[\text{Mi}\right]}{ka + kb_1\left[\text{Cl}_2\right] + kb_2\left[\text{PrH}\right] + kb_3\left[\text{TrCE}\right] + kb_i\left[\text{Mi}\right]}$$

III. 3

To obtain the individual rate constants $k_2{}''$, kb_1, kb_2, and ka it was necessary to chlorinate trichloroethylene over a range of chlorine and propane pressures. Details of each run were then fed into a computer i.e. for a series of experiments in which R^{PCE}_{nPrCl} was investigated as a function of chlorine and propane pressure, the pressures of each of the reactants were fed into the computer together with the experimentally observed selectivity ratios.

The computer was then programmed with a "theoretical" expression

for a selectivity ratio, obtained by modifying equation III 3 slightly so that it became

$$Rth = \frac{k_2''}{k_2'} \times \frac{[Cl_2] + (kb_2/kb_1)[PrH] + (kb_3/kb_1)[TrCE]}{ka/kb_1 + [Cl_2] + (kb_2/kb_1)[PrH] + (kb_3/kb_1)[TrCE]}$$

III. 4.

Ten arbitrarily chosen values of each of the rate constant ratios k_2''/k_2', kb_2/kb_1, and ka/kb_1 were also fed into the computer which then calculated Rth for every experimental value of chlorine, propane and trichloroethylene pressure and for every combination of the values of the rate constant ratios; i.e. for a particular combination of the values of k_2''/k_2', kb_2/kb_1, and ka/kb_1 Rth was calculated for every separate experimentally obtained chlorine, propane and trichloroethylene pressure.

The value of Rth, having been calculated for each set of pressures of the reactants for each run, was then subtracted from the experimentally observed selectivity ratio, R exp, corresponding to the reactant pressures, and the difference was squared. These squares of the differences were then summed for all the pressure dependences and for each combination of the rate constant ratios, the computer finally printing out a ten by ten by ten array of the sums of the squares of the differences for every combination of the rate constant ratios. The minimum value of these sums of squares of differences corresponded to the best fit of the experimental results and the derived rate constant ratios.

For the chlorine/propane pressure dependences in which the trichloro-ethylene pressure remained constant and small, the value of the parameter kb_3/kb_1 was assumed to be unity. It will be demonstrated later in this chapter that the collisioned deactivating efficiencies of all the gases studied were comparable, and so the error involved in making this approximation is negligibly small compared with the experimental errors.

For the chlorine/propane pressure dependences at $79^\circ C$ the minimum value of $\sum (Rth - Rexp)^2$ was obtained from the parameters.

$$\frac{k_2''}{k_2'} = 1.4, \quad \frac{ka}{kb_1} = 70, \quad \frac{kb_2}{kb_1} = 1.1$$

Hence
$$k_2'' = 1.4 \times 3.8 \times 10^{10} \text{ mole}^{-1}. \text{ l. sec.}^{-1}$$
$$= 5.3 \times 10^{10} \text{ mole.}^{-1} \text{ l. sec.}^{-1} \text{ at } 79^\circ C.$$

ka was evaluated from the parameter ka/kb_1 by making the assumption that the active intermediate, ACl*, was deactivated at every collision with chlorine. Thus kb_1 is the standard collision number for collisions of chlorine molecules with its active radical

i.e.
$$kb_1 = Z_1^\circ (ACl^*, Cl_2) = \pi \sigma_{12}^2 \frac{N}{10^3} \sqrt{\frac{8RT}{\pi \mu}}$$

where the collision diameter, δ, of the tetrachloroethyl radical was taken as 6.5 $\overset{o}{A}$ (47), that of its chlorine molecule was taken as 4.4. $\overset{o}{A}$ (63) and $\overset{o}{\delta}_{12} = \frac{1}{2}(\delta_{Cl_2} + \delta_{ACl^*})$. kb_1 for a standard pressure of 1 mm Hg is

therefore

$$kb_1 = Z^O \quad (ACl^*, Cl_2) \quad = 1.004 \times 10^7 \ (mm \ Hg)^{-1} \ sec.^{-1}$$

$$= 2.21 \times 10^{11} \ mole^{-1} l. \ sec.^{-1}$$

whence $\quad$ ka $\quad = 7.03 \times 10^8 \ sec.^{-1} \quad$ at 79^OC

The parameter kb_2/kb_1 gives the efficiency of deactivation of the hot radical by collision with propane relative to the collisional deactivating efficiency of chlorine (assumed to be unit efficient).

Hence $\quad \dfrac{kb_2}{kb_1} = x_2 \cdot \dfrac{Z \ (ACl^*, \ PrH)}{Z \ (ACl^*, \ Cl_2)}$

Where x_2 is the deactivating efficiency per collision of propane relative to chlorine. The collisional diameter of propane was taken as 5.01 $\overset{O}{A}$ (64) and therefore

$$\dfrac{kb_2}{kb_1} = x_2 \ \dfrac{1.316}{1.004}$$

Whence $\quad x_2 \quad = \quad 0.84$ as efficient as chlorine per collision.

A check on the sensitivity of the calculation to the individual rate constant ratios was accomplished by reprogramming the computer with the theoretical expression modified so that ka was calculated in relation to collisional deactivation by propane, the collisional deactivating efficiency of chlorine being calculated relative to propane.

The theoretical selectivity ratio then took the form

$$Rth = \frac{k_2''}{k_2'} \times \frac{[PrH] + (kb_1/kb_2)[Cl_2] + (kb_3/kb_2)[TrCE]}{\frac{ka}{kb_2} + [PrH] + (kb_1/kb_2)[Cl_2] + (kb_3/kb_2)[TrCE]}$$

III. 5.

The values of the rate constant ratios which gave a minimum in the expression $\sum (Rth - R\ exp)^2$ were

$$\frac{k_2''}{k_2'} = 1.4 \qquad \frac{kb_1}{kb_2} = 0.9 \quad i.e. \quad \frac{kb_2}{kb_1} = 1.1 \qquad and \qquad \frac{ka}{kb_2} = 74$$

whence the collisional deactivating efficiency of propane per collision relative to chlorine, x_2 is

$$x_2 = 0.84$$

ka was calculated making allowance for the decreased deactivating efficiency of propane and was found to be

$$ka = 74 \times 0.84 \times Z_0(ACl^*, PrH)$$

$$= 74 \times 0.84 \times 1.316 \times 10^7$$

$$= 8.18 \times 10^8 \quad sec^{-1}$$

From the parameter ka/kb_i it was possible to make a second internal check of the data. The ratio of ka/kb_1 to ka/kb_2 should correspond to the value of kb_2/kb_1 derived from the program in which the rate constants were evaluated relative to the collisional deactivating rate of chlorine; from the chlorine dependence.

$$ka/kb_1 = 70 \quad , \qquad \text{and } kb_2/kb_1 = 1.1 \ ;$$

from the propane dependence

$$ka/kb_2 = 74$$

$$\therefore \ \frac{ka/kb_1}{ka/kb_2} = \frac{kb_2}{kb_1} = \frac{70}{74} \approx 1.0$$

from the propane dependence

$$ka/kb_2 = 74$$

$$\therefore \ \frac{ka/kb_1}{ka/kb_2} = \frac{kb_2}{kb_1} = \frac{70}{74} \approx 1.0$$

Thus the method is internally consistent within its limits of experimental error.

The chlorination of trichloroethylene was investigated to see if the reaction had a heterogeneous component, by increasing the surface to volume ratio by a factor of ten. As can be seen from figure III 3 no detectable change was observed upon changing the surface to volume ratio and it was concluded that the reaction was homogeneous.

The dependence of R^{PCE}_{nPrCl} on chlorine/propane pressure was investigated at $133^{\circ}C$ (Tables III 5 and 6) at $40^{\circ}C$ (Tables III 7 and 8) and the chlorine pressure dependence was investigated at $56^{\circ}C$ to results of which are shown in Table III 9. The rate constants ka, k_2'' , kb_1 and kb_2 for all

these pressure dependences at the different temperatures were calculated by the computer "grid" method outlined above and are shown in Table III. 13. The computer program for the calculation of the rate constants is shown in Appendix (A).

The temperature dependence of the rate constant ratio k_2''/k_2' is shown in figure III. 12 and the derived activation energies and A factors are

$$A_2'' = 2.68 \pm 1.36 \times 10^{10} \text{ mole.}^{-1} \text{ l. sec.}^{-1}$$

$$E_2'' = -240 \pm 410 \text{ cal. mole}^{-1}$$

As stated in the introduction these were calculated using the following values of A_2' and E_2' as standard (31)

$$A_2' = 1.7 \pm 0.3 \times 10^{10} \text{ mole.}^{-1} \text{ l. sec.}^{-1} \text{ per H atom}$$

$$E_2' = 980 \pm 130 \text{ cal. mole}^{-1}$$

From figure III. 13

$$A_a \quad (\text{TrCE}) = 7.3 \pm 2.73 \times 10^{10} \text{ sec.}^{-1}$$

$$E_a \quad (\text{TrCE}) = 3260 \pm 380 \text{ cal. mole}^{-1}$$

The error limits were derived from reasonable maximum and minimum gradients of the graphs.

The deactivating efficiency per collision of trichloroethylene relative to chlorine was calculated from the results of the dependence of R_{nPrCl}^{PCE} on trichloroethylene pressure at 79°C (Table III. 11a). The program used for this calculation was an extension of the one used for calculating the

propane dependence, the theoretical selectivity ratio now taking the form

$$Rth = \frac{k_2''}{k_2'} \times \frac{[TrCE] + (kb_1/kb_3)[Cl_2] + (kb_2/kb_3)[PrH]}{ka/kb_3 + [TrCE] + (kb_1/kb_3)[Cl_2] + (kb_2/kb_3)[PrH]}$$

III. 6

Making use of the previously calculated collisioned deactivating efficiency

of propane the expression III 6 becomes

$$Rth = \frac{k_2''}{k_2'} \times \frac{[TrCE] + (kb_1/kb_3)[Cl_2] + (1.1 \times kb_1/kb_3)[PrH]}{ka/kb_3 + [TrCE] + (kb_1/kb_3)[Cl_2] + (1.1 \times kb_1/kb_3)[PrH]}$$

III. 7

From this program a minimum value of $\sum (Rth - R\ exp)^2$ was obtained for

the   trichloroethylene data   from the parameters

$$\frac{k_2''}{k_2'} = 1.4 \quad , \quad \frac{kb_1}{kb_3} = 0.7 \quad and \quad \frac{ka}{kb_3} = 50$$

Taking the collisional diameter, δ, of trichloroethylene to be 6.5

Å (64) the standard collision number for collision of the active radical with

trichloroethylene molecules at a standard pressure of 1 mm Hg is

$$Z\ (ACl^*,\ TrCE) = 9.86 \times 10^6\ (mm.Hg)^{-1}.\ sec.^{-1}$$

Hence

$$\frac{kb_1}{kb_3} = \frac{10.04}{x_3 \times 9.86} = 0.7$$

where x_3 is the deativating efficiency per collision of trichloroethylene relative to chlorine

$$\text{and} \quad x_3 = 1.45$$

Making allowance for the increased deactivating efficiency of trichloroethylene ka is

$$ka = 50 \times 1.45 \times 9.86 \times 10^6 \quad \sec^{-1}$$

$$= 7.15 \times 10^8 \quad \sec^{-1}$$

Finally $\quad \dfrac{kb_1}{kb_3} = \dfrac{ka/kb_3}{ka/kb_1} = \dfrac{50}{70} = 0.7$

The deactivating efficiencies of argon, carbon dioxide, and sulphur hexaflouride were obtained from the dependence of R^{PCE}_{nPrCl} as the pressures of each of these gases (Tables III 10, 11b, and 11c). The theoretical selectivity ratio had a form which was analogous to that used for the calculation of the trichloroethylene deactivating efficiency and was

$$Rth = \frac{k_2''}{k_2'} \times \frac{[Mi] + (kb_1/kb_i)[Cl_2] + (1.1 \times kb_1/kb_i)[PrH] + (1.43\overline{kb_i})[TrCE]}{\dfrac{ka}{kb_i} + [Mi] + (kb_1/kb_i)[Cl_2] + (1.1 \times kb_1/kb_i)[PrH] + (1.43kb_1)\dfrac{[TrCE]}{\overline{kb_i}}}^{kb_1}$$

$$\text{III. 8}$$

where the subscripts $i = 1$ refers to chlorine; $i = 2$ refers to propane; $i = 3$ refers to trichloroethylene; $i = 4$ refers to argon; $i = 5$ to carbon dioxide; and $i = 6$ to sulphur hexafluoride.

The rate constants derived from this program and the
experimental results are summarized in Table III. 13.

It should also be noted that the lines drawn through the points
in figures III 3 to III 11 are obtained by plotting Rth values against pressure,
the Rth values having been obtained by substituting in any of the theoretical
expressions (e. g. equations III 4, III 5 etc.) the values of the parameters
k_2''/k_2', k_a/kbl, etc. which gave a minimum value of $\sum (Rth-Rexp)^2$.
When both chlorine and propane pressure dependences of R_{nPrCl}^{PCE} were
obtained at a particular temperature, the parameters used in the
calculation of the "theoretical" line were obtained from a program which
incorporated the two pressure dependences.   Hence the same "theoretical"
line is drawn in figures III 3 and 4; 5 and 6; and 7, 8.

TABLE III 3

DEPENDENCE OF R^{PCE}_{nPrCl} ON CHLORINE PRESSURE. TEMPERATURE 79.5°C

Run No.	TrCE Pressure	PrH Pressure	Cl$_2$ Pressure	Total Pressure	nPrCl	TrCE	PCE	R^{PCE}_{nPrCl}
		mm. Hg				x 100 mv x 10^{-9}		
51 (I)	8.55	9.14	78.8	96.6	1310	-	1539	0.905*
52 (P)	8.55	9.14	39.6	57.3	101.6	942	23.1	0.591*
53 (I)	8.58	9.19	119.6	137.1	1338	-	58.4	1.12 *
54 (P)	8.55	9.03	45.1	62.6	132.3	1040	30.5	0.654*
55 (P)	8.58	9.14	22.8	40.5	94.2	1030	19.4	0.524*
56 (P)	8.35	9.11	36.2	51.9	165	1107	34.7	0.537*
57 (I)	8.63	9.02	202	220	2136	4990	859	1.02 *
59 (P)	8.76	9.23	65.5	93.5	280	1148	840	0.759*
60 (I)	8.68	9.45	139.3	157.2	2124	-	759	0.933*
62 (P)	8.76	9.44	79.5	97.6	141.5	113.5	43.2	0.79
63 (P)	8.58	7.39	23.02	41.1	46.4	1250	10.56	0.597*
66 (P)	8.67	9.36	80.5	98.3	125	1022	37.8	0.782*
67 (P)	8.58	9.44	46.0	63.9	103	955	26.24	0.622*
69 (P)	8.72	9.35	13.3	31.4	19.03	970	3.21	0.435*
70 (P)	8.55	9.15	13.4	31.1	15.8	1130	2.57	0.434*
71 (P)	8.66	9.09	20.34	38.1	19.33	1210	3.51	0.457*
72 (P)	8.72	9.06	45.3	63.1	69.15	-	17.19	0.620*
73 (I)	8.35	9.23	121.0	138.8	880	5540	261	0.77 *
74 (P)	8.58	9.14	34.9	52.7	97.95	1158	20.04	0.324*
75 (P)	8.67	9.23	53.7	71.6	11.11	-	3.71	0.852
76 (P)	8.62	9.32	53.2	71.1	121.8	1095	30.15	0.640
77 (I)	8.55	9.19	136.0	153.5	1551	5570	643	1.07
78 (P)	8.80	9.02	53.9	71.4	160.9	-	46.74	0.713
79 (P)	8.55	9.14	54.4	71.9	194.3	1389	52.29	0.691
80 (I)	8.55	9.19	64.3	81.9	804	6460	231	0.743
81 (P)	8.58	9.10	13.22	30.9	51.6	1433	9.2	0.453
82 (P)	8.68	9.06	12.96	30.7	26.68	1420	4.39	0.413
83 (P)	8.76	8.89	22.91	40.5	52.44	1425	8.58	0.399
84 (I)	8.34	8.72	35.3	52.3	447.6	10940	121.2	0.686
85 (I)	8.62	8.93	80.0	97.2	612	11240	170	0.708

*   Packed Vessel; surface/volume ratio x 10.   (P)   Peak areas planimetered

(I)   Peak areas measured by integrator.

TABLE III 4

DEPENDENCE OF R_{nPrCl}^{PCE} ON PROPANE PRESSURE TEMPERATURE 79.5°C.

| Run No. | Pressure | (mm.Hg) | | | $\times 100 \frac{m}{mv} \times 10^{-9}$ amp | | | |
		Cl_2 Pressure	PrH Pressure	Total Pressure	Area nPrCl	Area TrCE	Area PCE	PCE R_{nPrCl}
186	8.55	23.22	8.59	40.3	311.1	6780	69.2	0.537
188	8.46	23.04	19.67	51.5	144.8	7190	16.7	0.685
191	8.55	23.04	20.2	51.8	564.9	7450	51.6	0.519
196	8.68	23.40	66.00	98.1	702	7300	33.5	0.872
197	8.72	23.04	66.80	98.5	470.1	7410	17.64	0.693
199	8.55	23.04	20.3	52.0	393.9	7240	33.74	0.488
202	8.62	23.4	103.0	135.2	1121	7730	36.6	0.936
203	8.72	22.94	98.8	130.3	910	7610	27.45	0.822
209	9.55	23.10	43.3	74.9	932	7370	57.0	0.744
210	8.58	23.05	43.5	75.0	1042	7060	61.8	0.722
215	8.46	23.10	66.0	97.5	433.5	7120	19.2	0.832
217	8.51	23.04	157.7	189.0	1236	7340	25.8	0.932
219	8.62	23.18	8.68	40.3	503.7	6920	121	0.595
220	8.58	23.2	108.2	137.8	1061	7260	31.9	0.908
221	8.55	23.25	82.9	119.8	1167	6920	42.5	0.869
222	8.51	22.84	134.2	165.3	1306	7360	34.4	1.00
223	8.55	22.9	134.2	165.7	1293	7180	31.3	0.913
224	8.67	22.9	157.0	188.6	709	7290	18.3	1.12

All peak areas were measured by integrator.

TABLE III 5

DEPENDENCE OF R_{nPrCl}^{PCE} ON CHLORINE PRESSURE   TEMPERATURE $133^{\circ}C$

Run No.	mm.Hg				$100\ mv \times 10^{-9} amp$			R_{nPrCl}^{PCE}
	TrCE Pressure	PrH Pressure	Cl_2 Pressure	Total Pressure	Area nPrCl	Area TrCE	Area PCE	
88(P)	8.42	8.68	84.5	101.7	84.69	2114	13.16	0.384
89(P)	8.46	8.89	84.7	102.3	343.5	2116	45.2	0.332
90(P)	8.55	8.58	59.4	76.3	213.3	2180	21.09	0.239
91(P)	8.42	8.68	59.2	76.3	225.8	2174	30.99	0.339
92(P)	8.55	8.58	57.0	76.1	129.5	2130	14.34	0.267
93(I)	8.55	8.55	102.2	119.2	1342	10460	262.4	0.434
94(I)	8.55	8.62	103.1	120.1	1717	10520	282	0.398
95(P)	8.58	8.55	25.2	42.2	75.35	2210	6.22	0.198
96(I)	8.58	8.55	25.2	62.2	290.4	10120	14.5	0.120
97(I)	8.55	8.58	116.4	133.7	2223	10110	387	0.421
98(I)	8.55	8.76	116.2	133.6	1675	10790	312	0.460
99(I)	8.58	8.55	115.6	132.9	1356	9640	246.9	0.435
102(I)	8.35	8.58	212	228.2	1282	7530	351.6	0.663
103(I)	8.58	8.58	212.4	230.0	954	7530	275.1	0.623
104(P)	8.58	8.62	34.4	51.6	28.0	134.1	4.05	0.369
105(P)	8.62	8.55	34.6	51.8	27.1	-	3.36	0.294
108(I)	8.58	8.55	129.0	146.0	478.8	11050	82.5	0.418
109(I)	8.58	8.62	129.2	146.2	263	16720	56.1	0.515
110(P)	8.62	8.50	25.2	42.2	39.45	2638	3.0	0.180
111(P)	8.38	8.62	47.4	66.5	125.9	2530	11.3	0.216
112(P)	8.55	8.62	49.3	66.6	92.84	2550	9.15	0.236
113(I)	8.47	8.58	152.7	169.9	1806	11730	299	0.405
114(I)	8.62	8.42	153.4	170.6	980	-	1944	0.465
115(I)	8.58	8.62	153.8	170.9	570.3	-	98.7	0.42
116(I)	8.58	8.50	153.6	170.6	329.4	-	79.4	0.574
117(P)	8.58	8.50	15.17	32.3	10.42	-	0.95	0.216
118(P)	8.55	8.45	18.82	32.8	12.70	-	1.06	0.199
119(I)	8.58	8.76	15.57	32.9	68.25		6.58	0.236

(P)   Peak areas planimetered

(I)   Peak areas measured by integrator

TABLE III   6

$$\text{DEPENDENCE OF } R_{nPrCl}^{PCE} \quad \text{ON PROPANE PRESSURE TEMPERATURE } 133^\circ C$$

Run No.	mm. Hg				m100mv x 10^{-9} amp			
	PTrCE Pressure	Cl_2 Pressure	PrH Pressure	Total Pressure	Area nPrCl	Area TrCE	Area PCE	R_{nPrCl}^{PCE}
246	8.68	22.9	7.95	39.5	2137	6550	311.4	0.320
247	8.58	23.0	7.78	39.4	1134	6760	152.7	0.292
249	8.55	23.0	48.0	79.4	1269	6540	41.5	0.442
251	8.50	23.3	28.4	60.2	1350	6560	54.5	0.342
252	8.55	23.5	28.5	60.5	691	6730	33.2	0.384
253	8.72	23.2	47.7	79.7	872	6380	27.3	0.412
254	8.55	23.3	66.0	97.9	1465	6780	39.61	0.489
255	8.58	23.0	66.2	97.9	1818	6870	29.46	0.301
257	8.76	22.9	83.9	115.3	1694	8810	25.6	0.348
259	8.55	23.2	108.8	140.0	2097	7240	26.8	0.391
262	8.62	22.9	66.0	97.5	2390	6980	48.9	0.376
264	8.72	23.2	28.94	60.8	1442	6880	55.35	0.306
265	8.55	23.2	8.20	40.0	1260	6920	96.51	0.175
266	8.58	22.7	64.6	97.9	1928	7150	38.64	0.374
269	8.55	23.0	84.7	116.1	1735	-	31.4	0.432
270	8.72	23.0	85.1	116.9	1351	-	26.5	0.460
272	8.76	22.9	110.0	141.6	1556	-	28.56	0.553
273	8.55	22.8	132.1	163.1	8.31	-	11.55	0.517
274	8.55	22.8	132.0	163.4	1308	-	20.8	0.590
275	8.58	22.9	109.2	140.8	1108	-	15.7	0.433
276	8.62	22.9	154	185.3	3789	6790	44.4	0.502

All peaks were measured by integrator

TABLE III   7

DEPENDENCE OF R^{PCE}_{nPrCl} ON CHLORINE PRESSURE. TEMPERATURE $40^{\circ}C$

Run No.	TrCE Pressure	PrH Pressure	Cl_2 Pressure	Total Pressure	Area nPrCl	Area TrCE	Area PCE	PCE RnPrCl
		mm. Hg			$\times 100mv \times 10^{-9}$ amp			
122	8.55	8.67	23.4	40.6	115.9	4790	32.1	1.10
123	8.58	8.58	23.44	40.6	297	4740	101.1	0.835
125	8.55	8.67	31.6	48.9	53.4	5240	162	0.740
127	8.55	8.72	31.94	49.2	287.7	4600	89.7	0.766
128	8.55	8.55	50.60	67.8	1800	14650	834	1.11
137	8.55	8.72	93.8	111.1	583.5	78.10	373	1.57
138	8.55	8.55	108.9	126.0	475.2	7850	325.2	1.65
160	8.55	8.55	126.2	143.4	271.2	7950	185.4	1.65
144	8.67	8.46	129.4	142.1	364.4	8880	214.5	1.40
149	8.62	8.55	78.1	90.3	207.3	8200	120	1.38
150	8.55	8.55	78.1	90.3	134.3	8440	88.8	1.59
151	8.62	8.38	126.1	143.2	284.4	8100	186	1.47
158	8.35	8.67	68.6	85.8	135	7720	83	1.50
159	8.55	8.62	68.3	85.5	107.1	7810	65.1	1.48
160	8.50	8.67	68.7	85.8	92.9	8210	56.0	1.68
162	8.58	8.46	169.9	187.0	184.4	6950	123.9	1.59
163	8.55	8.67	167.0	186.8	100.7	7050	76.1	1.69
168	8.58	8.58	171.8	189.0	276.3	6700	174.6	1.52
170	8.62	8.50	193.5	210.6	145.7	6680	99.5	1.67
171	8.66	8.50	192.5	209.9	185.0	7250	120.8	1.56
172	8.35	8.29	49.8	66.8	51.2	7160	29.73	1.44
174	8.58	8.46	78.4	95.3	86.9	7100	50.5	1.42
176	8.55	8.55	94.4	111.8	202.7	7050	115.7	1.33
181	9.58	8.55	32.4	49.6	109.6	6820	53.3	1.18

TABLE III 8

$$\text{DEPENDENCE OF } R^{PCE}_{nPrCl} \text{ ON PROPANE PRESSURE· TEMPERATURE } 40^{\circ}C$$

Run No.	TrCE Pressure	Cl2 Pressure (mm. Hg)	PrH Pressure	Total Pressure	Area nPrCl	Area TrCE (x100 mv)	Area PCE (x 10^{-9} amp)	R^{PCE}_{nPrCl}
328	8.76	22.3	8.89	39.9	65.7	11090	26.4	0.983
230	8.58	23.10	22.30	54.0	560.1	10760	134.4	1.50
332	8.62	23.2	44.3	76.1	1097	10780	123.9	1.39
333	8.58	23.4	44.7	77.7	1000	9750	111.9	1.40
334	8.76	23.2	66.2	98.2	1854	10610	123 9	1.21
335	8.55	22.9	65.5	96.8	135.3	10680	93.3	1.27
336	8.62	23.1	86.7	118.3	1276	10490	72.0	1.36
337	8.55	22.9	86.9	118.3	1539	10400	84.3	1.34
338 (P)	8.55	23.2	110.0	141.4	406.3	2120	17.83	1.37
339 (P)	8.55	23.3	109.9	141.4	456	2320	18.83	1.27
341	8.62	23.4	22.4	54.4	436.5	10170	88.8	1.27
342	8.72	23.3	22.4	54.6	489.6	10170	86.7	1.11

(P) Peak area planimetered -
    all other peaks were measured by integrator

TABLE III 9

DEPENDENCE OF R^{PCE}_{nPrCl} ON CHLORINE PRESSURE TEMPERATURE $56^{o}C$

Run No.	TrCE Pressure	PrH Pressure	Cl_2 Pressure	Total Pressure	Area nPrCl	Area TrCE	Area PCE	R^{PCE}_{nPrCl}
		mm. Hg			x 100 mv x 10^{-9}amps			
225	8.58	8.89	71.5	88.9	344.4	7510	155.7	1.13
226	8.76	8.55	71.7	89.0	354.9	8050	157	1.04
228	8.50	8.76	34.1	51.4	129.7	7550	411.3	0.786
231	8.58	8.50	54.3	71.2	261.9	7820	121.9	1.11
232	8.62	8.67	91.0	108.3	604.8	7780	294.9	1.18
234	8.46	8.62	14.7	31.8	39.69	7670	11.44	0.700
233	8.55	8.55	90.0	108.0	303.3	7840	167.1	1.33
236	8.55	8.55	34.0	51.1	98.3	7370	34.59	9.845
237	8.76	8.50	109.4	126.8	424.2	7850	238.5	1.31
238	8.46	8.62	14.8	31.8	549.0	7710	21.69	0.97
239	8.46	8.80	110.8	127.8	831	7580	424.8	1.28
240	8.62	8.55	138.4	155.8	994	7690	616.2	1.48
241	8.55	8.62	139.2	156.6	1464	7520	863	1.43
242	8.50	8.55	163.7	180.8	423.6	7270	283.8	1.62
243	8.46	8.66	163.4	181.2	530.4	6860	309.9	1.63
244	8.62	8.62	192.5	209.7	607.2	7240	390.3	1.55
245	8.62	8.58	193.7	210.6	491.4	8270	292.8	1.43

TABLE III 10

DEPENDENCE OF R_{nPrCl}^{PCE} ON ARGON PRESSURE· TEMPERATURE 79°C

| | mm, Hg | | | | | | x100mv | x 10^{-9}amp | |
Run No.	TrCE Pressure	PrH Pressure	Cl$_2$ Pressure	Argon Pressure	Total Pressure	Area nPrCl	Area TrCE	Area PCE	R_{nPrCl}^{PCE}
345	8.58	8.55	22.1	142.0	181.8	254.4	1043	136.2	1.25
346	8.55	8.58	22.1	119.2	158.3	343.8	9630	152.4	1.07
347	8.72	8.63	22.1	120.0	159.1	386.1	9460	174.3	1.08
349	8.58	8.80	22.3	98.1	137.8	682	8930	253.2	0.91
350	8.63	8.76	22.2	74.0	113.1	505.2	9210	222	1.08
351	8.68	8.63	22.2	74.5	113.6	491.7	-	221.1	1.08
352	8.58	8.72	22.1	51.2	90.3	663	8670	266.4	0.979
353	8.63	8.94	22.2	51.5	90.6	816	8340	302.7	0.922
357	8.55	8.55	22.3	97.2	136.3	575.7	8830	251.7	1.65
258	8.55	8.55	22.4	143.0	183.0	530.5	8760	274.8	1.20
359	8.50	8.63	8.50	8.87	34.5	152.1	-	38.9	0.621
360	8.63	8.55	8.50	9.23	36.9	193.8	8880	41.1	0.503
361	8.63	8.85	8.29	20.5	46.3	139.6	8790	34.2	0.603
342	8.55	8.67	8.63	25.3	51.0	335.7	8610	72.0	0.524
363	8.58	8.58	8.50	44.3	69.8	135.6	9040	43.2	0.765
364	8.58	8.63	8.45	44.3	70.0	91.9	8980	28.4	0.746
365	8.58	8.63	8.50	63.4	88.9	117.9	9230	40.8	0.838
366	8.58	8.55	8.55	87.8	113.6	110.1	9010	89.9	0.865
367(P)	8.58	8.63	8.46	110.8	136.2	22.48	-	7.74	0.83

TABLE III   11

$$\text{DEPENDENCE OF } R^{PCE}_{nPrCl} \text{ on PRESSURE. TEMPERATURE } 79^{\circ}C$$

(a) TRICHLOROETHYLENE PRESSURE

Run No.	TrCE Pressure	PrH Pressure	Cl$_2$ Pressure	Total Pressure	Area nPrCl	Area TrCE	Area PCE	R^{PCE}_{nPrCl}
	mm. Hg						x100mv x 10^{-9}amp	
298 (P)	13.0	4.36	4.27	21.6	0.926	-	0.579	0.504
299 (P)	21.4	4.62	4.14	30.2	0.802	-	0.738	0.478
300 (P)	12.93	4.36	4.23	21.5	0.968	-	0.479	0.408
301 (P)	21.4	4.53	4.32	30.3	0.883	-	0.892	0.515
304 (P)	4.36	4.32	4.66	13.3	3.349	-	0.625	0.302
306 (P)	47.1	4.62	4.27	55.99	1.712	-	4.865	0.667
310 (P)	17.10	4.27	4.27	25.64	3.505	-	2.755	0.472
311 (P)	17.10	4.36	4.18	25.44	3.44	-	2.697	0.494
369 (P)	37.2	4.02	4.11	45.4	5.685	-	10.81	0.492
307 (P)	47.0	4.57	4.23	56.0	1.51	-	5.304	0.82
312 (P)	51.3	4.27	4.18	59.75	1.845	-	8.115	0.88
370 (P)	37.2	4.01	4.18	45.4	5.766	5810	10.58	0.476
396 (P)	37.2	4.19	4.27	45.6	4.05	-	9.55	0.631

(P)   Peak areas planimetered

TABLE III 11

DEPENDENCE OF R_{nPrCl}^{PCE} ON INERT GAS PRESSURE TEMPERATURE $79^{\circ}C$

(b)   CARBON DIOXIDE PRESSURE

Run No.	mm. Hg						x100mv	x 10^{-9} amp	
	TrCE Pressure	PrH Pressure	Cl_2 Pressure	CO_2 Pressure	Total Pressure	Area nPrCl	Area TrCE	Area PCE	R_{nPrCl}^{PCE}
374	8.63	8.46	8.55	88.0	113.7	87.8	98400	36.1	0.966
375	8.85	8.58	8.33	24.7	50.5	169.8	9640	50.3	0.723
376	8.58	8.80	8.63	63.2	89.3	189.6	9840	64.4	0.836
377	8.63	8.98	8.84	64.5	71.0	187.2	9430	59.0	0.789
378	8.58	8.85	8.85	167.3	160.8	192.6	9540	72.4	0.921
379	8.63	8.80	8.58	9.10	35.10	327.6	9420	76.5	0.576
380	8.55	8.55	8.55	8.58	34.2	282.0	9660	78.3	0.666
381	8.68	8.68	8.50	112.1	137.3	190.5	9320	70.2	0.885
382	8.68	8.58	8.85	182.5	208.2	349.8	11040	135.0	0.920

TABLE III   11

DEPENDENCE OF R^{PCE}_{nPrCl} ON INERT GAS PRESSURE   TEMPERATURE   79°C

(c)   SULPHUR HEXAFLUORIDE PRESSURE

| Run No. | mm.Hg | | | | | $x100mv \times 10^{-9}$ amp | | | R^{PCE}_{nPrCl} |
	TrCE Pressure	PrH Pressure	Cl$_2$ Pressure	SF$_6$ Pressure	Pressure	Area nPrCl	Area TrCE	Area PCE	
384	8.58	8.84	8.55	25.3	51.2	217.2	8990	60.6	0.694
385	8.63	8.50	8.58	82.8	108.3	126.9	9030	47.7	0.891
386	8.63	8.55	8.58	8.55	34.2	1171	9630	326	0.66
387	8.58	8.68	8.63	46.60	72.4	183.9	9170	54	0.712
388	8.58	8.67	8.62	63.8	89.6	177.8	9490	62.7	0.857
389	8.62	8.55	8.62	8.55	34.4	278.1	9130	69.6	0.594
390	8.58	8.58	8.76	186.3	212.8	68.3	9080	24.7	0.869
391	8.50	8.55	8.58	135.6	161.3	168.2	9240	47.5	0.764
394	8.62	8.58	8.55	47.0	72.7	88.9	9260	31.5	0.846
395	8.55	8.55	8.55	112.3	138.0	68 5	9920	7.5	0.974

TABLE III

Molecule Mi	Temp °C	ka/kbi (mmHg)	kb₁/kbi	ka/kbi / ka/kbi ie kb₁/kbi	Collisional diameter $\sigma \times 10^8$ cm	$Z^*(ACl^*, Mi) \times 10^{-7}$ (mmHg^{-1} sec^{-1})	Collisional efficiency relative to Cl_2, XI	ka $\times 10^{-8}$ sec^{-1}	k_2''/k_2
1 Cl_2	40	32	1	1	4.4(63)	1.065	1	3.41	1.9
2 PrH	40	-	1/0.7	1	5.01(64)	1.401	0.53	-	1.9
1 Cl_2	56	54	1	1	4.4	1.034	1	5.59	1.9
2 PrH	56	-	1/0.7	-	5.01	1.355	0.53	-	1.9
1 Cl_2	79	70	1	1	4.4	1.004	1	7.03	1.4
2 PrH	79	-	1/0.9	-	5.01	1.316	1.84	-	1.4
2 PrH	79	74	0.9	1.0	5.01	1.316	0.84	8.18	1.4
3 TrCE	79	50	0.7	0.7	6.5(64)	0.986	1.45	7.15	1.4
4 Ar	79	74	0.8	1.0	8.12(63)	1.018	1.23	9.25	1.5
5 CO_2	79	60	1.0	0.9	4.49(63)	1.21	0.83	6.04	1.8
6 SF_6	79	54	0.9	0.8	5.51(63)	0.950	1.17	6.04	1.3
1 Cl_2	133	136	1.0	1	4.4	0.938	1.0	12.67	0.9
1 Cl_2	133	140	1.0	1.0	4.4	0.938	1.0	13.11	0.9
2 PrH	133	-	1/1.2	-	5.01	1.228	0.92	-	0.9
1 Cl_2	133	168	1.0	1.0	4.4	0.938	1.0	15.77	1.0
2 PrH	133	-	1/1.2	-	5.01	1.228	0.92	-	1.0

The internal consistency of the "grid" method is shown by comparing values of kb_1/kbi with values ka/kbi ie $\dfrac{kb_1/kbi}{ka/kbi}$

The different values of ka/kb_1 at 133°C for the chlorine /propane pressure dependence correspond to the same value of $(Rth-Rexp)^2$

Dependence of R_{nPrCl}^{PCE} on Chlorine Pressure

Temperature 79.5°C

Chlorine Pressure = Variable
P_{PrH} = 9.2 mm. Hg
P_{TrCE} = 8.6 " "

R_{nPrCl}^{PCE}

⦶ Surface/Volume Ratio × 10

Figure III 3

1.0

0.6

0.2

50   200

Total Pressure (mm Hg)

Dependence of R_{nPrCl}^{PCE} on Propane Pressure

Temperature 79.5°C

Propane Pressure = Variable

P_{TrCE} = 8.6 mm Hg

P_{Cl_2} = 23.2 „ „
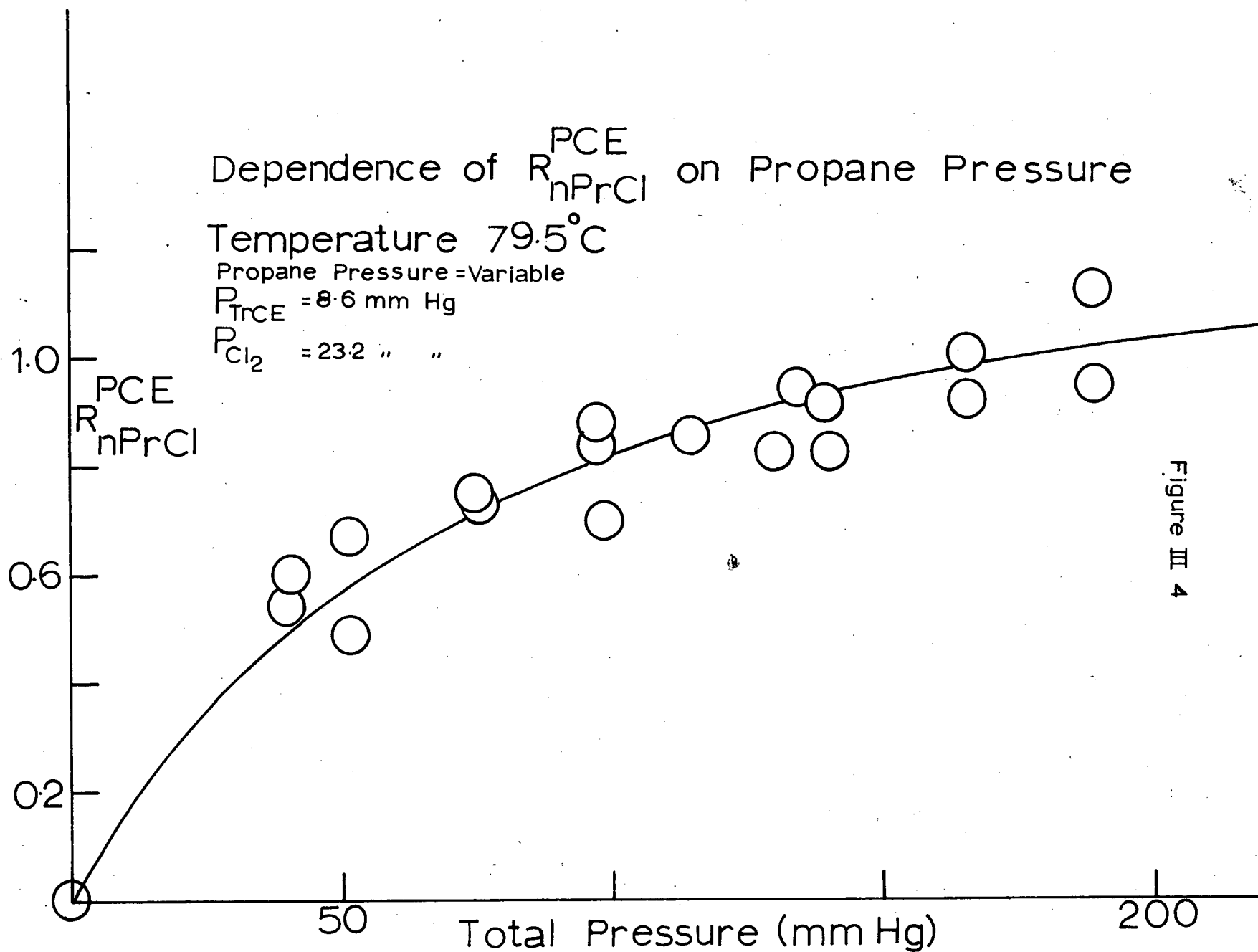
R_{nPrCl}^{PCE}

Total Pressure (mm Hg)

Figure III 4

Dependence of R^{PCE}_{nPrCl} on Chlorine Pressure

Temperature 133°C

Chlorine Pressure = Variable

$P_{PrH} = P_{TrCE} = 8.6$ mm. Hg
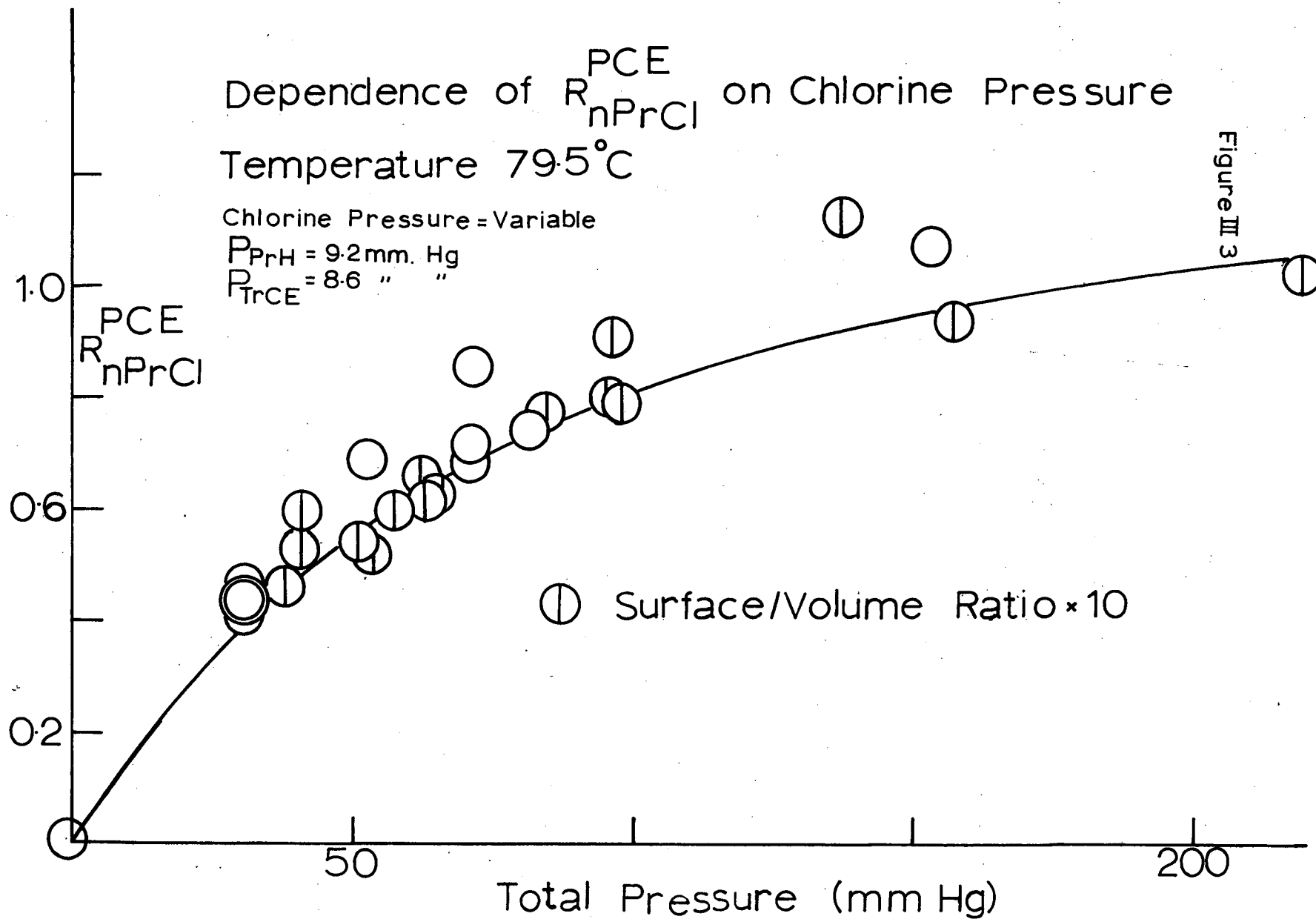
Figure III 5

R^{PCE}_{nPrCl}

Total Pressure (mm Hg)

Dependence of R_{nPrCl}^{PCE} on Propane Pressure

Temperature 133°C

Propane Pressure = Variable

$P_{TrCE} = 8.6$ mm. Hg

$P_{Cl_2} = 23.0$ " "

Figure III 6

R_{nPrCl}^{PCE}

1·0

0·6

0·2

50   200

Total Pressure (mm Hg)

Dependence of R_{nPrCl}^{PCE} on Chlorine and Propane Pressure

Temperature 40.1°C

R_{nPrCl}^{PCE}

◯ Chlorine Pressure Variable

⬭ Propane   "   "

Total Pressure (mm Hg)
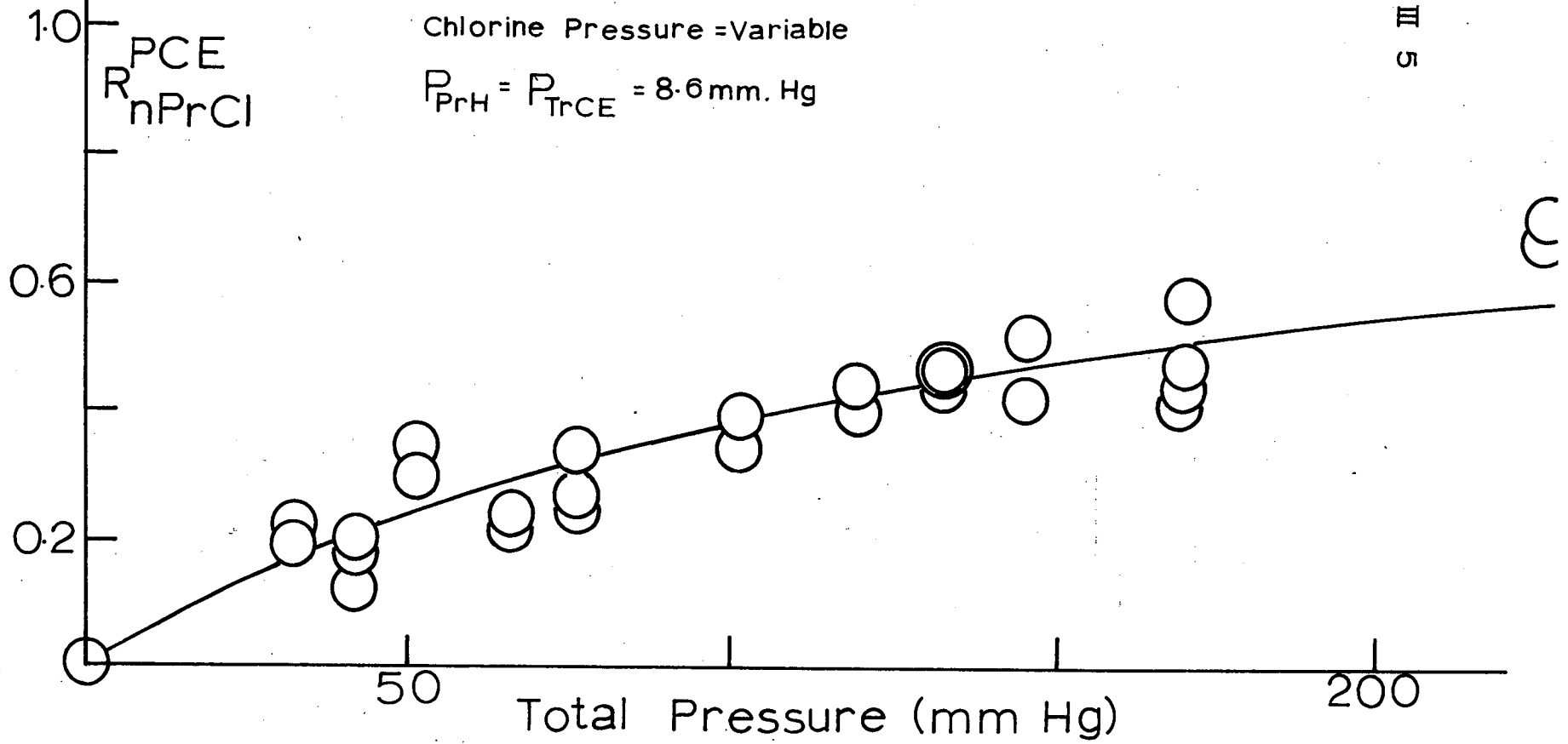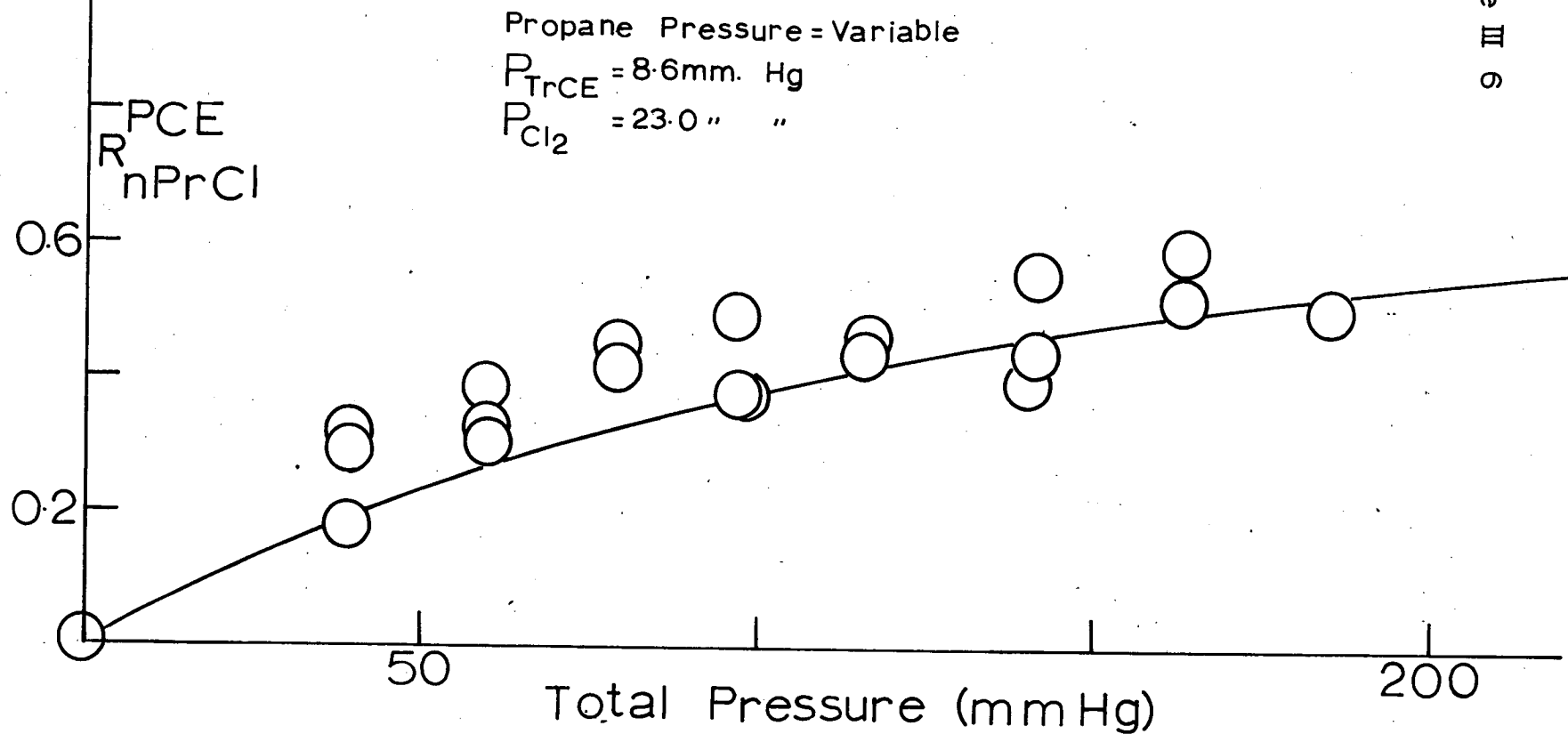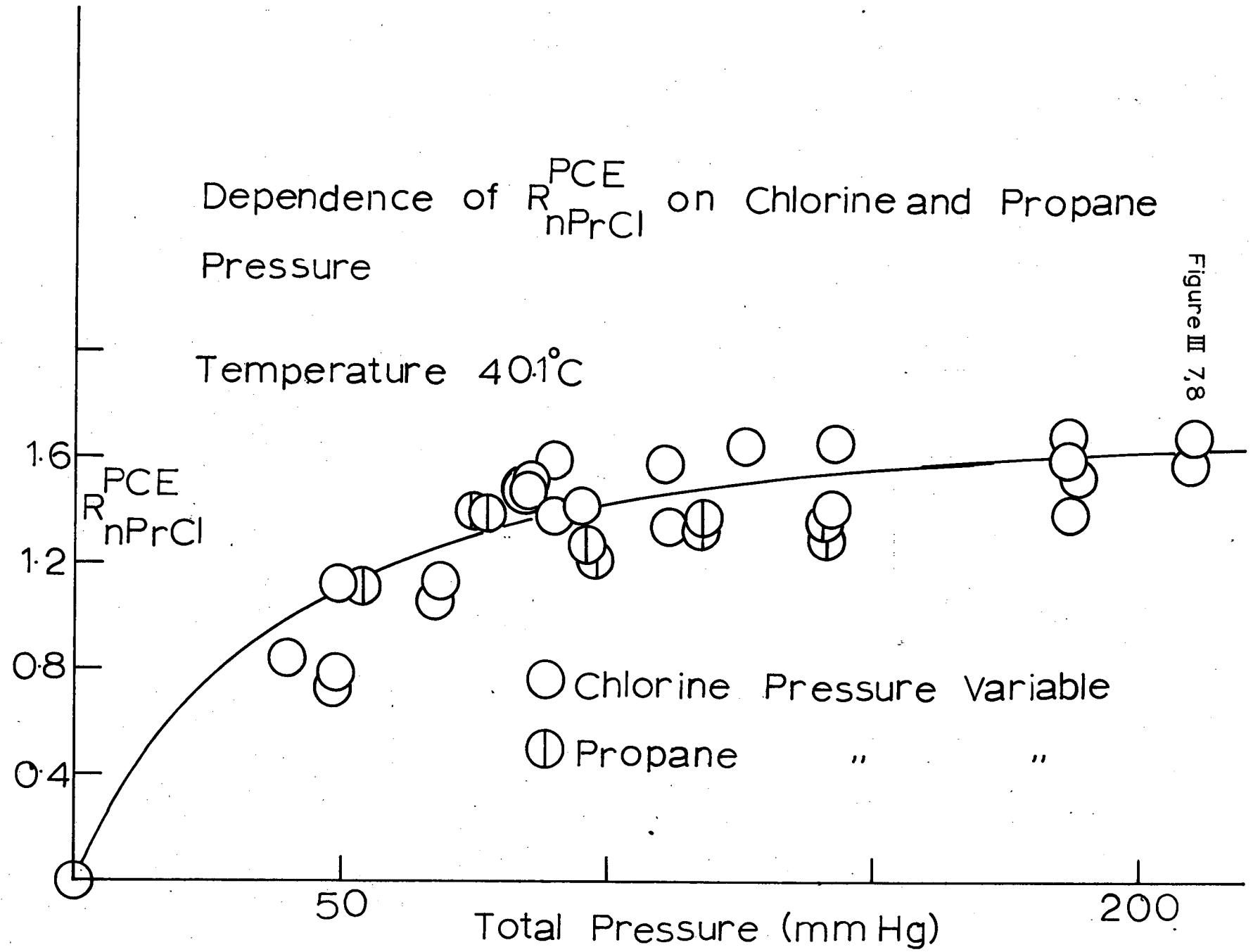
Figure III 7,8

Dependence of R_{nPrCl}^{PCE} on Chlorine Pressure
Temperature 560°C

Chlorine Pressure = Variable

$P_{PrH} = P_{TrCE} = 8.6mm$ Hg

Figure II 9

R_{nPrCl}^{PCE}

1.6

1.2

0.8

0.4

50   Total Pressure (mm Hg)   200
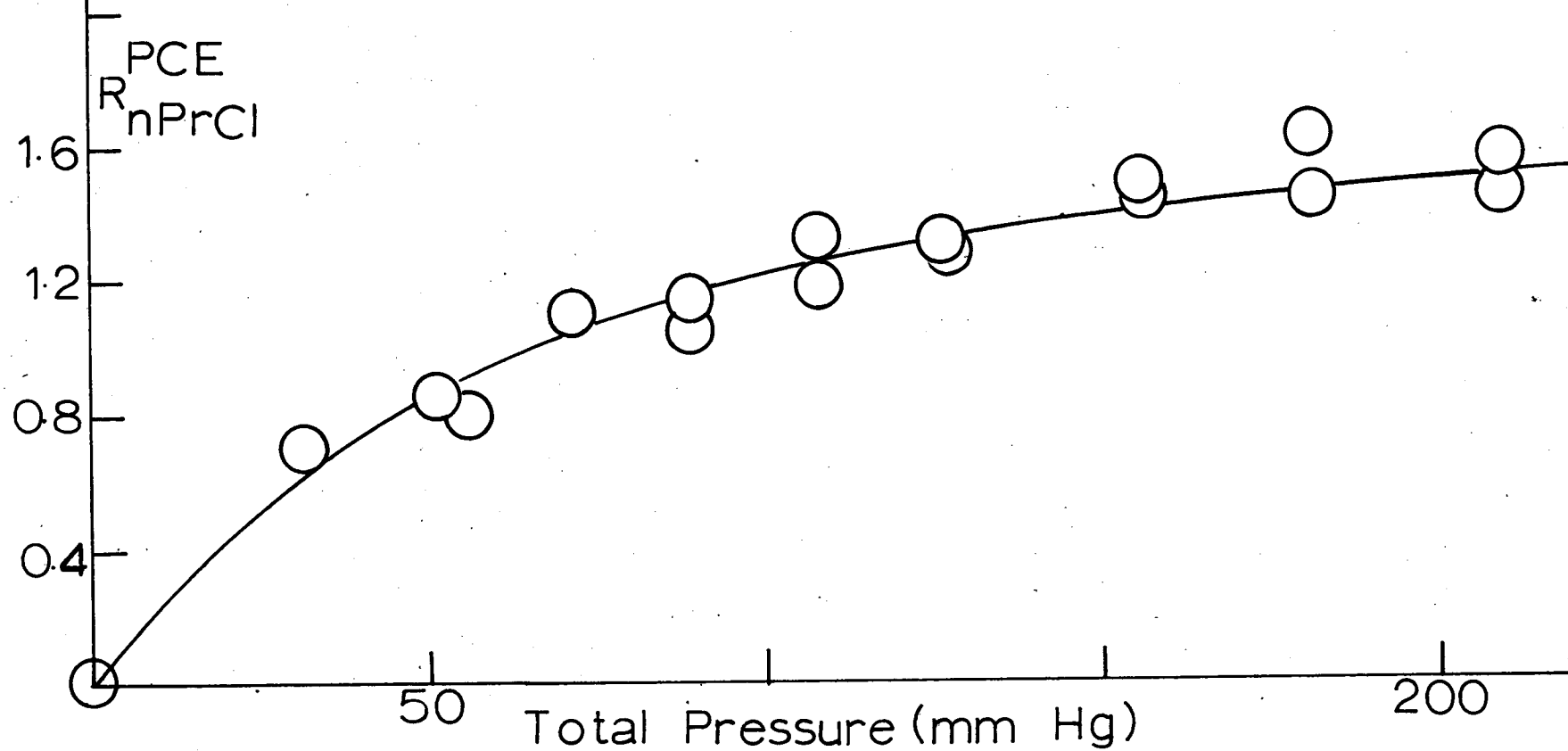
Dependence of R_{nPrCl}^{PCE} on Argon Pressure
Temperature 79·5°C

Argon Pressure = Variable
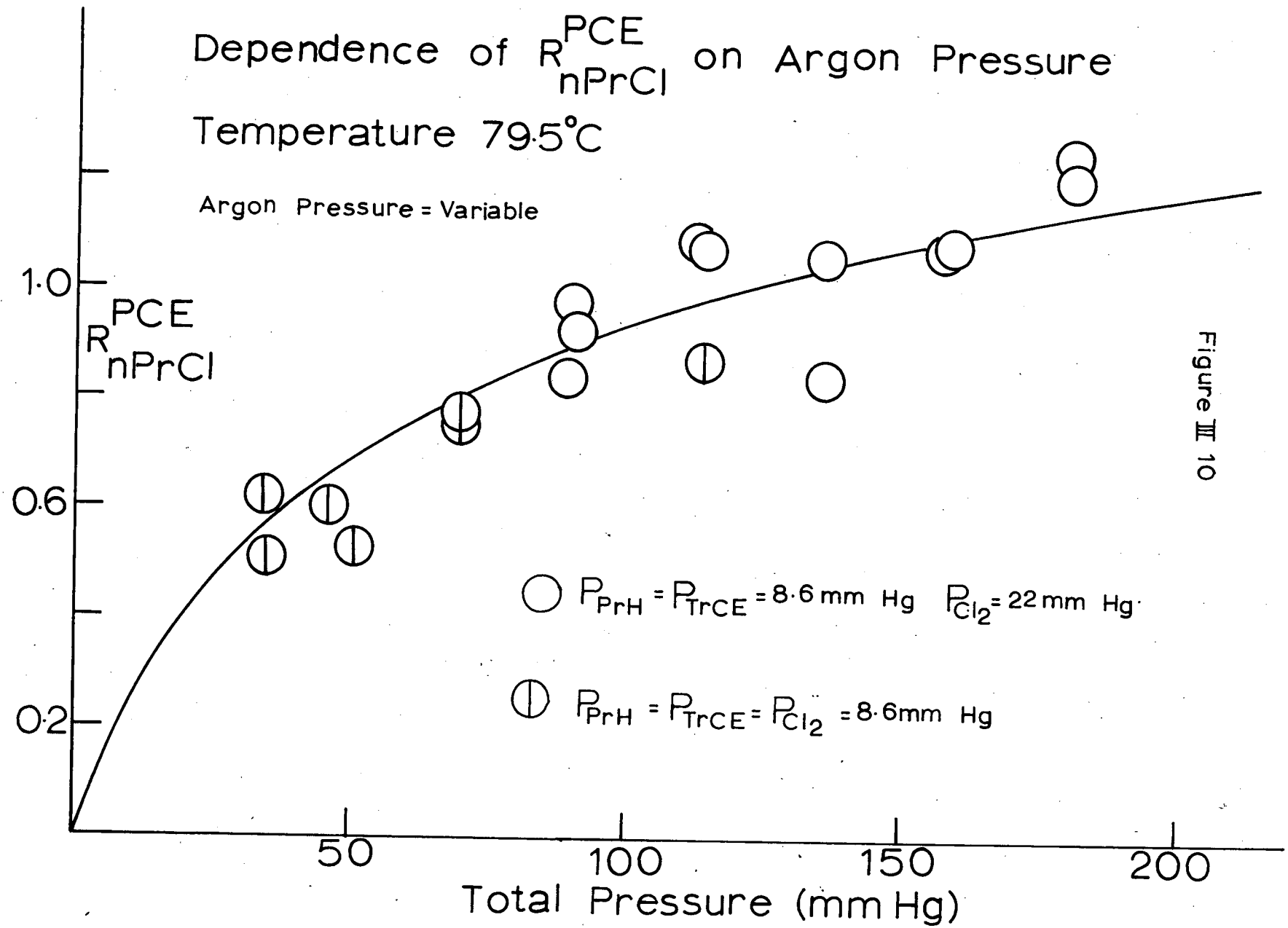
R_{nPrCl}^{PCE}

$\bigcirc$ $P_{PrH} = P_{TrCE} = 8·6\,mm\ Hg$ $P_{Cl_2} = 22\,mm\ Hg$

$\oplus$ $P_{PrH} = P_{TrCE} = P_{Cl_2} = 8·6\,mm\ Hg$

Total Pressure (mm Hg)

Figure III 10

Dependence of R_{nPrCl}^{PCE} on Inert Gas Pressure
Temperature 79.5°C

TrCE

SF$_6$

CO$_2$

1.0

R_{nPrCl}^{PCE}

0.6

0.2

● TrCE Pressure Variable
○ CO$_2$ „   „
⦶ SF$_6$ „   „

Figure III 11

50   Total Pressure (mm Hg)   200

Arrhenius Plot for k_2''/k_2' for TrCE

$\log k_2''/k_2'$

$(1/T) \times 10^3$

Figure III 12

Arrhenius Plot for k_a

Figure III 13

Tetrachloroethylene was chlorinated in competition with propane as a function of carbon dioxide pressure to try to observe experimentally the gradation in radical lifetimes in going from the trichloroethyl radical, through the tetrachloroethyl radical, to the pentachloroethyl radical. However since the selectivity ratio R^{HCE}_{nPrCl} was independent of pressure over the accessible pressure range i. e. from 6 mm to 200 mm only a lower limiting value of 2×10^{-8} seconds of the pentachloroethyl radical lifetime could be obtained.

Several factors conspire against the evaluation of the rate constants for the chlorination of tetrachloroethylene by the competitive techniq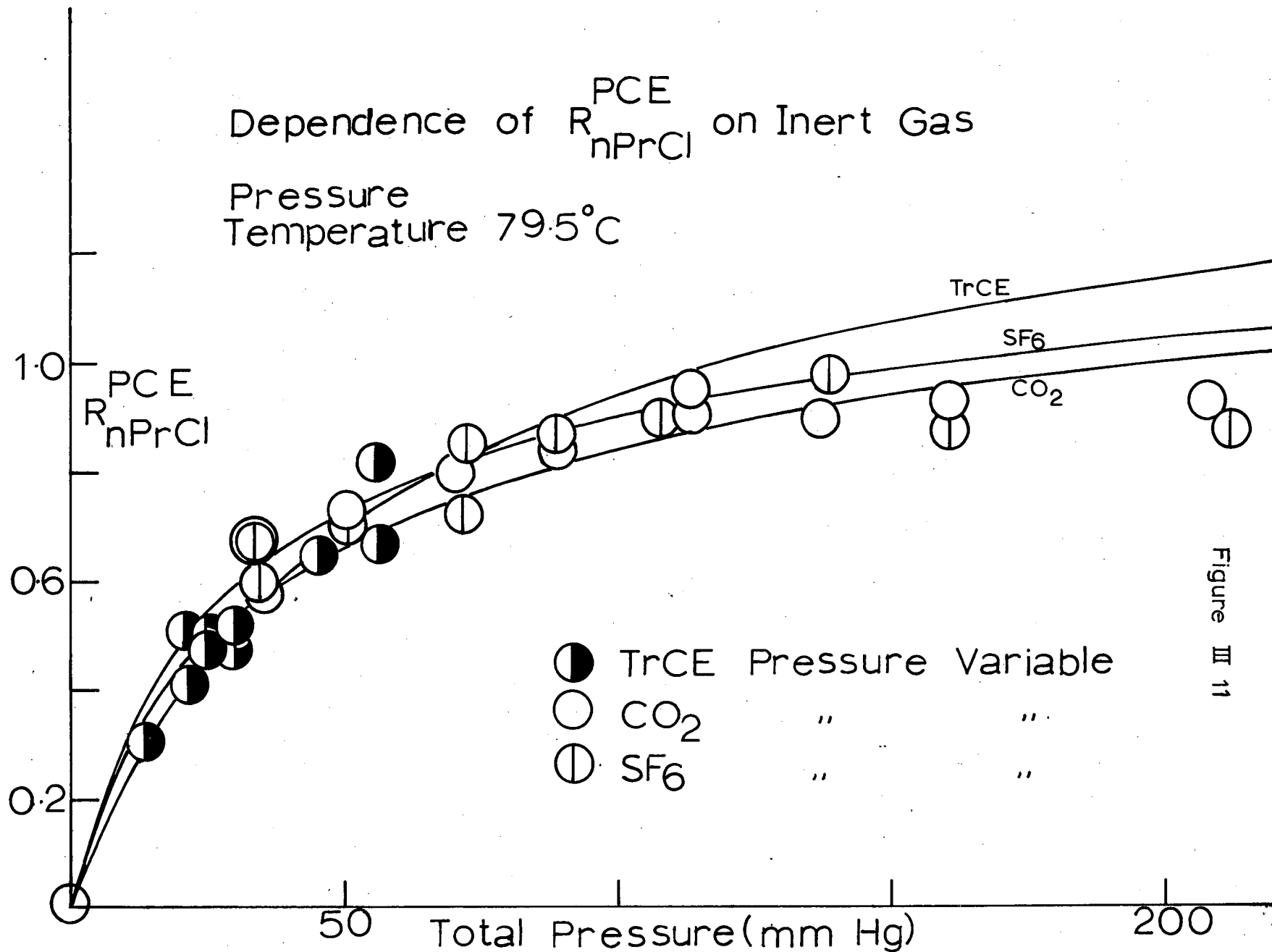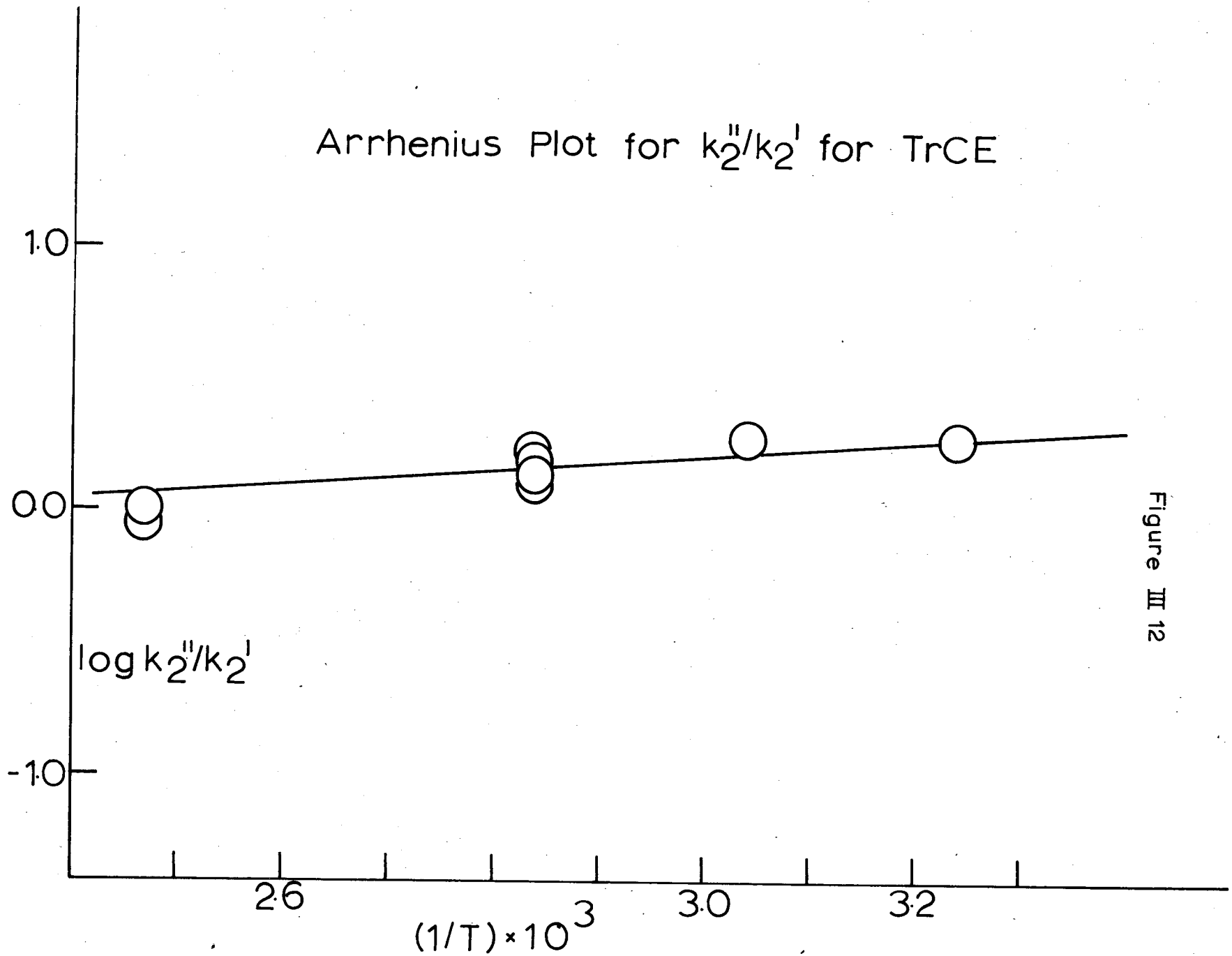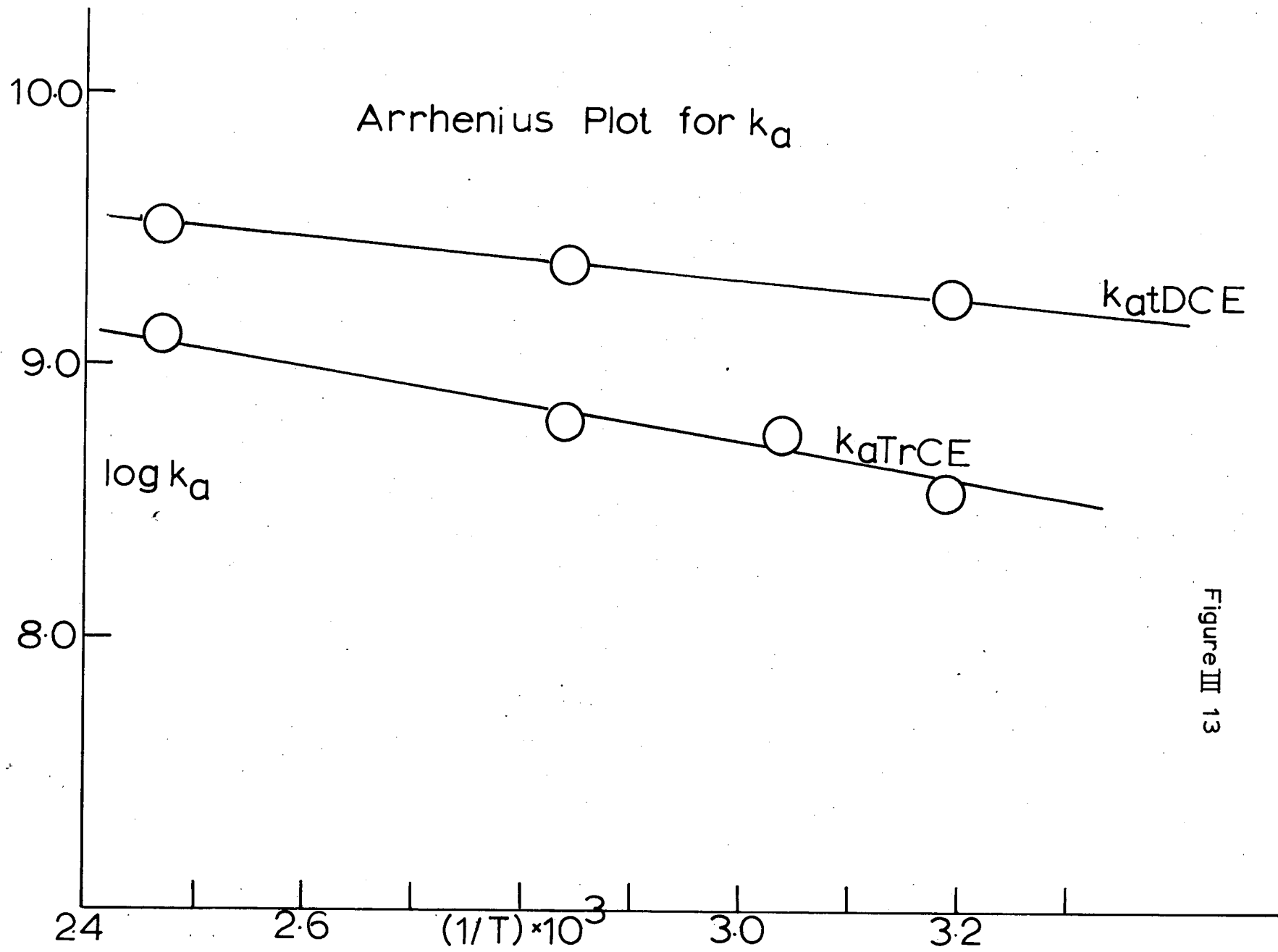ue in a static system. These are (1) the unreactivity of chlorine to tetrachloroethlene as exemplified by the low rate of formation of the addition compound relative to photosubstitution of propane (2) the insensitivity of the flame ionication detector to hexachloroethane and (3) the long length of the radical lifetime which, in order that the rate of unimolecular decomposition of the radical be evaluated, necessitates working at extremely low pressures. This incurs problems of the accurate measurement of small pressures together with the estimation of small amounts of products, which are themselves insensitive to the type of detection employed.

Assuming that all the pentachloroethyl radicals formed in reaction (2'') are deactivated by collision at the pressures studied k_2''/k_2' can be equated with the limiting value of R^{HCE}_{nPrCl} . From figure III 14

$$R_{nPrCl}^{HCE} = 0.1 = k_2''/k_2'$$

Whence $k_2'' = 0.24 \times 10^{10}$ mole^{-1}.1. sec^{-1} at 79°C

This value of k_2'' for tetrachloroethylene is the same as that obtained by Goldfinger (46).

TABLE III   14

DEPENDENCE OF R^{HCE}_{nPrCl} on CARBON DIOXIDE PRESSURE TEMPERATURE 79°C

Run No.	TetraCE Pressure	PrH Pressure	Cl$_2$ Pressure	CO$_2$ Pressure	Pressure	Area nPrCl	Area TetraCE	Area PCE	HCE R_{nPrCl}
	mm. Hg					x100mv x 10^{-9} amp			
400	8.55	8.62	8.58	192.3	208.2	2310	10300	9.1	0.105
401	8.58	8.55	8.55	182.7	208.2	1984	9800	8.8	0.117
405	8.62	8.62	8.30	135.5	161.1	2535	-	8.53	0.09
406	8.58	8.50	8.55	-	2565	639	9920	3.1	0.118
407	8.76	8.55	8.33	9.76	34.4	2571	10320	8.58	0.087
408	4.27	4.31	4.23	-	12.82	530	-	1.56	0.078
409	2.14	2.26	2.18	-	6.58	221	2694	1.08	0.129
410	8.50	8.55	8.45	88.0	114.2	2362	9980	9.51	0.090
411	8.58	8.58	8.55	44.9	76.7	2790	10230	0.085	
412	8.55	8.55	8.55	8.55	34.20	2169	-	8.88	0.108

Dependence of R_{nPrCl}^{HCE} on CO_2 Pressure

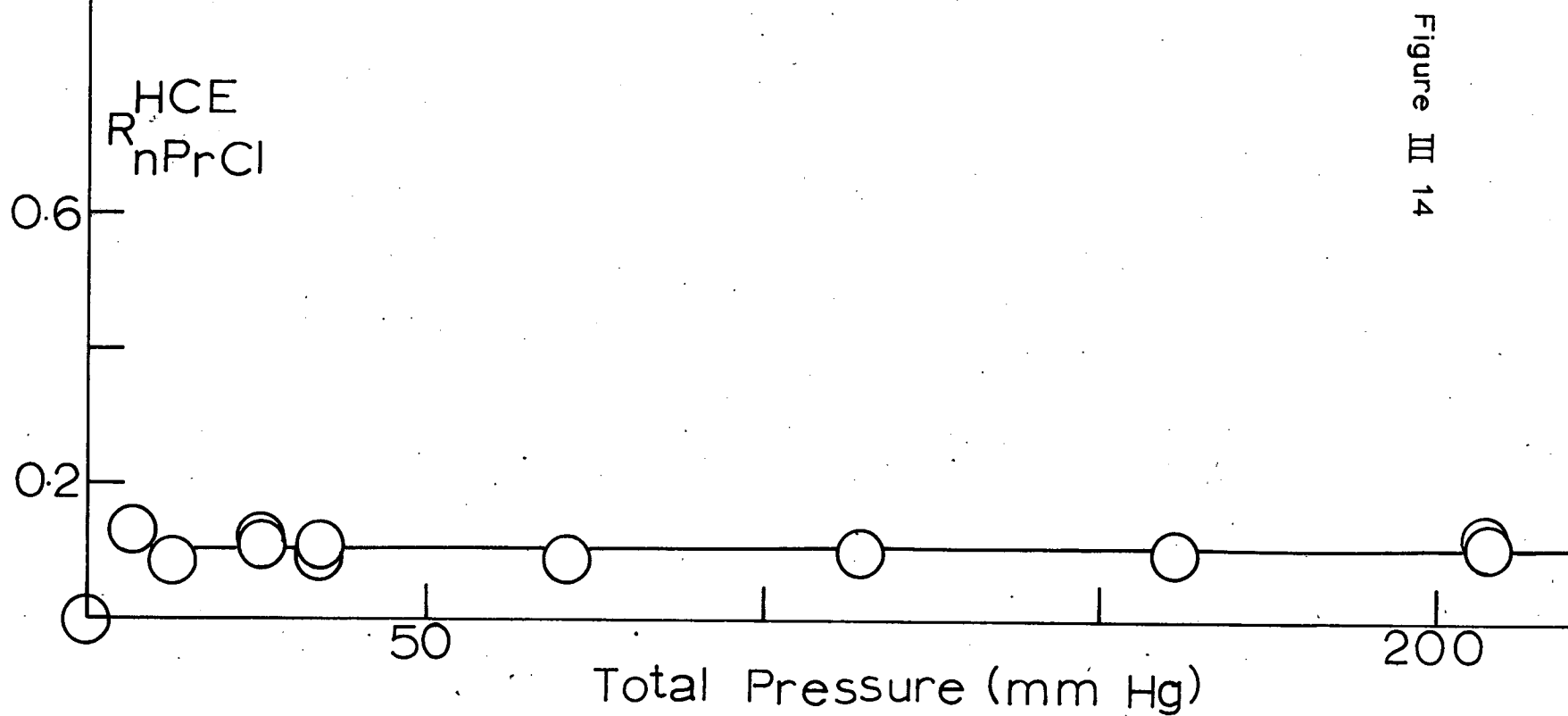Temperature 79.5°C

Figure III 14

R_{nPrCl}^{HCE}

Total Pressure (mm Hg)

To complete the series ethylene and vinyl chloride were chlorinated in competition with propane. The chlorination of ethylene has been investigated by the competitive technique by Hagopian, Knox and Thomson (65) and by the rotating sector technique by Dainton, Lomax and Weston (55). In the former case the authors found considerable surface reaction whereas the latter authors found the surface reaction to be negligibly small.

As can be seen from Table III 15 the chlorination of ethylene has a considerable rate in the dark. This heterogeneous component of the reaction has been investigated. By inhibiting the reaction with large quantities of NOCl in the inhibition manifold and by not degassing at $-120^{\circ}C$ and still finding considerable surface reaction it has confirmed that the surface effect is occurring only in the reaction vessel.

It was thought that the surface effect might be connected with the degree of chlorination of the olefin - it has been demonstrated in this work that the chlorination of trichloroethylene has a negligible heterogeneous component - and so vinyl chloride was chlorinated in competition with propane in the hope that it would exhibit a smaller amount of surface reaction. However, here again, there was a considerable heterogeneous component which, as far as can be gathered from the results was dependent on the nature of the surface (Table III 16). Although the percentage dark reaction was a minimum on a hexamethyldisilazane surface its rate was greater than the homogeneous reaction in full light intensity, making it impossible to study the system directly.

TABLE III   15

PRESSURE DEPENDENCE OF CHLORINATION OF ETHYLENE   TEMPERATURE 79°C

Run No.	mm Hg					$\times 100$ mV $\times 10^{-9}$ amp		
	C_2H_4 Pressure	PrH Pressure	Cl_2 Pressure	CO_2 Pressure	Total Pressure	Area nPrCl	Area $C_2H_4Cl_2$	$R\frac{C_2H_4Cl_2}{nPrCl}$
414	8.58	8.06	8.55	–	25.6	2577	4170	3.64
413	8.55	8.55	8.55	182.3	2080	1254	1834	3.28
415	8.50	8.55	8.50	–	25.6	984	1330	3.03
416	8.55	8.35	8.55	–	25.7	462	2495	12.3
417	8.60	8.58	8.55	–	25.7	249.9	1091	9.82
418 (I)	8.58	8.55	8.58	–	25.8	1344	6336	10.58
419 (L)	8.50	8.50	8.55	–	25.6	500	6770	30.0
420 (NI)	8.58	8.55	8.55	–	25.7	96	1446	33.6
421 (NI)	8.55	8.55	8.50	–	25.6	120.6	6999	129.1

(L)   Large volume of NOCl added; no pumping at -120°C

(NI)   No illumination; dark time 5 minutes

TABLE III 16

CHLORINATION OF VINYL CHLORIDE

		mm Hg			x100mV x 10^{-9} amp				
Run No,	Temp $^{\circ}$C	VC Pressure	PrH Pressure	Cl$_2$ Pressure	Area nPrCl	Area C$_2$H$_3$Cl$_3$	R $\frac{C_2H_3Cl_3}{nPrCl}$	Dark Time	Surface
430	79	8.58	8.94	8.67	20.0	185.9	10.34	7 mins	Urea formaldehyde
433	40	8.76	8.62	8.62	\3	18.9	156	5 mins	P.V.C.
4.9	40	8.58	8.29	8.67	92	280	7.55	10 mins	HMDS
440	40	8.55	8.55	8.42	1197	2106	4.96	15 mins	"
442	40	8.80	8.62	8.55	77.1	651	20.9	10 mins	"
443	40	8.80	8.55	8.55	74.1	722	25.8	15 mins	"
444	40	8.58	8.94	8.55	329.7	366	1.11	4 mins	" (a)
445	40	8.58	8.90	8.58	37.9	675	44.0	6 mins	"
446	40	8.67	8.55	8.55	606	1197	488	4 mins	" (b)
447	40	8.55	8.65	8.55	67.1	1284	47.3	6 mins	"

(a)   Dark Time 4 mins Illuminated for 2 mins, on 140 V

(b)   "   "   "   "   " 2 mins, on 240 V

H.M.D.S.   = Hexamethyl disilazane

P.V.C.   = Polyvinylchloride

CHAPTER IV

DISCUSSION

As shown in the introduction both the bimolecular and the unimolecular

rate constants are susceptible to absolute calculation, if the properties of

A, Cl, ACl^{*}, and ACl^{+} are sufficiently well defined.

According to the transition state theory the rate constant for reaction

(2") may be expressed as

$$k_{2"} = (kT/h) \; (q^{+}/q_A q_{Cl}) \; \exp(-\Delta Eo^{+}/kT) \qquad\qquad \text{IV} \quad 1$$

(equation 1a65)

where q^{+}, q_A and q_{Cl} are the partition functions measured from the lowest

vibrational state of the molecules for the activated complex, the olefin, and

Cl; ΔEo^{+} is the difference in energy of the lowest vibrational states of

the reactants and the complex. Inserting the expressions for the partition

functions gives

$$k_{2"} = \left(\frac{kT}{h}\right) \left(\frac{M^{+}}{M_A}\right)^{3/2} \left(\frac{A^{+}B^{+}C^{+}}{A_A B_A C_A}\right)^{\frac{1}{2}} \frac{\sigma_A}{\sigma^{+}} \left(\frac{8\pi^3 I^{+} kT}{h^2}\right)^{\frac{1}{2}} \left(\frac{h^2}{2\pi M_{Cl} kT}\right)^{3/2} x$$

$$\frac{\overset{12}{\prod}(1-\exp(-h\nu_A/kT)) \; \exp(-\Delta Eo^{+}/kT)}{\underset{13}{\prod}(1-\exp(-h\nu^{+}/kT))} \qquad\qquad \text{IV} \quad 2$$

The superscript $^{+}$ refers to the transition state complex and the sub-

scripts A and Cl refer to the olefin molecule and the chlorine atom; M is

the molecular mass; A B C is the product of the moments of inertia about the principal axes of rotation; σ is the symmetry number; the $\vee$ are the fundamental vibration frequencies; and I^+ is the reduced moment of inertia of the complex for internal rotation. k, T, and h have their usual meanings.

Experimental A factors are obtained from plots of ln k (exp) against 1/T. The appropriate quantity calculable from any theoretical expression for a rate constant is:

$$A \text{ calc} = k \exp (d \ln k / d \ln T) \qquad\qquad IV. 3$$

If the theoretical expression can be cast into the form

$$k = P \, f (T) \exp (- E/kT) \qquad\qquad IV. 4$$

where P is a temperature independent factor, then

$$A \text{ calc} = P \, f(T) \exp (d \ln f(T) / d \ln T)$$
$$= P \, f (T) \exp (n) \qquad\qquad IV. 5$$

Equation IV. 2 for k_2'' gives

$$\ln f(T) = \sum^{12} \ln (1 - \exp (- h \vee_A / kT)) \; - \; \sum^{13} \ln (1 - \exp(-h \vee^+ / kT)) - \frac{E_0^+}{kT}$$

$$IV. 6$$

and therefore

$$\frac{d \ln f(T)}{d \ln T} = n = \sum^{13} \frac{h \vee^+}{kT} (\exp(h \vee^+/kT) - 1)^{-1} \; - \; \sum^{12} \frac{h \vee_A}{kT} (\exp (h \vee_A /kT) - 1)^{-1}$$
$$\frac{+ E_0/kT}{} \qquad\qquad IV. 7$$

Substituting equation IV. 7 into equation IV. 5 gives

$$A_{calc} = \left(\frac{kT}{h}\right)\left(\frac{M^+}{M_A}\right)^{3/2}\left(\frac{A^+B^+C^+}{A_AB_AC_A}\right)^{\frac{1}{2}}\frac{\sigma_A}{\sigma^+}\left(\frac{8\pi^3 I^+ kT}{h^2}\right)^{\frac{1}{2}}\left(\frac{h^2}{2\pi M_{Cl}kT}\right)^{3/2}x$$

$$\frac{\overset{12}{\prod}(1-\exp(-h\nu_A/kT))\;\exp(n)}{\overset{13}{\prod}(1-\exp(-h\nu^+/kT))}$$

IV. 8

The products of the moments of inertia about the principal axes A, B,

C are obtained by a method derived by Hirschfelder (66) which is a particular

case of a method due to Crawford (67) for the calculation of a generalised

moment. Hirschfelder obtains the product of the three principal moments

of inertia, A, B, C, from the determinant of the momental dyad

$$A_A \quad B_A \quad C_A \quad = \quad \begin{vmatrix} G & -D & -E \\ -D & H & -F \\ -E & -F & K \end{vmatrix}$$

where $M = \sum_i m_i$;

and

$$G = \sum_i m_i(y_i^2 + z_i^2) - \frac{1}{M}\left(\sum_i m_i y_i\right)^2 - \frac{1}{M}\left(\sum_i m_i z_i\right)^2,$$

$$H = \sum_i m_i(x_i^2 + z_i^2) - \frac{1}{M}\left(\sum_i m_i x_i\right)^2 - \frac{1}{M}\left(\sum_i m_i z_i\right)^2,$$

$$K = \sum_i m_i(x_i^2 + y_i^2) - \frac{1}{M}\left(\sum_i m_i x_i\right)^2 - \frac{1}{M}\left(\sum_i m_i y_i\right)^2,$$

$$D = \sum_i m_i x_i y_i - \frac{1}{M}\left(\sum_i m_i x_i\right)\left(\sum_i m_i y_i\right),$$

$$E = \sum_i m_i x_i z_i - \frac{1}{M}\left(\sum_i m_i x_i\right)\left(\sum_i m_i z_i\right),$$

$$F = \sum_i m_i y_i z_i - \frac{1}{M}\left(\sum_i m_i y_i\right)\left(\sum_i m_i z_i\right),$$

Since the properties of ACl^* and ACl^+ must be guessed it is assumed that the molecules of ACl, ACl^*, and ACl^+ are identical in structure and differ only in their internal energy and its distribution. It has been deduced for D C E (53) that there is free rotation about the C-C bond in all forms of ACl. It is also assumed that the vibrational frequencies of the radical are the same as those of the saturated hydrocarbon except for the frequencies assigned to the three C-H vibrational modes which are absent in the radical.

The fundamental vibrational frequencies of trans - D C E are 3080, 1274, 3073, 1578, 1200, 895, 846, 817, 763, 350, 250, and 227 cm^{-1} (58). The fundamental frequencies, given by Harrison and Kobe (68), for CH_2Cl. $CHCl_2$ are as follows : the modes whose frequences are bracketted are assumed absent in the radical : 3014, 2998, (2964), 1437, (1306), 1206, (1204), 1162, 1050, 936, 792, 742, 676, 422, 390, 332, 225, and 180 cm^{-1}. The lowest frequency, 180 cm^{-1}, is assigned to torsion about the the C-C bond. The energy barrier to internal rotation in ethanes has been calculated from thermodynamic considerations to be between 3 and 6 k.cal mole^{-1} (69). This has been recalculated by Allen, Brier and Lane (70) from far infra-red and Raman spectral data to be about 9 k.cal. for trichloroethane, 11 k. cal for tetrachloroethane, and 14 k. cal. for pentachloroethane. However, since the separation of the rotating groups will be greater in the radical than in the hydrocarbon, the barriers to internal rotation in the radicals will be less than the values calculated by Allen, Brier and Lane. Initially, then, the torsional vibrational mode in the hydrocarbon is taken

as a free internal rotation in the radical. There is also a considerable weight of experimental evidence to support this assumption (51, 53).

The vibrational mode in ACl which becomes the reaction co-ordinate is taken as the C-Cl stretch with the lowest frequency; in trichloroethane this is 742 cm^{-1}.

The product of the moments of inertia about the principal axes $A^+B^+C^+$ depend on the angle of rotation of the two ends of the radical. The values in Table IV. 1 refer to configurations of the radical which have planes of symmetry.

The fundamental frequencies of trichloroethylene, given by Houser, Bernstein, Mekka, and Angus (71), are : 3085, 1587, 1245, 930, 840, 780, 628, 450, 381, 274, 211, and 172 cm^{-1}. Those of sym-tetrachloroethane have been determined by Kagarise (72) and are : 2980, (2980), 1279, (1244), 1216,1276, (1199), 1024, 975,907, 801, 795, 748, (682), 353, 290, 178, and 88 cm^{-1}. The frequency at 88 cm^{-1} is assigned to torsion about the C-C bond; this mode is assumed to be freely internally rotating in the radical. The lowest C-Cl stretching frequency, 682 cm^{-1}, is regarded as the reaction co-ordinate and the three other bracketted frequencies are the C-H vibrational modes absent in the radical.

The fundamental frequencies of tetrachloroethylene were evaluated by Bernstein (73) and are : 1571, 1000, 931, 782, 512, 447, 404, 347, 318,

288, 237, and 194 cm^{-1} and those of pentachloroethane are : (2985), (1255), (1210), 1022, 835, 821, 773, 725, (584), 405, 328, 278, 238, 224, 176, 166, 32 8, and 85 cm^{-1} (74, 75). The frequency of pentachloroethane at 85 cm^{-1} was assigned to torsion about the C-C bond and that at 584 cm^{-1} was regarded as the the reaction co-ordinate.

The calculation of A_2 and n apparently involves the evaluation of 13 + 12 factors. However, many frequencies can be cancelled between A and ACl^+ ; the frequencies which give significant contributions together with other relevant data are listed in Table IV. 1.

TABLE IV. 1

DATA FOR CALCULATING A_2

Quantity	Value for cis A + Cl	Value for trans A + Cl	Value for C_2Cl_3 + Cl	Value for C_2Cl_4 + Cl	Units
$\frac{kT}{h}$	0.743×10^{13}	0.743×10^{13}	0.743×10^{13}	0.743×10^{13}	sec^{-1}
$A_A B_A C_A$	1.01×10^{-114}	$0.44 \times 10^{-114*}$	0.59×10^{-114}	0.25×10^{-114}	g^3 cm^6
$A^+ B^+ C^+$	9.7×10^{-114}	$15.3 \times 10^{-114*}$	6.05×10^{-114}	0.39×10^{-114}	g^3 cm^6
I^+	3.7×10^{-39}	$3.7 \times 10^{-39*}$	14.5×10^{-39}	17.5×10^{-39}	g cm^2
non cancelling					
frequencies in: A	571,173	763,350,227	450,211 / 1229,307	1571,512,447 / 821,725	cm^{-1}
in ACl	390,232,255	675,422,390,322	801,794,748	224,166	cm^{-1}
$(M^+/M_A)^{3/2}$	1.60	1.60	1.43	1.32	
$(A^+B^+C^+/A_AB_AC_A)^{1/2}$	3.10	5.90	3.23	1.24	
Q^+ vib/Q vib A	1.14	0.95	0.52	2.71	
Q^+ (int rotn)	37	37	63.1	59.3	
σ_A	2	2	1	6	
QCl (transl)	2.62×10^{26}	2.62×10^{26}	2.62×10^{26}	2.62×10^{26}	l mole^{-1} sec^{-1}
P f (T)	6.2×10^{9}	1.00×10^{10}	2.64×10^{9}	3.23×10^{10}	
n =	0.01	0.245	-0.655	0.938	
A calc	6.2×10^{9}	1.28×10^{10}	1.37×10^{9}	7.80×10^{10}	l mole^{-1} sec^{-1}
A (exp)	8.0×10^{10}	3.0×10^{10}	2.68×10^{10}	0.242×10^{10}	mole^{-1} l sec^{-1}
A(exp)/A calc	13	2	20	0.03	

* reference (26)

The A factors which are finally derived are:

$$A \text{ calc (cis DCE)} = 6.2 \times 10^{9} \text{ mole}^{-1} \cdot 1 \cdot \sec^{-1} \tag{53}$$

$$A \text{ calc (trans DCE)} = 1.28 \times 10^{10} \text{ mole}^{-1} \cdot 1 \cdot \sec^{-1}$$

$$A \text{ calc (TrCE)} = 1.37 \times 10^{9} \text{ mole}^{-1} \cdot 1 \cdot \sec^{-1}$$

$$A \text{ calc}_c \text{(Tetra CE)} = 7.80 \times 10^{10} \text{ mole}^{-1} \cdot 1 \cdot \sec^{-1}$$

The values for cis-dichloroethylene, trans-dichloroethylene and tri-chloroethylene are respectively 13, 2 and 20 times lower than these obtained experimentally. The discrepancy is not large for this type of calculation and suggests that the frequencies assigned to the bending vibrations of the C-Cl bond in the complex were too high. However, the assumption of free rotation in the activated complex is essential to obtain even reasonable agreement between theory and experiment. A calc would be 20 to 40 times lower if this mode were a torsional vibration.

The theoretical A factor for tetrachloroethylene is, however, about 30 times greater than the experimentally observed value. This together with the fact that the energy barrier to internal rotation in pentachloroethane is 14.2 Kcal (70) which, though lowered in the radical, might still be sufficiently high to prohibit free internal rotation in the radical, suggests that internal rotation in the pentachloroethyl radical might be restricted. Assuming this mode to be a torsional vibration of frequency 85 cm^{-1} the A factor becomes

$$A \, calc \, (Tetra \, CE) \quad = \quad 0.87 \times 10^{10} \, mole^{-1} \cdot l \cdot sec^{-1}$$

It seems reasonable to assume, therefore, that the pentachloroethyl radical cannot rotate freely about the C-C bond.

The concept of the lowering or "softening" of certain vibrational frequencies is of particular significance in the calculation of the unimolecular rate constant. Equations 1a70 and 1a71 show that the energy dependent unimolecular rate constant is proportional to the ratio of the number of quantum states of the activated complex to the number of quantum states of the active radical. Obviously changes in frequency values will have a marked effect on the numbers of configurations accessible to the activated complexand to the active radical and hence on the final value of the unimolecular rate constant.

The experimentally derived unimolecular rate constant, ka, is an average value for all values of the excess energy E^+ greater than zero or all values of E^* greater than Ea and can be related to the energy dependent unimolecular rate constant $k_3(E^*)$ (equation 1a98) by the equation

$$ka \quad = \quad \int_{Ea}^{\infty} k_3(E^*) \, f(E^*) \, dE^* \Big/ \int_{Ea}^{\infty} f(E^*) \, dE^* \qquad \qquad IV9$$

where $f(E^*) dE^*$ is the fraction of ACl^* molecular with energies between E^* and $E^* + dE^*$. $f(E^*)$ depends on the energy distribution among the reactants - the olefin and Cl

Evaluation of $k_3(E^*)$ (eqn 1a98)

where

$$k_3(E^*) = \frac{kT}{h} \quad \frac{P_1^+ P_r^+}{P_1 \, P_a} \quad \frac{\Gamma(s)\,\Gamma(t/2)}{\Gamma(r/2+1)} \quad \frac{\prod_i (h\nu_i) \sum P(Ev)\left(\frac{E^+ - Ev}{kT}\right)^{r/2}}{\int_{z=0}^{E^+} (E^*+Eo-z)^{s-1}\left(\frac{z}{kT}\right)^{t/2-1} dz}$$

<div align="right">IV 10</div>

requires a knowledge of the number of internal rotations of the activated complex, r; the number of internal rotations of the active radical, t; and the number of vibrational degrees of freedom of the active radical, s. For the tetrachloroethyl radical $t = r = 1$ and $s = 14$ (there are $3 \times 7 - 6 = 15$ internal degrees of freedom, one is a free internal rotation and 14 are vibrations). Equation IV 10 therefore becomes

$$k_3(E^+) = \frac{kT}{h} \quad 2. \quad \frac{P_1^+ Pr^+}{P_1 \, P_a} \quad 13! \quad \frac{\prod_i (h\nu_i) \sum P(Ev)\left(\frac{E^+ - Ev}{kT}\right)^{\frac{1}{2}}}{\int_{z=0}^{E^+} (E^*+Eo-z)^{s-1} (z/kT)^{-\frac{1}{2}} dz}$$

<div align="right">IV 11</div>

The above equation was simplified using the relationship

$$\Gamma(\tfrac{1}{2} + 1) = \tfrac{1}{2}\Gamma(\tfrac{1}{2}) = \tfrac{1}{2}\sqrt{\pi}$$

If it is assumed that there is little change in the structure of ACl in the process $ACl^* \longrightarrow ACl^+$ the partition function ratio $P_1{}^+ Pr^+ / P_1 Pa$ will be unity. Almost certainly the ratio will not exceed 2. From the listed energies it is found that $Eo = 18, 180$ cal mole^{-1}. Assuming that $Ea = 20,000$ cal mole^{-1} and writing $E^+/Eo = \alpha$ the integral in the denominator of IV 11 can be evaluated by successive integrations by parts and can be expressed as

$$I = (kT)^{\frac{1}{2}} Eo^{s-\frac{1}{2}} \sum_n^s \left[\frac{2^{2n} n! \, (s-1)!}{(2n)! \, (s-n)!} \times \alpha^{(n-\frac{1}{2})} \right] \qquad \text{IV 12}$$

where $s = 14$ and α can have any value greater than 1.10.

The summation in equation IV 12 is plotted as a function of $E^+ = E^* - Ea$ in figure IV 1.

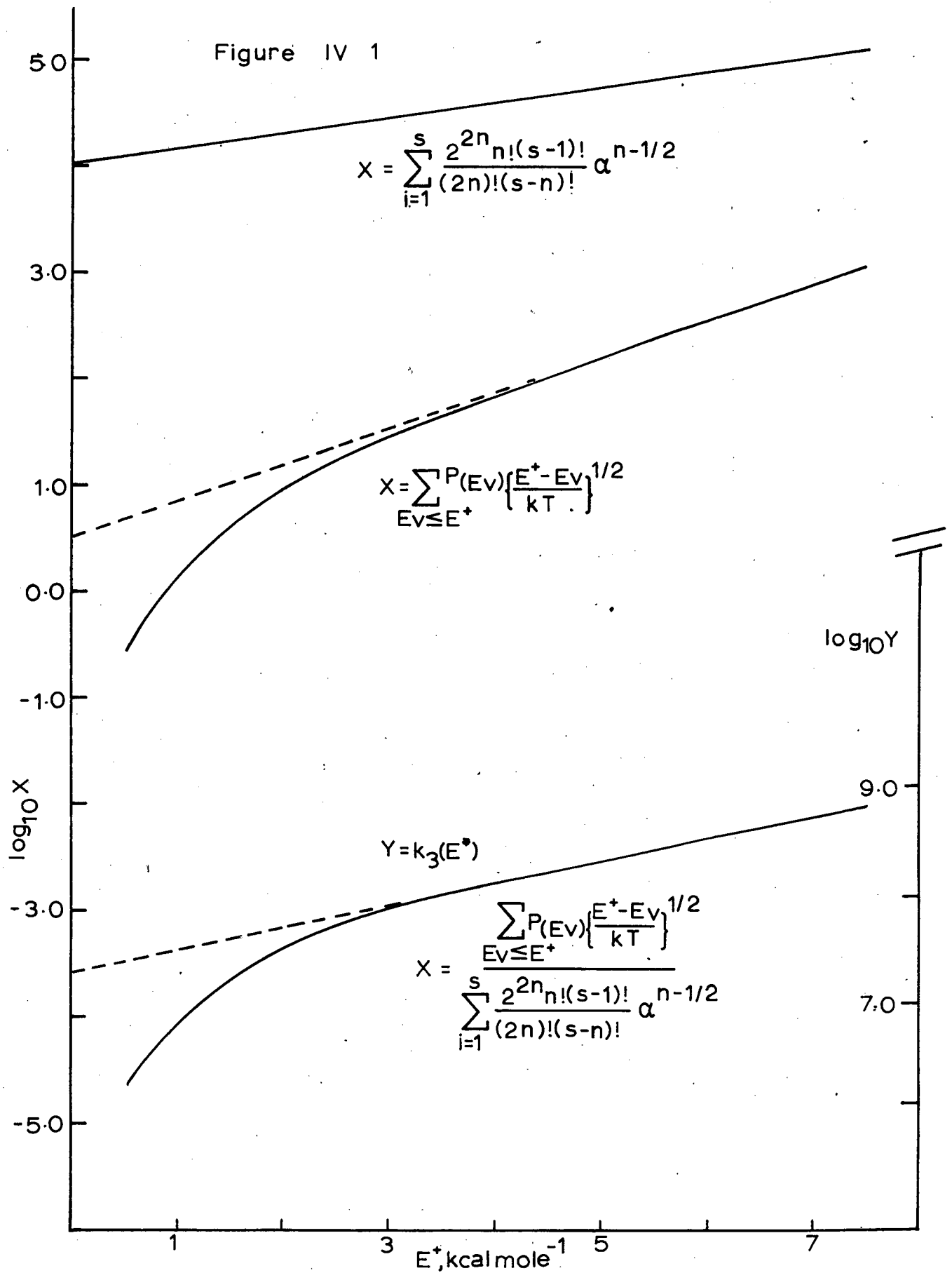The summation in the numerator of equation IV 11 can be evaluated

explicitly only for low values of Ev which the number of combinations of frequencies is limited. The first five Ev are 0, 510, 830, 870, and 1580 cal mole^{-1} and for each $P(Ev) = 1$. For higher energies the number of combinations multiplies so rapidly that an approximate treatment is required.

The method used in this work has been described by Fowler (67) and has been used to interpret mass spectral data (77). The method involves the frequencies being arranged in multiples of the lowest energy and yields $P(Ev)$ values as coefficients of a polynomial generated by expansion of a number of power series. The computer was programmed so that it calculated the coefficients of each term of each series, the products of the coefficients being summed subject to certain energy restrictions. These sums of products were printed out by the computer and corresponded to the number of vibrational energy states at a given energy.

The vibrational frequencies of the tetrachloroethyl radical fall reasonably well into four groups and the members of each group are assumed to have equal frequencies, the group frequencies themselves being simple multiples of each other; thus for the tetrachloroethyl radical there are : 3 frequencies at 770 cal. mole^{-1} (510, 830 and 970 cal. mole^{-1} mean = 770 cal. mole^{-1}); 5 frequencies at 2310 cal. mole^{-1} (1475, 1948, 2140, 2280, and 2284, mean = 2100 cal. mole^{-1}); 5 frequencies at 3080 cal mole^{-1} (2590, 2760, 2930, 3470, and 3660, mean); and 1 frequency at 8520 cal. mole^{-1}. The degeneracy of each level is plotted as a function of the excess energy

Figure IV 1

$$X = \sum_{i=1}^{s} \frac{2^{2n} n! (s-1)!}{(2n)! (s-n)!} \alpha^{n-1/2}$$

$$X = \sum_{Ev \leq E^+} P(Ev) \left\{ \frac{E^+ - Ev}{kT} \right\}^{1/2}$$

$Y = k_3(E^*)$

$$X = \frac{\sum\limits_{Ev \leq E^+} P(Ev) \left\{ \frac{E^+ - Ev}{kT} \right\}^{1/2}}{\sum\limits_{i=1}^{s} \frac{2^{2n} n! (s-1)!}{(2n)! (s-n)!} \alpha^{n-1/2}}$$

E^+ and, by drawing a smooth curve, the approximate number of energy levels per 200 cal. mole^{-1} energy range may be found. The summation may then be evaluated for different values of E^+ by adding terms for every 200 cal. mole^{-1} interval. The computer program for calculating "Fowler's polynomials" is given in appendix B and the sums of degeneracies of the vibrational energy levels per quantum up to 100 quanta excess energy are given in appendix C. The final value for the summation is plotted against E^+ in figure IV. 1 along with the derived values of $k_3(E^*)$. $k_3(E^*)$ increases rapidly with E^* and at high values (broken line) has the form

$$\log k_3 (E^+) = 7.28 + 0.208 E^+ \text{ (k cal. mole}^{-1}\text{)}.$$

It is convenient here to question the accuracy of the "semi-classical" count for the number of vibrational/rotational energy levels per unit energy of the active radical. Several authors (23, 24, 78) have noted the original classical expression for the number of vibrational energy levels, $N^*(E^*) \, dE^*$ d.., in the range E^* to $E^* + dE^*$ given by

$$N^*(E^*) \, dE^* = \frac{(E^*)^{s-1}}{\Gamma(s) \prod_i^s (h \nu_i)} dE^*$$

based on integration over all energies less than E^* using Dirichlet's integral (25) to be seriously at fault at energies of experimental interest. Marcus and Rice (23) suggested the "semi-classical" expression for the average number of vibrational energy levels per unit energy. Thus

$$N^*(E^*) = \frac{(E^* + Eo)^{s-1}}{\Gamma(s) \prod_i^s (h\nu_i)} \qquad \text{IV.13}$$

$$\text{where } Eo = \frac{1}{2} \sum_{i=1}^s (h\nu_i) \qquad \text{IV.14}$$

Rabinovitch and Diesen (79) have modified equation IV.13 by the inclusion of an empirical correction factor. It gives

$$N^*(E^*) = \frac{(E^* + \gamma Eo)^{s-1}}{\Gamma(s) \prod_i^s (h\nu_i)} \qquad \text{IV.15}$$

The factor γ has been evaluated by Rabinovitch and Current (80) for several frequency patterns - cyclo C_3H_6, cyclo C_3D_6, $CHCl_3$ and CH_3Cl - by comparison of the accurate computer summation of the energy level degeneracy factors up to various total energies with an integrated form of IV.15 Thus

$$\sum_{Ev=0}^{E^*} P_{(Ev)} = \frac{(E^* + \gamma Eo)^s}{\Gamma(s+1) \prod_i^s (h\nu_i)} \qquad \text{IV.16}$$

The γ values for these cases lie on a band whose value approaches unity at high energies when the semi-classical approximation holds.

The spread of the γ values is made more clear (81) by use of the semi-classical defect quantity $\Delta = 1 - \gamma$. At energies above $E^* = 2 Eo$, the spread becomes insignificant since the use of the energy unit Eo, characteristic of each molecule, reconciles much of the difference between

different molecules. The situation is more critical at lower energies. Since the spread arises as a consequence of the difference in vibrational patterns this suggests a correlation by a frequency dispersion parameter. The ratio

$$\mathbb{V} = \left\langle \nu_i^{*\,2} \right\rangle / \left\langle \nu_i^{*} \right\rangle^2$$

is such a measure. However, the modified dispersion parameter

$\beta = (s-1)\mathbb{V} / s$

$$\text{i.e} \qquad \beta = (s-1)\sum \nu_i^{*\,2} / (\sum \nu_i^{*})^2 \qquad\qquad \text{IV. 17}$$

where s is the number of vibrational degrees of freedom provides an even better correlation and correction factor. The quantity Δ/β has a greatly reduced spread for all molecules of the study (81), when plotted against E^*/E_0 i.e. α. A set of preferred values of Δ/β called ω was selected from this narrow band and form the basis of the "corresponding vibrational states" type of approximation.

The modified approximation expression is

$$\sum_{E_v = 0}^{E^*} P_{(E_v)} = \frac{(E^* + (1 - \beta\omega)E_0)^s}{\Gamma(s+1) \prod_i (h\nu_i)} \qquad\qquad \text{IV. 18}$$

$$\log \sum_{E_v = 0}^{E^*} P_{(E_v)} = s\log(\alpha + 1 - \beta\omega) + C$$

$$\text{IV. 19}$$

where $c = s \log E_0 - \log s! - \sum \log h\nu_i$ and α is in units of E_0.

Thus for the evaluation of $\sum P(E_v)$ for any molecule, the molecular frequencies are used to find β and E_0 and equation IV. 18 or 19 is applied together with the selected values of ω. Rabinovitch claims counts within a few per cent of the exact value for the 45 molecules studied at $\alpha > 0.25$.

It was considered, therefore, that some form of correction factor would have to be applied to the zero point energy of the radical in equation IV. 12 in order to obtain a more nearly correct value of the number of rotational and vibrational energy states of the radical.

However, according to the unmodified equation (eqn 1a97) the total number of vibrational/rotational quantum states of the active radical per unit energy is

$$N^*(E^*) = \frac{Pa}{kT \ \Gamma(s) \Gamma(t/2) \ \prod\limits_{i}^{s}(h\nu_i)} \int_0^{E^*} (E_a + E^+ + E_0 - z)^{s-1} \left\{\frac{z}{kT}\right\}^{t/2-1} dz$$

IV. 20

which reduces to

$$N^*(E^*) = \frac{Pa \ E_0^{s-\frac{1}{2}}}{13! \sqrt{\pi}(kT)^{\frac{1}{2}} \prod\limits_{i}^{s}(h\nu_i)} \sum\limits_{n}^{S} \left[\frac{2^{2n} n! (s-1)!}{(2n)! (s-n)!} \alpha^{n-\frac{1}{2}} \right]$$

IV. 21

where Pa is the partition function of the t active rotations of the active radical.

The total number of vibrational/rotational energy levels per unit energy

of the activated complex is given by the integral of equation 1a88

i.e.
$$\int_{0}^{E^+} N_2 (E^+ - y)\,dy = \frac{2P_r^+}{\sqrt{\pi}} \sum_{Ev=0}^{E+} P(Ev)\left(\frac{E+ - Ev}{kT}\right)^{\frac{1}{2}}$$

IV. 22

As described earlier in this section it has been ~ssible to obtain an exact count of $\sum P_{(Ev)}((E^+-Ev)/kT)^{1/2}$ as a function of energy (figure IV. 1) which at high energies (broken line) has the form

$$\log \left(\sum P_{(Ev)}((E^+-Ev)/kT)^{\frac{1}{2}} = 0.5 + 0.344\, E^+ k\, cal. mole^{-1}\right.$$

It should be possible, then, to equate the number of vibrational/rotational energy levels obtained from an extrapolated form of the exact count with the number of vibrational/rotational levels derived from the semi-classical count.

Over the energy range of interest for the tetrachloroethyl radical i. e from 20 k cal. mole^{-1} to 26 k cal. mole^{-1} the number of energy states given by the extrapolated exact count is $2.7 \times 10^7 \times Pr^+$ to $3.1 \times 10^9 \times Pr^+$, whilst the number of states obtained from the semi-classical count is $4.52 \times 10^6 \times$ Pa to $5.03 \times 10^8 \times$ Pa. Assuming $Pr^+ = Pa$, one obtains reasonable agreement between the two calculations which supports both the assumption and the view that the semi-classical approximation requires no modification at the energies with which we are concerned. Indeed to obtain a better corre-

spondence between the two calculations γ would need to be greater than unity which contradicts the whole meaning of the correction factor.

Finally, the energy distribution of the active molecules is required. ACl^* is formed by association of Cl atoms whose energies have a Maxwell-Boltzmann distribution and trichloroethylene molecules in various vibrational states. If it is assumed that the ACl^* radicals possess the same translational and rotational energy spectrum as the original trichloroethylene molecules the internal energy distribution of the ACl^* can be obtained. This is achieved by superimposing on each vibrational stationary state a Maxwell-Boltzmann distribution of translational energies attenuated by the fraction of the total number of molecules in that particular vibrational state. The total distribution function which is the sum of each individual vibrational/translational distribution function is shown in figure IV.2. The distribution approximates at high energies to

$$\log \ f(E^*) \ = \ 1.00 \ - \ 0.400 \ E^+ \ (k \ cal. \ mole^{-1})$$

The approximation will tend to overestimate the amount of energy in the internal modes of ACl^* since it is equivalent to assuming that all the translational energy of the Cl atom is converted into vibrational or internal rotational energy of the active radical. The function $f(E^*) \ k_a(E^*)/k_a$ and the normalized vibrational translational distribution function is shown in figure IV.3 together with $k_3(E^*)$. The figure shows that molecules with energy slightly more than the mean energy contribute most to the reaction
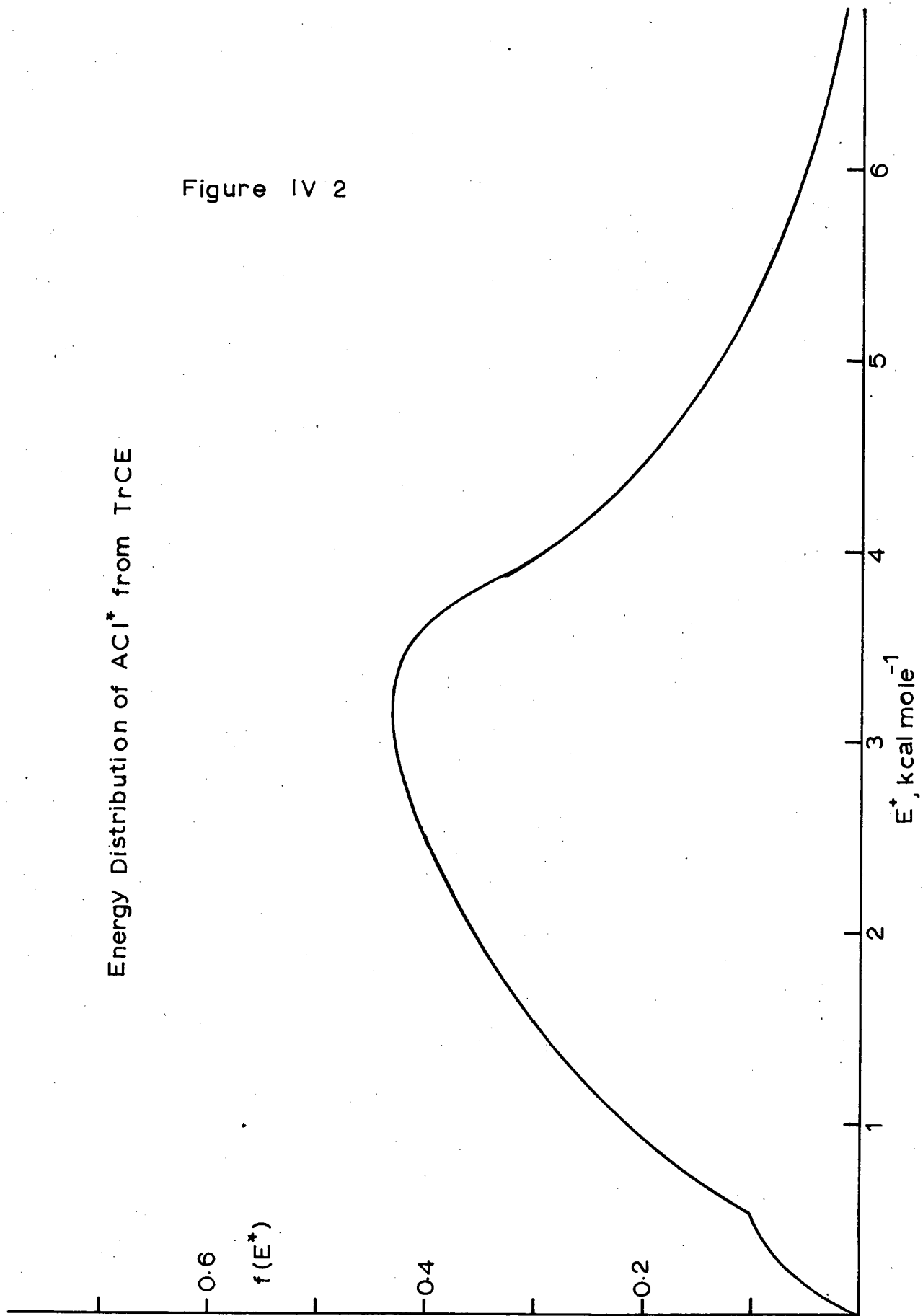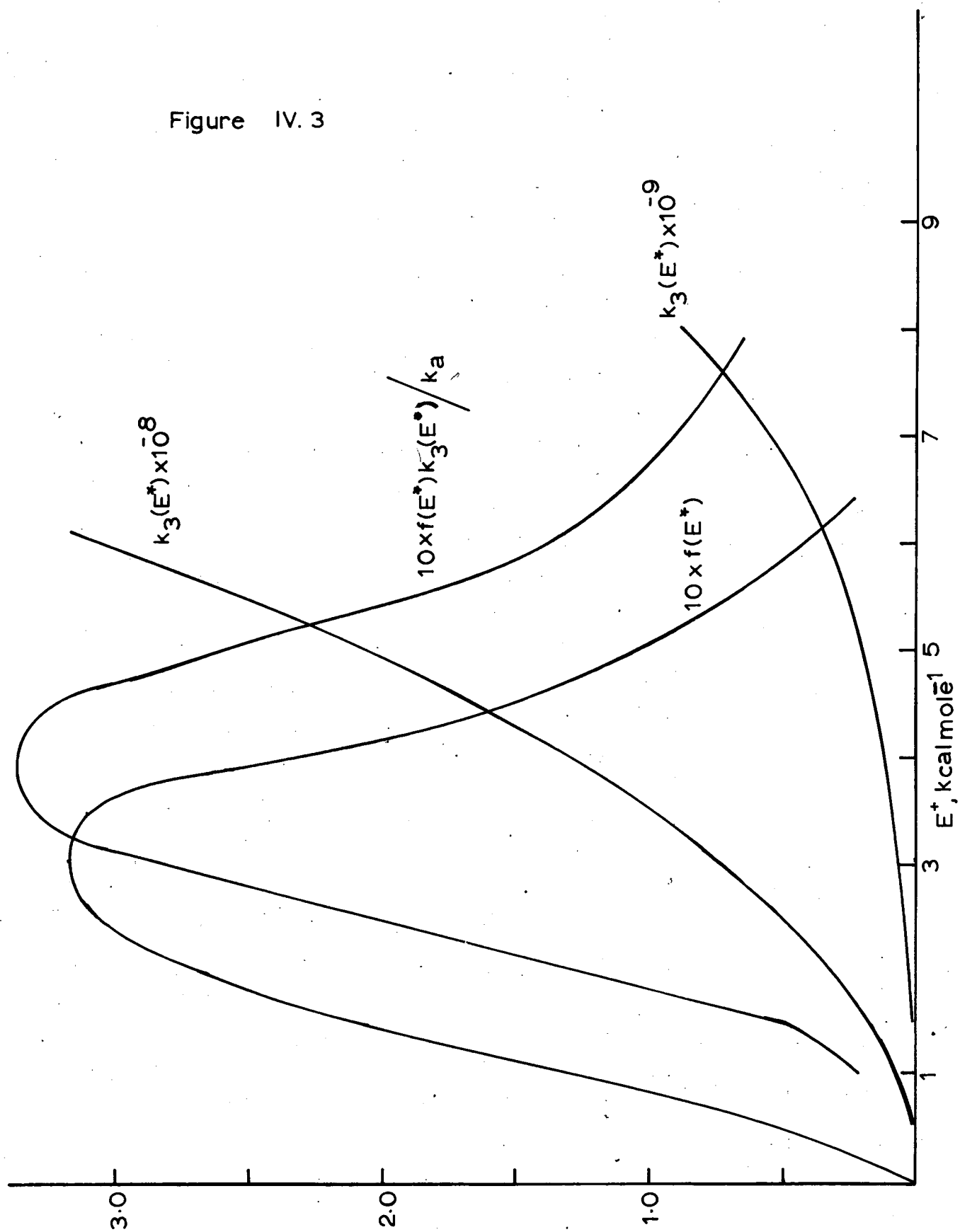
Figure IV 2

Energy Distribution of ACl* from TrCE

Figure   IV. 3

rate. The average value of ka was obtained by integrating the area under the curve of $k_3(E^*)$ times the normalized distribution function, against energy. A value of ka = 0.92×10^8 sec^{-1} is obtained which is to be compared with the experimental value of 7.0×10^8 sec^{-1} at 79°C.

The discrepancy between theory and experiment is smaller than for the bimolecular calculation; the agreement however could be improved. Though the assumption of the lowest possible value of the partition function ratio for the adiabatic modes probably underestimates this value, the internal energy of the complex E^+ has probably been overestimated. These factors will oppose each other. Further, the correspondence between the two methods of calculating the number of rotational and vibrational quantum states of the active radical obtained assuming the partition functions of the internal rotational modes to be equal makes the assumption appear reasonable. There remain four other explanations for the discrepancy.

First, it was assumed that there exist no inactive degrees of freedom. The presence of such degrees of freedom will tend to reduce the denominator in equation IV.11 thereby increasing $k_3(E^*)$. Secondly it is likely that the vibration frequencies of at least two modes are considerably lower in the complex than in the active radical. This will tend to increase P(Ev) by a considerable factor. Thirdly, the value of ka which has been estimated assumes an equilibrium distribution of activated molecules. Because a considerable proportion of the active molecules were in fact deactivated in

the experiments, the lower energy states will be more depleted by collision than the higher energy states since they decompose more slowly. The average collision frequency of ACl^{*} with other molecules at the pressure used in this work was about $5 \times 10^{8} sec^{-1}$. Thus the observed k_a will be somewhat higher than the k_a calculated assuming that no deactivation occurs.

Fourthly, apart from any inadequacies in the calculations, the experimental value of k_a is based on the assumption that deactivation of ACl^{*} by Cl_2 is 100% efficient. The experimental k_a would be lower if chlorine was less efficient, agreement between theory and experiment thereby being improved. Knox (26) has argued that, since the calculated bimolecular A factors for cis and trans dichloroethylene are 13 and 4 times less than the experimental values, incorrect vibrational frequencies have been assumed for two vibrations in the transition state complexes. It would, therefore, be expected that, since the bimolecular and unimolecular reactions proceed via the same transition state, the discrepancy between the theoretical and experimental values for the unimolecular rate constant would be the same as that for the bimolecular A factor. Comparing the factor of 20 for the discrepancy between the theoretical and experimental unimolecular rate constants for dichloroethylene, Knox suggests that if the error is caused entirely by inefficiency of deactivation, Cl_2 is between 20 and 50% efficient.

Whilst the results of this work do not contradict the suggestion that deactivation of ACl^{*} occurs as a result of 2 to 5 collisions with chlorine, the coincidence that argon and chlorine both deactivate the active radical by the same multistage process (according to this work they have the same deactivating efficiency), indicates that the de-excitation process is more

The high efficiency of deactivation by chlorine which has in its infra-red spectrum a band at 526 cm^{-1} (86), by propane whose vibrational levels are : 372, 748, 870, 923, 1053 cm^{-1} etc. (87), by CO_2 whose vibrational levels are at 667, 1388, 2077 cm^{-1} etc. (88) by SF_6 which has a great number of vibrational levels between 500 and 1000 cm^{-1} e. g. at 546, 605, 626, 693, 705, 940, 984, and 995 cm^{-1} (89) and by trichloroethylene, whose vibrational spectrum has been given, can be easily understood. De-excitation of the active radical probably occurs either by resonance energy transfer or by a complex collision (90) in which most of the vibrational quantum received by the deactivant is transferred into one of its vibrational modes, the remaining energy going directly to translation. It is not surprising then that these gases have comparably high efficiencies; the slight preference of the active radical for deactivation by trichloroethylene might infer the predominance of resonance energy transfer over the complex collision mechanism.

However, the results of this work show that argon is equally as efficient as the more complex molecules in deactivating the active species. This result appears genuine having been obtained by studying the dependence of the selectivity, R_{nPrCl}^{PCE}, on argon pressure over the same pressure range as employed in the determination of the other deactivating efficiencies.

Energy transfer theory (82) predicts that the efficiency of deactivation

increases with an increase in mass of the deactivant and with a decrease in the amount of energy transferred. Since the active radical is a highly vibrating species whose oscillators will be expected to be in a fairly high quantum state, and since the energy jumpt between a high vibrational quantum state and the next lower state will be relatively small, the transfer of this energy to translation in the heavy argon atom should occur readily. It seems reasonable, therefore, that all the gases studied in this work should have the same deactivating efficiency. A useful test of the dependence of the efficiency of deactivation on mass would be to study the dependence of R_{nPrCl}^{PCE} on hydrogen pressure.

Dainton (59) has stated that the unimolecular rate constants obtained by Knox and Riddick (53) are too high by a factor of 10^3. This statement is based on the fact that complete deactivation of the active intermediate requires 10^3 collisions. Whereas it is true that 10^3 collisions are required to deactivate the active radical to the ground state (this is due to the innefficiency of the de-excitation of the $v = 1$ to $v = 0$ state) it is our contention that only a small critical excess energy, on average about 3 k. cal., need be removed to render the active radical incapable of decomposition.

Our results on the deactivating efficiencies of the gases studied agree with those of Goldfinger et al (92) who have recently reinvestigated the chlorination of ethylene in competition with ethane and have obtained the following results for the deactivating efficiencies per collision of the various

gases relative to ethane:

Cl_2	C_2H_4	C_2H_6	SF_6	CO_2
0.46	0.45	1.00	0.30	0.48

The rate constant for the unimolecular decomposition of the active mono-chloroethyl radical was found to be

$$ka = 2.0 \times 10^9 \; sec^{-1}$$

However, these results cannot be regarded with too great confidence. Apart from following the reaction manometrically, they noted a considerable amount of dark reaction (up to 20% of the photo rate at $310^\circ K$) which was so rapid at higher temperatures that further investigation was made impossible. This dark reaction has been attributed to a thermal process which is claimed to have the same rate as the photochemical reaction precluding the necessity of correcting for it.

In this work on the chlorination of trichloroethylene and of trans-dichloroethylene, both of which have been shown to be homogeneous, no detectable dark reaction occurred in the time required for adequate mixing at $40^\circ C$. The thermal chlorine atom concentration at this temperature is so small that amounts of reaction in ca 100 seconds is negligible (38). In the work on ethylene and vinyl chloride, however, considerable dark reaction was noted at $79^\circ C$ and $40^\circ C$ which has been shown to be surface dependent. That it should occur at the same rate as the photochemical reaction would seem fortuitous.

Finally, since the energy dependent unimolecular rate constant $k_3(E^*)$ is proportional to the ratio of the number of quantum states of the activated complex to the number of quantum states of the active radical its value is dependent not only on the size of the quanta attributed to each vibrational mode but also on the nature of the frequency assignment.

For dichloroethylene (26) and trichloroethylene agreement between the theoretical and experimental unimolecular and bimolecular rate constants is only obtained by assuming that the lowest vibrated frequency, attributed to torsion in the saturated hydrocarbon, is in fact a free rotation in the radical. In the case of tetrachloroethylene, however, correspondence between the theoretical and experimental bimolecular rate constants is achieved by assuming that internal rotation is restricted in the pentachloroethyl transition state.   This has a considerable influence on the calculation of the overall unimolecular rate constant.

According to equation 1a78 the energy dependent unimolecular rate constant $k_3(E^*)$ has the form

$$k_3(E^*) = \frac{P_1^+}{hP_1} \times \int_{x=0}^{E^+} \frac{N_2(x)\,dx}{\sum\limits_{Ei=0}^{E^*-Ea} \left(N^*(E^* - Ei)\,DEi \right)}$$

IV 23

where P_1^+ and P_1 are the adiabatic degrees of freedom of the activated complex and the active radical modes when their energy is Ei.

If, as in the calculation of the unimolecular rate constant for trichloro-ethylene, Ei is assumed to be zero and P_1^+/P_1 is assumed equal to unity, equation IV. 23 reduces to

$$k_3(E^*) = \frac{1}{h} \quad \frac{E^+ \overset{\sum}{\geq} Ev \quad P(Ev)}{N^*(E^*)}$$

IV 24

for purely vibrational degrees of freedom in the transition state.

The sum of the degeneracies of the vibrational levels of the activated complex $\sum P(Ev)$ can be obtained by a computer calculation of Fowler's polynomials having first arranged the frequencies of the pentachloroethyl radical into three groups which are multiples of the lowest frequency viz 3 frequencies at 400 cal. mole^{-1} (234, 472, and 500 cal. mole^{-1}, mean = 400 cal. mole^{-1}), 6 frequencies at 800 cal. mole^{-1} (643, 680, 794, 937, 937, and 1158, mean = 860) and 5 frequencies at 2400 cal. mole^{-1} (2070, 2210, 2350, 2380, and 2920, mean = 2386). Log $\sum P(Ev)$ is plotted as function of E^+ in figure IV 4.

The number of quantum states of the active radical per unit energy, No. (E^*), is obtained from an integrated form of the Marcus semi-classical expression (eqn IV 13 Thus)

$$N^*(E^*) = \frac{(E^* + Eo)^s}{\Gamma(s+1) \quad \prod_i (h\nu_i)} s$$

From the listed energies Eo = 8.23 kcal and Ea was taken as 17 k. cal mole^{-1} (49).

Figure IV 4
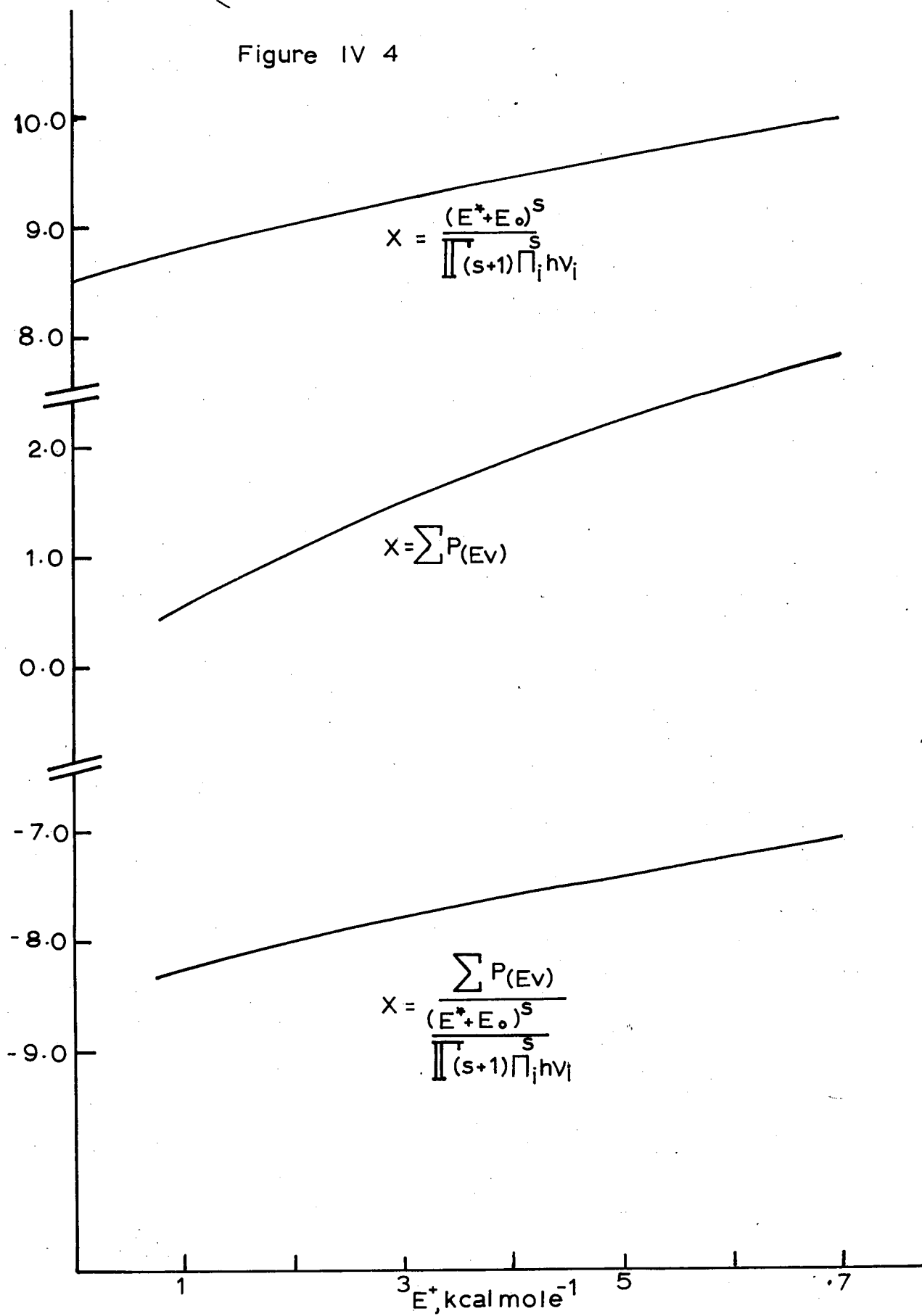
The logarithm of $N^*(E^*)$ together with the log of the ratio $\sum P(EV)/N^*(E^*)$ is plotted as a function of $E+$ in figure IV 4; the energy dependent unimolecular rate constant is plotted as a function of E^r in figure IV. 5. The vibrational/translational energy distribution was again obtained by superimposing on each vibrational stationary state a Maxwellian distribution of translational energies of the chlorine atoms, attenuated by the fraction of the total number of olefin molecules in any particular vibrational energy state. The total distribution function was obtained by summation over all energies; the normalized curve is shown in figure IV.5.

The overall unimolecular rate constant ka was obtained by integrating the area under the curve of $k_3(E^*)$ $f(E^*)$ as a function of the excess energy E^+, from which a final value of ka = 0.2×10^7 sec^{-1} was obtained. The lifetime of the active pentachloroethyl radical is therefore 5×10^{-7} seconds at 79°C.

Experimentally, we have estimated a lower limit on the lifetime to be 2×10^{-8} seconds. This estimate was arrived at from the fact that the curve of R_{nPrCl}^{HCE} against pressure showed no dependence on pressure down to a total reactant pressure of 6 mm. As a rule of thumb the pressure independent region of the rate of addition occurs when the collision frequency of ACl^* with other molecules is about 10 times greater than the rate of unimolecular decomposition of the active intermediate. Making this assumption, since the limiting high pressure value is obtained at 6 mm. i.e. $Z^o = 6 \times 10^7$

Figure IV 5
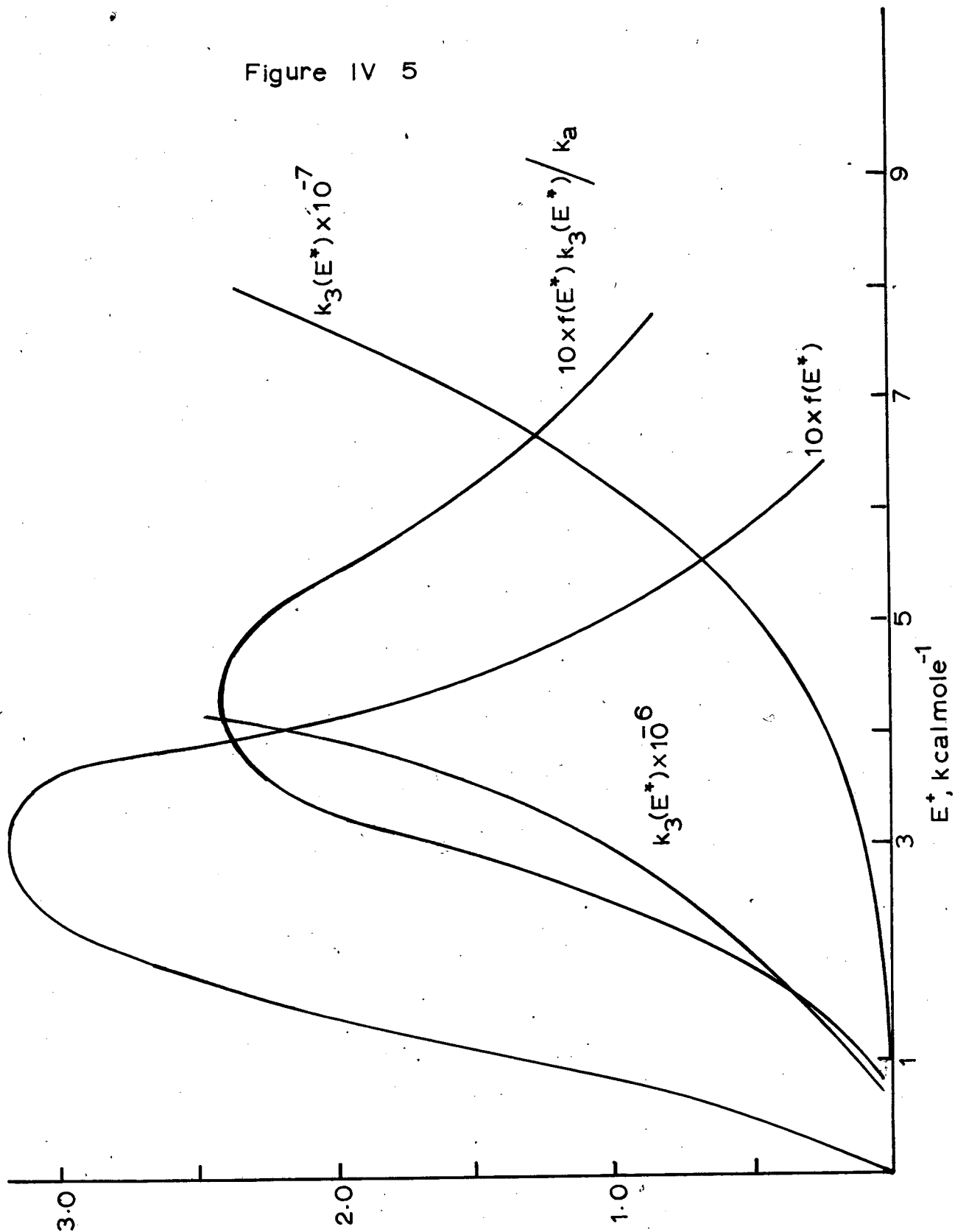
collisions sec^{-1} one obtains an estimate of the radical lifetime to be 2×10^{-7} seconds. Here again, agreement between theory and experiment is good; but as in the bimolecular case it is necessary to assume that the pentachloroethyl radical cannot rotate freely about the C-C bond.

CONCLUSION

The good agreement between theory and experiment gives support for the overall mechanism used in this work. The activated complexes and active radicals in the chlorination of dichloroethylene (53) and trichloroethylene can apparently rotate freely about the C-C bond, and their vibration frequencies may be taken as the same as those in similar molecules apart from two in each of the complexes which are probably lower. In the chlorination of tetrachloroethylene there is no internal rotation in the activated complex or the active radical.

The similarity of the efficiencies of collisional deactivation for a set of molecules of widely varying structure supports the assumption that the active radicals are deactivated at every collision and that reactions of the type

$$ACl^* + Cl_2 = ACl_2 + Cl$$

are unlikely. This type of collisional deactivation resulting from chemical affinity and leading to anomalously high efficiencies of deactivation has been widely reported in the literature (93-96).

Experimental determination of the rate of unimolecular decomposition of the pentachloroethyl radical in a static system would necessitate working in the pressure range 0-6 mm. which could be measured accurately by an extremely sensitive form of bellows pressure measuring device.

(It operates by following the minute movement of the glass bellows with a micrometer the movement of which is monitered on a pen recorder). Alternatively, the chlorination of tetrachloroethylene could be studied absolutely in a fast flow system. Chlorine atoms can be generated by a microwave generator (97) and measurement of their concentration can be achieved either by calibrating the intensity of the orange-red glow resulting from their recombination (98) or by measuring the heat evolved from their recombination on a platinum thermocouple. This fast flow system is particularly attractive since it affords the possibility of obtaining not only the rate constants of the chlorination of tetrachloroethylene absolutely, but also the absolute rate constants for the chlorination of hydrocarbons e.g. methane and chloroform, allowing a check to be made on the rate constants of the latter two molecules, previously determined by a competitive technique. The method suffers from one severe restriction though, in that it is impossible to use it to measure bimolecular reactions whose rates exceed $10^9 \text{ mole.}^{-1} \text{ l. sec}^{-1}$ due to limitations in rates of flow in the reaction tube.

Although Goldfinger et al. have reinvestigated the chlorination of ethylene and have obtained values of k_a and of collisional deactivating efficiencies, their methods are less than satisfactory. It would be interesting, theoretically, to try to determine the parameters of the chlorination of ethylene and vinyl chloride to observe the effect of a small change in structure on the rates of bimolecular and unimolecular

reaction over the complete series of halogenated ethylenes.   The difficulty

in the ethylene and vinyl chloride chlorinations lies in the fast rate of

heterogeneous addition;   the method of investigation must therefore

inhibit diffusion to the walls   e. g. by carrying out the reaction in a flow

system in the middle of an annulus of inert gas or by using a technique

similar to flash photoysis in which the rates of production and decay of

atoms is faster than their rate of diffusion to the walls.

A very difficult but fairly elegant experiment would be to attach

an infra-red spectrophotometer to the end of a flow tube.   This would

afford not only the absolute overall rate constants for the chlorination of

an olefin, but also, by observing the infra-red chemiluminescence at different

points down the tube one could obtain the relative rates of reaction into

various vibrational levels.   If the experiment were carried out with cis

or transdichloroethylene a complete energy determination of the

bimolecular and unimolecular reactionscould be obtained.

The Arrhenius parameters for the reaction

$$A + Cl \qquad ACl^* \qquad 2''$$

in the series $A = C_2H_nCl_{4-n}$ (n = o to 4) are given in the following table:
the values of k_2'' at $350^0 C$ have also been included.

Reaction	log A_2'' (1. mole^{-1} sec^{-1}.)	E (k. cal. mole^{-1}.)	log k_2''	Reference
$C_2H_4 + Cl$	10.2 ± 0.1	O	10.2	65
	10.6	O	10.6	92
$C_2H_3Cl + Cl$	10.3 ± 0.6	1.5 ± 1.0	9.4	57
Cis. $C_2H_2Cl_2 + Cl$	10.3 ± 0.4	1.2 ± 0.7	9.6	52
	10.9 ± 0.2	0.19 ± 0.25	10.8	53
trans $C_2H_2Cl_2 + Cl$	10.5 ± 0.2	-0.17 ± 0.23	10.6	53
$C_2HCl_3 + Cl$	10.3 ± 0.6	1.5 ± 1.0	9.4	57
	9.75	O	9.75	50
	10.4 ± 0.1	-0.24 ± 0.41	10.7	this work
$C_2Cl_4 + Cl$	9.2	O	9.2	46
	9.4	O	9.4	this work

It is difficult to draw any conclusion about the general trend of these
results since the disagreement between different workers for a given
reaction is almost as large as the spread for all the reactions.

Nonetheless, since the standard collision number for the collision
of a chlorine atom with an olefin is about 10^{11} mole^{-1}. 1. sec^{-1}, the steric
factor for the collision is about 0.1 for the series ethylene to trichloro-
ethylene.   For the chlorine atom tetrachloroethylene reaction, however,
only one in one hundred collisions is effective.   This must result from a
high entropy of activation associated with a rigid transition state complex.
This gives further weight to the idea that internal rotation is restricted in
the pentachloroethyl transition state complex.

APPENDIX B

COMPUTER PROGRAM IN ATLAS AUTOCODE FOR THE CALCULATION OF FOWLER'S POLYNOMIALS

FOR THE TETRACHLOROETHYL RADICAL

```
Integer        N, M, O, P, I, Z, D, C, B
Integer        K1, K3, K4, K11,
Integer        J1, J3, J4, J11
Integerarray   N1, (1:101), M1 (1:103), 01 (1:101), P1 (1:111)
Integerarray   A (1:101)
Read           (N, M, O, P)
Cycle          I = O, 1, 100
N1 (I) = 0
01 (I) = 0
A (I) = 0
Repeat
Cycle          I = 0, 1, 102
M1 (I) = 0
Repeat
Cycle          I = 0, 1, 110
P1 (I) = 0
Repeat
Cycle          I = 0, 1, 100
If             N = 1  Then→   1
If             I = 0  Then    Z = (( N + I - 1 ) *Z)/(I)
If             I = 0  Then    Z = 1
N1 (I) = Z;→ 2
1 : N1 (I) = 1
2 : Repeat
Cycle          I = 0, 3, 102
If             M = 1  Then→ 3
If             I = 0  Then    Z = (( M + (I/3) - 1) *Z)/(I/3)
If             I = 0  Then    Z = 1
M1 (I) = Z; → 4
3 : M1 (I) = 1
4 : Repeat
Cycle          I = 0, 4, 100
If             O = 1  Then → 5
If             I = 0  Then    Z = (( O + (I/4) - 1) *Z)/(I/4)
If             I = 0  Then    Z = 1
O 1 (I) = Z; → 6
5 : O1 (I) = 1
6 : Repeat
Cycle          I = 0, 11, 110
If             P = 1  Then → 7
If             I = 0  Then    Z = ((P + ( I/11) - 1) *Z )/(I/ 11)
```

```
If              1 = 0    Then   Z = 1
P1 (I) = Z ;  →  8
7 : P1 (I) = 1
8 : Repeat
Cycle           1 = 0, 1, 100
J1 = I
Print           (J1,  3, 0)
Newline
K1 = N1 (I)
Cycle           C = 0, 3, 102
J3 = J1 +C
If              J3   100   Then  →  15
K3 = K1 * M1 (C)
Cycle           B = 0, 3, 100
J4 = J3 + B
If              J4   100    Then  →  16
K4 = K3*O1 (B)
Cycle           D = 0, 11, 110
J11 = J4 + D
If              J11   100   Then  →  17
K11 = K4 * P1 (D)
A (J11) = A (J11) + K11
Repeat
17 : Repeat
16 : Repeat
15 : Repeat
Cycle              I = 0, 1, 100
Print   A ( I )
Newline
Repeat
End of Program
3  5  5  1
→ Z
3  5  5  1
```

Excess Energy in Quanta	No. of States
44	29960992
45	36560251
46	44472442
47	53931440
48	65208431
49	78617775
50	94521608
51	113336526
52	135541830
53	161686951
54	192400869
55	228402211
56	270569863
57	319856731
58	376903705
59	443452841
60	520666101
61	610085296
62	713450352
63	832722420
64	970110751
65	1128098751
66	1309474677
67	1517364635
68	1755268751
69	2027100986
70	2337234669
71	2690545185
72	3092465014
73	3549042102
74	4066996980
75	4653790201
76	5317698141
77	6067889157
78	6914509766
79	7868777621
80	8943080137
81	10151086455
82	11507885147
83	13030005274
84	14735758722
85	16645191348
86	18780335006
87	21165363729
88	23826778227
89	26793606715
90	30097617101
91	33773548507
92	37859355765
93	42396470667
94	47430131764
95	53009590344

Excess Energy in Quanta:	No. of States
96	69188535229
97	86025402282
98	73588746929
99	81932646462
100	91147136074

BIBLIOGRAPHY

(1) S. Arrhenius,   Z. physik, Chem., 1889, 4, 226.

(2) W.C. McC. Lewis,   J. Chem. Soc., 1918, 113, 471.

(3) J. Perrin,   (a) Ann. phys., 1919, 11, 5.
                                                 (b) Trans. Faraday Soc., 1922, 17, 546.

(4) I. Langmuir,   J. Amer. Chem. Soc., 1920, 42, 2190.

(5) G.N. Lewis and D.F. Smith,   J. Amer. Chem. Soc., 1925, 47, 1508.

(6) F.A. Lindemann,   Trans. Faraday Soc., 1922, 17, 598.

(7) C.N. Hinshelwood and H.W. Thomson,   Proc. Roy. Soc., 1926, 113, A, 221.

(8) C.N. Hinshelwood,   ibid., 1927, 114, A, 84.

(9) C.N. Hinshelwood and P.J. Askey,   ibid., 1927, 115, A, 215.

(10) H.C. Ramsperger,   J. Amer. Chem. Soc., 1927, 49, 912, and 1495.

(11) D.J. McKenney and K.J. Laidler,   Canad. J. Chem., 1963, 41, 1984.

(12) K.J. Laidler and M. Eusuf,   ibid., 1965, 43, 268.

(13) M.H. Jones and E.W.R. Steacie,   J. Chem. Phys., 1953, 21, 1018.

(14) S. Toby and K.O. Kutschke,   Canad. J. Chem., 1959, 37, 672.

(15) J.A. Kerr, D.H. Slater, and J.C. Young,   J. Chem. Soc., A, 1966, 104.

(16) C.N. Hinshelwood,   Proc. Roy. Soc., 1926, 113, A, 230.

(17) C.S. Elliot and H.M. Frey,   Trans. Faraday Soc., 1966, 62, 895.

(18) F. J. Fletcher, B. S. Rabinovitch
F. W. Watkins and D. J. Locker,   J. Phys. Chem., 1966, 70, 2823.

(19) L. S. Kassel,   J. Phys. Chem., 1928, 32, 225.

(20) O. K. Rice and H. C. Ramsperger,   J. Amer. Chem. Soc., 1927, 49, 1617.

(21) H. Eyring,   J. Chem. Phys., 1935, 3, 107.

(22) For a review of London's ideas
see   "Theory of Rate Processes",

S. Glasstone, K. J. Laidler and
H. Eyring   McGraw-Hill, (N. Y.), 1941.

(23) R. A. Marcus and O. K. Rice,   J. Phys. Chem., 1951, 55, 894.

(24) R. A. Marcus,   J. Chem. Phys., 1952, 20, 359.

(25) R. C. Tolman,   "Principles of Statistical Mechanics," Oxford University Press, 1938, 492.

(26) J. H. Knox,   Trans. Faraday Soc., 1966, 62, 1206.

(27) H. O. Pritchard, J. B. Pyke
A. F. Trotman-Dickenson,   J. Amer. Chem. Soc., 1955, 77, 2629.

(28) J. H. Knox,   Chem. and Ind., 1955, 1631.

(29) P. C. Anson, P. S. Fredricks
and J. M. Tedder,   J. Chem. Soc., 1959, 918.

(30) P. S. Fredricks and J. M. Tedder,   ibid., 1960, 144.

(31) J. H. Knox and R. L. Nelson,   Trans. Faraday. Soc., 1959, 55, 937.

(32) J. H. Knox,   Trans. Faraday Soc., 1962, 58, 275.

(33) W. H. Rodebush and W. C. Klingelhoeffer,   J. Amer. Chem. Soc., 1933, 55, 130.

(34) E. Wrede,   Z. Physik., 1929, 54, 51.

(35) H. Steiner and E. K. Rideal,   Proc. Roy. Soc., 1939, 173, A, 503.

(36) A. Farkas, Z. physik. Chem., 1930, B, 10, 419.

(37) G. C. Fettis and J. H. Knox, "Progress in Reaction Kinetics Vol. 2", Pergamon Press, (London) 1964.

(38) S. W. Benson and J. H. Buss, J. Chem, Phys., 1958, 28, 301.

(39) S. W. Benson, ibid., 1952, 20, 1605.

(40) P. G. Ashmore and J. Chanmugam, Trans. Faraday Soc., 1953, 49, 254.

(41) P. G. Ashmore and J. Chanmugam, ibid., 1953, 49, 270.

(42) T. T. Jones and H. W. Melville, Proc. Roy. Soc., 1940, 175, A, 392.

(43) W. G. Burns and F. S. Dainton, Trans. Faraday Soc., 1950, 46, 411.

(44) J. Adam, P. Goldfinger and P. A. Gosselain, Bull. Soc. Chim, Belg., 1956, 65, 561.

(45) S. Dusoleil, P. Goldfinger, A. M. Mahiew-Van der Auwera, G. Martens and D. Van der Auwera, Trans. Faraday Soc., 1961, 57, 2197.

(46) P. Goldfinger, G. Huybrechts and G. Martens, ibid., 1961, 57, 2210.

(47) F. S. Dainton, D. A. Lomax and M. Weston, ibid., 1957, 53, 460.

(48) K. L. Muller and H. J. Schumacher, Z. physik. Chem., B, 1937, 35, 285.

(49) J. Adam, P. Goldfinger and P. A. Gosselain, Bull. Soc. Chim. Belg., 1956, 65, 549.

(50) G. Huybrechts, L. Meyers and G. Verbeke, Trans. Faraday Soc., 1962, 58, 1128.

(51) P. B. Ayscough, A. J. Cocker and F. S. Dainton, ibid., 1962, 58, 284.

(52) P. B. Ayscough, A. J. Cocker,
F. S. Dainton and S. Hirst, ibid., 1962, 58, 295.

(53) J. H. Knox and J. Riddick, ibid, 1966, 62, 1190.

(54) R. J. Cvetanovic, "Advances in Photochemistry Vol I",
Interscience Publishers, 1963, 115.

(55) F. S Dainton, D. A. Lomax and
M. Weston, Trans. Faraday Soc., 1962, 58, 308.

(56) P. B. Ayscough, F. S. Dainton and
B. E. Fleischfresser, ibid, 1966, 62, 1838.

(57) P. B. Ayscough, A. J. Cocker,
F. S. Dainton and S. Hirst, ibid, 1962, 58, 318.

(58) K. S. Pitzer and J. L. Hollenberg, J. Amer. Chem. Soc., 1954, 76,
1493.

(59) P. B. Ayscough, F. S. Dainton
and B. E. Fleischfresser, Trans. Faraday Soc., 1966, 62, 1846.

(60) R. E. Dodds and P. L. Robinson, "Experimented Inorganic Chemistry",
Elsevier Publ. Co. (London), 1954.

(61) D. H. Desty, "Gas Chromatography" Butterworth,
1960.

(62) P. G. Ashmore, Catalysis and Inhibition of Chemical
Reactions, Butterworth's (London),
1963.

(63) J. O. Hirschfelder, C. F. Curtis
and R. B. Bird, "Molecular Theory of Gases and Liquids",
Wiley, (N. Y.), 1954.

(64) R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids",
McGraw-Hill, (London), 1958.

(65) A. K. E. Hagopian, J. H. Knox,
and Miss E. A. Thomson, Bull. Soc. Chim. Belg., 1962, 71, 764.

(66) J. O. Hirschfelder,   J. Chem. Phys., 1940, $\underline{8}$, 431.

(67) B. L. Crawford,   ibid., 1940, $\underline{8}$, 273.

(68) R. H. Harrison and K. A. Kobe,   J. Chem. Phys., 1957, $\underline{26}$, 1411.

(69) J. D. Kemp and K. S. Pitzer,   ibid., 1936, $\underline{4}$, 749.

(70) G. Allen, P. N. Brier and
     G. Lane,   Trans. Faraday Soc., 1967, $\underline{63}$, 824.

(71) T. J. Houser, R. B. Bernstein,
     R. G. Mekka and J. C. Angus,   J. Amer. Chem. Soc., 1959, $\underline{77}$, 6202.

(72) R. E. Kagarise,   J. Chem. Phys., 1956, $\underline{24}$, 300.

(73) H. J. Bernstein,   ibid., 1950, $\underline{18}$, 478.

(74) G. Allen and H. J. Bernstein,   Canad. J. Chem., 1954, $\underline{32}$, 1124.

(75) J. R. Nielson, C. Y. Liang and
     L. W. Daasch,   J. Opt. Soc. Amer., 1953, 43, 1017.

(76) R. H. Fowler,   "Statistical Mechanics", Cambridge University Press, 1936, 2nd Ed., P31-33.

(77) B. Steiner, C. F. Giese and
     M. G. Inghram,   J. Chem. Phys., 1961, $\underline{34}$, 189.

(78) H. M. Rosenstock,   J. Chem. Phys., 1961, $\underline{34}$, 2182.

(79) B. S. Rabinovitch and R. W. Diesen,   J. Chem. Phys., 1959, $\underline{30}$, 735.

(80) B. S. Rabinovitch and J. H. Current,   J. Chem. Phys., 1961, $\underline{35}$, 2250.

(81) G. Z. Whitten and B. S. Rabinovitch,   J. Chem. Phys., 1963, $\underline{38}$, 2466.

(82) R. N. Schwartz, Z. I. Slawsky
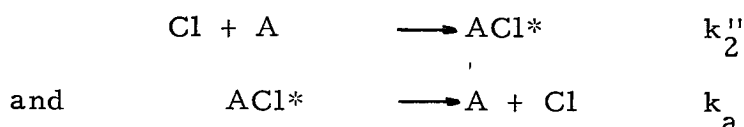   and K. F. Herzfeld,   J. Chem. Phys., 1952, $\underline{20}$, 1591.

(83) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases", Butterworths, (London), 1961.

(84) T. L. Cottrell, R. C. Dobbie, J. McLean and A. W. Read, Trans. Faraday Soc., 1964, $\underline{60}$, 241, (and earlier papers).

(85) C. C. Chow and E. F. Greene, J. Chem. Phys., 1965, $\underline{43}$, 324.

(86) J. Collins and L. D'Or, ibid., 1955, $\underline{23}$, 397.

(87) H. L. Murray and V. Thornton, ibid., 1951, $\underline{19}$, 1014.

(88) J. H. Taylor, W. S. Benedict and J. Strong, ibid., 1952, $\underline{20}$, 1884.

(89) R. T. Lagemann and E. A. Jones, ibid., 1951, $\underline{19}$, 534.

(90) J. D. Lambert, A. J. Edwards, D. Pemberton and J. L. Stretton, Discuss Faraday Soc., 1962, $\underline{33}$, 61.

(91) P. J. Kurtz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner and C. E. Young, J. Chem. Phys., 1966, $\underline{44}$, 1168.

(92) J. A. Franklin, P. Goldfinger, and G. Huybrechts, Preprint International Conference on Photochemistry, Munich, Sept 1967.

(93) R. C. Millikan, J. Chem. Phys., 1963, $\underline{38}$, 2860.

(94) A. Euken and R. Becker Z. physik. Chem., (Leipzig), 1934, $\underline{27}$, B, 235.

(95) N. Basco, A. B. Callear and R. G. W. Norrish, Proc Roy. Soc., 1961, $\underline{A260}$, 459.

(96) K. L. Wray, J. Chem. Phys., 1962, $\underline{36}$, 2597.

(97) E. A. Ogryzlo,   Canad. J. Chem., 1961, <u>39</u>,
                                              2556.

(98) L. W. Bader and A. E. Ogryzlo,   J. Chem, Phys., 1964, <u>41</u>, 2926.

ABSTRACT OF THESIS

Name of Candidate ..... KENNETH CHARLES WAUGH,

Address ..... 11 Cochrane Place, Leith, Edinburgh, 6.

Degree ..... Doctor of Philosophy ..... *Date* ..... August 1967

Title of Thesis ..... Competitive Chlorination of Substituted Ethylenes

The Arrhenius parameters of the rate constants of the reactions

$$Cl + A \longrightarrow ACl^* \qquad k_2''$$

$$\text{and} \qquad ACl^* \longrightarrow A + Cl \qquad k_a$$

(where ACl^* is an active chloroalkyl radical and A on olefin) have been determined by the competitive technique for trichloroethylene and tetrachloroethylene. In the latter case, however, only a rough estimate could be made of the rate of unimolecular decomposition of the active pentachloroethyl radical.

When A = trichloroethylene, the parameters are

$$k_2'' \, (TrCE) = 2.68 \pm 1.36 \times 10^{10} \, \exp \, (+0.24 \pm 0.41/RT) \, \text{mole}^{-1} . \, \text{l. sec}^{-1}$$

and $k_a \, (TrCE) = 7.33 \pm 2.73 \times 10^{10} \, \exp \, (-3.26 \pm 0.38/RT) \, \text{sec}^{-1}$

where the activation energies are in k. cal. mole^{-1}.

The efficiency of various gases in deactivating the active tetrachloroethyl radical by the reaction

$$ACl^* + Mi \longrightarrow ACl^0 + Mi \qquad \text{(bi)}$$

(where ACl^0 is an inactive chloroalkyl radical), has been found to be

	Cl_2	PrH	TrCE	CO_2	Ar	SF_6
Efficiency per collision relative to chlorine	1	0.85	1.46	0.83	1.23	1.17

The bimolecular A factor for trichloroethylene has been calculated by absolute rate theory to be $1.37 \times 10^9 \, \text{mole}^{-1} . \, \text{l. sec}^{-1}$; this value has to be compared with the experimental value of $2.68 \times 10^{10} \, \text{mole}^{-1} . \, \text{l. sec}^{-1}$. The unimolecular rate constant has been calculated by the Marcus theory to be $0.92 \times 10^8 \, \text{sec}^{-1}$ which compares well with the experimental value of $7.0 \times 10^8 \, \text{sec}^{-1}$ at $79^\circ C$. This reasonable agreement between the experimental and theoretical bimolecular A factors and unimolecular rate constants was achieved only after it was assumed that the activated complex and active radical rotate freely about the C-C bond.

Use other side if necessary.

When A = tetrachloroethylene a value of A_2'' of 0.24×10^{10} mole^{-1}.l.sec^{-1} at 79°C was obtained experimentally which is to be compared with the value 0.87×10^{10} mole^{-1}.l.sec^{-1}, calculated from absolute theory of reaction rates. In this case, however, to achieve this degree of agreement between the theoretical and experimental bimolecular A factors it is necessary to assume that internal rotation, of the transition state complex, about the C-C bond is restricted; the assumption of free rotation in the transition state complex gives a theoretical value 30 times higher than the experimental one. Further, making the assumption of a rigid activated complex the lifetime of the penta-chloroethyl radical is calculated by the Marcus theory to be 5×10^{-7} seconds which compares well with the experimentally estimated lifetime of 2×10^{-7} seconds.