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Chlorine-catalysed Pyrolysis of 1,2-Dichloroethane

Part 2.—Unimolecular Decomposition of the 1,2-Dichloroethyl Radical and its Reverse Reaction

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Fall-off curves for the unimolecular rate constant k_2 of the reaction

 $\dot{C}_2H_3Cl_2 \xrightarrow{2} C_2H_3Cl + \dot{C}l$

have been calculated by the Forst and RRKM methods and compared with the experimental results reported in Part 1 and by Huybrechts *et al.* The Forst calculations can be fitted to the Part 1 results, but then predict $k_2^{(\infty)}$ values that lie below the experimental results of Huybrechts *et al.* which refer to lower temperatures and higher pressures. In contrast RRKM calculations using higher Arrhenius parameters give fall-off curves that are compatible with all available experimental data. The preferred RRKM models without allowance for the centrifugal effect have $E_2^{(\infty)} \approx 19.6$ kcal mol⁻¹ (82 kJ mol⁻¹) and $A_2^{(\infty)} \approx 10^{14.0}$ s⁻¹. When a reasonable centrifugal effect is allowed for the early transition state $(I^+/I \approx 2)$ the preferred models have $E_2 \approx 20.0$ kcal mol⁻¹ (84 kJ mol⁻¹) and $A_2^{(\infty)} \approx 10^{14.3}$ s⁻¹. Our experimental evaluations of $k_{-2}^{(m)}$ are used in conjunction with earlier experimental results and RRKM-based calculations for the reverse reaction

$$\dot{C}_1 + C_2 H_3 C_1 \rightarrow \dot{C}_2 H_3 C_1_2$$

to evaluate $A_{-2}^{(\infty)}$ and $E_{-2}^{(\infty)}$.

The decomposition of 1,2-dichloroethane (DCE) catalysed by chlorine or by chlorine plus nitric oxide proceeds by the chain-propagating steps (1) and (2) with competition from step (3)

$$\dot{C}l + C_{a}H_{a}Cl_{a} \rightarrow \dot{C}_{a}H_{a}Cl_{a} + HCl$$
⁽¹⁾

$$\dot{C}_2 H_3 Cl_2 \rightarrow C_2 H_3 Cl + \dot{C}l \tag{2}$$

$$\dot{C}_2 H_3 Cl_2 + Cl_2 \rightarrow C_2 H_3 Cl_3 + \dot{C}l.$$
(3)

The competitive reactions allow evaluation of k_2/k_3 and experimental studies¹ have shown that k_2 is in the unimolecular fall-off region for pressures p between 8 and 150 Torr.[†] Extensive measurements of $\gamma_{\exp p}^{(p)} = k_2^{(p)}/k_3$ as a function of p were made at five temperatures between 520 and 572 K. The mean values $\bar{k}_2^{(p)}$ were calculated at chosen levels of p using the published² Arrhenius parameters for k_3 and are here shown in table 1 with the standard errors of the means.

It is clearly of importance to see how these results conform with various theories

$$\dagger$$
 1 Torr = 101 325/760 N m⁻².

TABLE	1.—Mean values of $\vec{p}, \vec{k}_2^{\rm c}$	^{p)} (with standal	RD ERRORS OF MEA TEMPERATURES	NS AND NUMBERS	of runs) of <i>p</i> _{DCE}	$k_2^{(p)}, k_2^{(p)}$ in vese	l B at the
572 K	$\tilde{p}\pm$ s.E./Torr $\hat{k}_2^{(p)}\pm$ s.E./ 10^5 s^{-1} no. of runs	$9.0 \pm 0.08 \\ 0.92 \pm 0.03 \\ 19$	$\begin{array}{c} 22.8 \pm 0.33 \\ 2.04 \pm 0.05 \\ 18 \end{array}$	$\begin{array}{c} 36.5 \pm 0.29 \\ 2.82 \pm 0.03 \\ 19 \end{array}$	$63.4 \pm 0.614.03 \pm 0.0824$	$101.2 \pm 0.58 \\ 5.30 \pm 0.09 \\ 23$	$134.6 \pm 0.90 \\ 6.13 \pm 0.13 \\ 11$
560 K	$\vec{p} \pm \text{s.e./Torr}$ $\vec{k}_2^{(p)} \pm \text{s.e./10}^5 \text{ s}^{-1}$ no. of runs	$\begin{array}{r} 9.2 \pm 0.13 \\ 0.88 \pm 0.04 \\ 5 \end{array}$	$\begin{array}{rrr} 24.5 \pm 0.66 \\ 1.84 \pm 0.06 \\ 8 \end{array}$	36.8 ± 0.48 2.22 ± 0.10 7	$64.3 \pm 0.963.12\pm 0.126$	$100.4 \pm 1.51 \\ 3.82 \pm 0.14 \\ 6$	$138.3 \pm 1.82 \\ 4.51 \pm 0.11 \\ 4$
547 K	$\overline{p} \pm \text{s.e./Torr}$ $\overline{k}_2^{(p)} \pm \text{s.e./10}^5 \text{ s}^{-1}$ no. of runs	$\begin{array}{ccc} 9.3 \pm 0.33 \\ 0.63 \pm 0.66 \\ 4 \end{array}$	$\begin{array}{c} 22.5 \pm 0.38 \\ 1.31 \pm 0.06 \\ 4 \end{array}$	$36.8 \pm 0.76 \\ 1.75 \pm 0.08 \\ 5$	$\begin{array}{c} 65.0 \pm 1.26 \\ 2.30 \pm 0.12 \\ 4 \end{array}$	$\begin{array}{r} 97.3 \pm 0.90 \\ 2.72 \pm 0.11 \\ 6 \end{array}$	
534 K	<i>p</i> ±s.E./Torr <i>k</i> ² ^{p)} ±s.E./10 ⁵ s ⁻¹ no. of runs	$9.4 \pm 0.12 \\ 0.38 \pm 0.01 \\ 6$	$\begin{array}{c} 23.0 \pm 0.26 \\ 0.85 \pm 0.03 \\ 6 \end{array}$	$\begin{array}{c} 35.6 \pm 0.78 \\ 1.14 \pm 0.03 \\ 6 \end{array}$	$65.2 \pm 1.35 \\ 1.65 \pm 0.03 \\ 6 \\ 6$	$100.2 \pm 1.35 \\ 1.97 \pm 0.07 \\ 6 \\ 6$	$131.7 \pm 2.33 \\ 2.17 \pm 0.08 \\ 4 \\ 4$
521 K	$\vec{p} \pm \text{s.e.}/\text{Torr}$ $\vec{k}_a^{(p)} \pm \text{s.e.}/10^5 \text{ s}^{-1}$ no. of runs	9.6 ± 0.46 0.26 ± 0.03 5	$ \begin{array}{r} 18.6 \pm 0.25 \\ 0.37 \pm 0.01 \\ 9 \end{array} $	$\begin{array}{c} 27.3 \pm 0.46 \\ 0.58 \pm 0.03 \\ 11 \end{array}$	$\begin{array}{c} 55.0 \pm 0.38 \\ 0.83 \pm 0.02 \\ 11 \end{array}$	$\begin{array}{c} 91.8 \pm 0.77 \\ 1.20 \pm 0.04 \\ 11 \end{array}$	$134.8 \pm 1.57 \\ 1.35\pm 0.02 \\ 4$

P. G. ASHMORE, A. J. OWEN AND P. J. ROBINSON

of unimolecular fall-off. Our first theoretical calculations were based on the Forst approach³ which requires a detailed knowledge of molecular parameters only for the reacting species. These did not result in a completely satisfactory explanation of the experimental results. However, full RRKM calculations gave a much more satisfactory explanation of our own and of other investigators' results reported in Part 1. The agreement between theory and experiment led to the evaluation of the parameters $A_2^{(\infty)}$ and $E_2^{(\infty)}$ of the high-pressure rate constant $k_2^{(\infty)}$ which is inaccessible by direct experiment.

CALCULATIONS OF FALL-OFF CURVES AND FIT TO THE EXPERIMENTAL $k_{2}^{(p)}$ DATA

FORST CALCULATIONS

Programs were written by P.J.R. to calculate the collision rate constant k_{coll} , the density of states $N(E_{vr})$ by the Hoare and Ruijgrok⁴ method of steepest descent, the partition function Q_2 for the radical, and hence $k(E) = A_2^{(\infty)}N(E - E_2^{(\infty)})/N(E)$ (with $E > E_2^{(\infty)}$) for suitable pairs of $A_2^{(\infty)}$ and $E_2^{(\infty)}$. Finally $k_2^{(p)}$ was calculated from eqn (X)*

$$k_{2}^{(p)} = \frac{1}{Q_{2}} \int_{E_{2}^{(\infty)}}^{\infty} \frac{k(E)}{1 + k(E)/k_{\text{coll}}[\mathbf{M}]} N(E) \exp(-E/\mathbf{R}T) \,\mathrm{d}E \qquad (X)^{*}$$

with M, the collision partner, at p = 5, 10, 25, 50, 75, 100, 125, 150 and 200 Torr. The first calculations ignored the centrifugal effect,⁵ partly for simplicity, partly because the low level of $A_2^{(\infty)}$, $E_2^{(\infty)}$ values led to the view that the transition state was formed early in the dissociation (2) of the radical, with some tightening due to rapid formation of the π -bond before the C—Cl bond is much extended. This kind of transition state would give rise to comparatively low values for I^{\neq}/I and hence a small centrifugal effect. This point is taken up later in this paper.

Molecular parameters for the dichloroethyl radical have been proposed by previous workers.^{6,7} As exemplified later, the two sets of parameters gave very similar results, and once this was settled, the Beadle, Knox, Placido and Waugh (BKPW)⁶ parameters were used in the Forst calculations. In later calculations, convenient groupings of frequencies, based on the BKPW values, were used to simplify the computations. The BKPW and other required parameters for the radical $\dot{C}_2H_3Cl_2$ are given in table 2.

Calculations of $k_{2}^{(p)}$ with a wide range of $A_{2}^{(\infty)}$ and $E_{2}^{(\infty)}$ values identified a comparatively small network of values that gave $k_{2}^{(p)}$ close to the experimental $\bar{k}_{2}^{(p)}$ means at 572 K. From this network pairs of $A_{2}^{(\infty)}$, $E_{2}^{(\infty)}$ values could be selected that gave $k_{2}^{(100)}$ for p = 100 Torr equal to the value obtained from short interpolation to p = 100 Torr between the experimental means. These pairs lie on the line $k_{2}^{(100)}$ shown in fig. 1(a), and show a compensation effect (high A_{2} goes with high E_{2} , and low A_{2} with low E_{2}) similar to that in pairs of $A_{2}^{(\infty)}$, $E_{2}^{(\infty)}$ required to produce a given $k_{2}^{(\infty)}$. However, the higher pairs produce a fall-off curve that lies below the experimental $\bar{k}_{2}^{(p)}$ value at p < 100 Torr and above them at p > 100 Torr, *i.e.* is too straight. In contrast, the lower pairs lead to $k_{2}^{(p)}$ above the experimental values for p < 100 Torr and below those at p > 100 Torr, *i.e.* is too bent. The result is, of course, that each pair gives a different value of the high-pressure rate constant $k_{2}^{(\infty)}$.

These changes of shape of the calculated curves passing through $\overline{k_2^{(100)}}$ can be applied to identify $A_2^{(\infty)}$ and $E_2^{(\infty)}$ and hence $k_2^{(\infty)}$ within closer limits. A simple way is to repeat the procedure used for the $k_2^{(100)}$ curve for a much lower pressure. Thus the line $k_2^{(25)}$ in fig. 1 (a) represents values of $A_2^{(\infty)}$ and $E_2^{(\infty)}$ that give $k_2^{(25)}$ equal to the experimental

^{*} Equations with lower numbers are in Part 1.1

UNIMOLECULAR DECOMPOSITION $\dot{C}_2H_3Cl_2 \rightarrow C_2H_3Cl + \dot{C}l$

internal rotatio	(a) D on $I = 33 \times 10^{-40}$	Data for radical g cm ² , degenera	cv 1. symmetry	number 1
vibration frequencies/cm	$^{-1}$ [ref. (6)]	3005 (2), 29 1052, 986	957, 1450, 1304 , 768, 754, 709,	, 1264, 1230, 301, 220
grouped frequencies/cm ⁻ collision diameter collision bath C ₂ H ₄ Cl ₂	-1	3000 (3), 12 0.55 nm	280 (4), 1020 (2), 754 (3), 301, 220
	(b) Data	a for Forst mode	els	
model	Α	В	С	D
$E_{572}^{(\infty)}/\text{kcal mol}^{-1}$	17.15	17.40	17.80	16.00
$\log_{10}(A_{572}^{(\infty)}/s^{-1})$	12.60	12.80	13.00	12.00
	(c) Data fo	or RRKM comp	lexes	
$\log_{10} A_{572}^{(\infty)}/$	$\Delta S_{572}^{\neq}/$	$E_{\rm o}/$	$E_{572}^{(\infty)}/$	grouped frequencies

TABLE 2.—PARAMETERS FOR FORST AND RRKM CAI	LCULATIONS
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complex	$\frac{\log_{10}A_{572}^{(\infty)}}{s^{-1}}/$	$\Delta S_{572}^{\neq}/$ cal mol ⁻¹ K ⁻¹	$E_0/$ kcal mol ⁻¹	$E_{572}^{(\infty)}/$ kcal mol ⁻¹	grouped frequencies /cm ⁻¹
F	13.70	0.864	16.30	19.12	3008 (3), 958 (3), 777 (2), 447 (3), 199 (2), 131 (1)
G	14.00	2.241	16.60	19.57	3025 (3), 957 (3), 777 (2), 431 (3), 175 (2), 93 (1)
Н	14.30	3.613	16.81	20.03	3028 (3), 957 (3), 737 (2), 379 (3), 157 (2), 89 (1)
(<i>d</i>) Da	ta for RRKM	complexes which	allow for the ce	entrifugal effect	with $I^{\neq}/I = 2.0$

$E_0/\text{kcal mol}^{-1}$		16.5			17.0			17.5	
$E_2^{(\infty)}/\text{kcal mol}^{-1}$ $A_2^{(\infty)}/10^{14} \text{ s}^{-1}$	X ₁ 0.7	19.5 X ₂ 0.8	X ₃ 0.9	Y ₁ 1.7	20.0 Y ₂ 1.8	Y ₃ 2.0	Z ₁ 4.0	20.5 Z ₂ 4.4	Z ₃ 5.0

value obtained by short interpolations of the experimental means to p = 25 Torr. The intersection of the two lines $k_2^{(25)}$ and $k_2^{(100)}$ gives the values of $A_2^{(\infty)}$ (close to $10^{12.7}$ s⁻¹) and $E_2^{(\infty)}$ (close to 17.5 kcal mol⁻¹) that give a fall-off curve passing through the experimental means $k_2^{(p)}$ close to p = 25 and 100 Torr. Two more sophisticated procedures confirmed the results of the simple procedure.

Method (1), based on Szirovica and Walsh,⁸ involved comparison of the locus of $A_2^{(\infty)}$, $E_2^{(\infty)}$ values fitting the slope of the Lindemann reciprocal plot $(1/k_2^{(p)})$ against 1/p at a given temperature with the locus of the values fitting $k_2^{(p)}$ at a specific pressure. Lindemann plots of two Forst calculations for 572 K are shown in fig. 2; they are nearly linear over the pressure range of interest. A network of values of theoretical slopes can be constructed for suitable ranges of $A_2^{(\infty)}$ and $E_2^{(\infty)}$, and pairs



FIG. 1.—Pairs of $A_{2}^{(\infty)}$, $E_{2}^{(\infty)}$ values that give (a) Forst calculations that fit $k_{2}^{(100)}$, $k_{2}^{(25)}$ and L (the slope of the Lindemann plot for experimental $k_{2}^{(p)}$) at 572 K, and (b) RRKM calculations that fit $k_{2}^{(100)}$, $k^{(25)}$ and $k_{3}^{(10)}$ at 572 K.



FIG. 2.—Lindemann plots of $1/k_2^{(p)}$ for Forst calculations with model B (\bigcirc) and with model D (\triangle) (see table 2) at 572 K.

of $A_2^{(\infty)}$, $E_2^{(\infty)}$ values can be found, by interpolation, that give slopes equal to that of the line fitted (by least-mean-square procedures) to the Lindemann plot of $1/\bar{k}_2^{(p)}$ against 1/p. These pairs are plotted as line L in fig. 1 (a). The three lines intersect within a small range of $A_2^{(\infty)}$, $E_2^{(\infty)}$ values which are therefore consistent with the shape of the fall-off curve at 572 K. Table 3 shows the 572 K values using method (1) and BKPW parameters.

Method (2) involved the direct fitting of empirical equations for the theoretical fall-off

FAR 1

(XI)

UNIMOLECULAR DECOMPOSITION
$$C_2H_3Cl_2 \rightarrow C_2H_3Cl+Cl_3$$

T/K	$\log_{10}A_2^{(\infty)}/s^{-1}$	$E_2^{(\infty)}/{ m kJ}~{ m mol}^{-1}$	$E_2^{(\infty)}$ /kcal mol ⁻¹
521	12.85	74.2	17.7
534	12.90	73.8	17.6
547	12.60	71.9	17.2
560	12.60	71.9	17.2
572	12.80	73.0	17.4
572ª	12.70	72.3	17.3
572 ^b	12.80	73.4	17.5

TABLE 3.— $A_2^{(\infty)}$, $E_2^{(\infty)}$ values fitting experimental data and Forst calculations. Unless noted otherwise, method (1) and BKPW parameters were used.

^a Method (2) and BKPW⁶ parameters; ^b method (2) and SR⁷ parameters.

curves to the experimental $k_2^{(p)}$, p points. No simple function will describe these curves over a wide range of pressures. However, quartic polynomials in p, developed over the range 1-250 Torr, could be fitted accurately to $k_2^{(p)}(\text{calc})$ over the more limited range 5-150 Torr for each pair of $A_2^{(\infty)}$, $E_2^{(\infty)}$ values. The sum of the squares of the residuals (s.s.r.) of the experimental points from the quartic curve could then be computed, and a small network of $A_2^{(\infty)}$, $E_2^{(\infty)}$ pairs was identified with the lowest s.s.r. An additional discrimination was obtained by examining the distribution of the signs of the residuals over the pressure range. The results for 572 K, shown in table 3 for both BKPW and SR parameters, are very close to those found by method (1) or the simple method.

Method (1) was applied, using the BKPW parameters, at four other temperatures with results also shown in table 3. Giving equal weightings to these values at the five temperatures, the mean values found for the Arrhenius parameters are

$$E_{2}^{(\infty)} = 72.9 \pm 1.1 \text{ kJ mol}^{-1} = 17.42 \pm 0.26 \text{ kcal mol}^{-1}$$
$$\log_{10}(A_{2}^{(\infty)}/\text{s}^{-1}) = 12.75 \pm 0.25$$
$$\log_{10}(k_{2}^{(\infty)}/\text{s}^{-1}) = 12.75 - \frac{17420}{4.576 T/\text{K}}.$$

i.e.

and

In fig. 3 the values of $\bar{k}_{2}^{(p)}$ are plotted for each temperature with the theoretical Forst curve (full line) appropriate to the overall mean $A_{2}^{(\infty)}$, $E_{2}^{(\infty)}$ values. The overall pattern from fig. 3 indicates that the mean Arrhenius parameters $A_{2}^{(\infty)}$ and $E_{2}^{(\infty)}$ give a reasonable fit to the fall-off at all five temperatures.

However, they are much lower than the values found by Huybrechts *et al.*⁹ for fairly high pressures $[E_2 = 20.7 \text{ kcal mol}^{-1} \text{ and } \log_{10}(A_2/\text{s}^{-1}) = 14.33]$. Moreover, eqn (XI) predicts values of $k_2^{(\infty)}$ that lie *below* those found experimentally by Huybrechts *et al.* until very low temperatures are reached, as illustrated in fig. 4 by the positions of the lines (XI) and (XII)⁹

$$\log_{10}(k_2^{(\infty)}/s^{-1}) = 14.33 - \frac{20\,700}{4.576\,T/K}.$$
 (XII)

This conflict might arise from errors in our fitting procedures, which is unlikely because of the cross-checks from different procedures, or from systematic errors in the experimental results (those of Huybrechts *et al.*⁹ and our own¹) or from the acknowledged³ decrease in accuracy of the Forst method at lower pressures. Incorpor-



FIG. 3.—Calculated Forst curves for the mean $A_2^{(\infty)}$, $E_2^{(\infty)}$ optimum values at the five temperatures (see table 3) with mean $k_2^{(p)}$ for \diamondsuit 572; \bigcirc , 560; \bigtriangledown , 547; \triangle , 534 and \Box , 521 K.



FIG. 4.—Arrhenius plots of k_2 from the experiments of Huybrechts *et al.*⁹ (XII), of $k_2^{(\infty)}$ from our Forst calculations (XI) and of $k_2^{(\infty)}$ from our RRKM calculations (XII).

684 UNIMOLECULAR DECOMPOSITION
$$\dot{C}_2H_3Cl_2 \rightarrow C_2H_3Cl + \dot{C}l$$

ation of the centrifugal effect would make only minor changes in the calculations. The Forst estimates of $k_2^{(\infty)}$ suggest that our experimental pressure range lies just below p_{i} , where the Forst method would still be reliable. On the other hand, extrapolation of the Huybrechts results to our temperatures indicates k_2 values well above the predicted Forst $k_2^{(\infty)}$, which would mean that our experimental pressure range is well below the true p_{i} . It is therefore possible that the discrepancies result from inaccuracies of the Forst method under these conditions.

A reaction of the same kind as (2) is the decomposition of the ethyl radical

 $C_2H_5 \rightarrow C_2H_4 + \dot{H}$

for which the experimental value of k is given by

 $\log_{10}(k/s^{-1}) = 14.4 - 31\,800 \text{ K}/4.576T \text{ [ref. (10)]}$ $\log_{10}(k/s^{-1}) = 13.6 - 32400 \text{ K}/4.576T \text{ [ref. (11)]}.$

or

e

Benson¹² has pointed out that for the ethyl radical there is a positive contribution to
$$\Delta S^{\neq}$$
 of 3.6 cal mol⁻¹ K⁻¹ by loss of symmetry; this loss does not occur in forming the complex from $\dot{C}_2H_3Cl_2$, and for reaction (2) ΔS^{\neq} might be 3.0 cal mol⁻¹ K⁻¹ lower, *i.e.* A_2 might be expected to lie between 10^{13.6} and 10^{12.8} s⁻¹. This appears to favour lower $A^{(\infty)}$, $E^{(\infty)}$ values. On the other hand, the higher A_2 , E_2 values from Huybrechts' relatively high-pressure experiments appear to fit well with accepted bond energies (such as R · CHCl—H where R = CH₃, CH₂Cl, CHCl₂, CCl₃) and the estimated standard (1 atm) entropies of the radicals R · CHCl.⁹

We therefore conclude that our estimation of $A_{2}^{(\infty)}$, $E_{2}^{(\infty)}$ values from the fall-off curves using Forst calculations is not satisfactory, and it is desirable to see whether full RRKM calculations give a better description of our own and the Huybrechts results.

RRKM CALCULATIONS

Full RRKM calculations were first done for 572 K neglecting the centrifugal effect. A series of activated complexes were constructed to give selected values of $A_{b}^{(\infty)}$ at 572 K. Details of the assignments are not critical since RRKM fall-off calculations are insensitive to the detailed structure of the activated complex, the shape and position of the fall-off curve being determined essentially by the resulting ΔS^{\neq} and by $E^{(\infty)}$ [ref. (13), pp. 152 and 178].* State sums for the complexes were generated by exact count and densities for the radical by the Whitten-Rabinovitch method.¹⁴

Suitable complexes $(A_2^{(\infty)})$ and values of $E_2^{(\infty)}$ were investigated to locate those that gave fall-off curves close to the experimental mean values $\bar{k}_{2}^{(p)}$, using the procedure tested during the Forst calculations. Fig. 1(b) shows pairs of $A_2^{(\infty)}$, $E_2^{(\infty)}$ values that gave calculated $k_2^{(p)}$ in agreement with the experimental values for p = 100, 25 and 10 Torr. As can be seen, the intersection indicated $A_2^{(\infty)}$ and $E_2^{(\infty)}$ values substantially higher than in the Forst calculations, viz. close to $\log_{10}(A_2^{(\infty)}/s^{-1}) = 14.0$ and $E_{b}^{(\infty)} = 19.6 \text{ kcal mol}^{-1} \text{ at } 572 \text{ K}$. These parameters define complex G (table 2).

The differences between $k_{2}^{(p)}$ values calculated for this complex and the individual experimental values are expressed in table 4 as the sum $\Sigma R_i^{(p)}$ of the residuals $R_i^{(p)} = [k_i^{(p)}(\exp) - k_i^{(p)}(\mod i)]$ and the sums $\Sigma V_i^{(p)}$ of the corresponding variances for the experimental pressure ranges at 572 K. The results of applying a t-test at the 1% level of significance are also shown; model G predictions are not significantly

* Note
$$E_{\mathrm{T}}^{(\infty)} = E_0 + \mathbf{R}T + \langle E^{\neq} \rangle - \langle E \rangle$$
 and $\ln (A_{\mathrm{T}}^{(\infty)}/\mathrm{s}^{-1}) = \ln [(ekT/h)/\mathrm{s}^{-1}] + \frac{\Delta S_{\mathrm{T}}^{\neq}}{\mathbf{R}}$.

intal means $ar{p}$ and $ar{k}_2^{(p)}$ with the standard errors of the means and the sums $\Sigma R_i^{(p)}$ of the residuals a and the sums $\Sigma V_i^{(p)}$	or RRKM models F, G, H. Differences between model and experimental results are indicated as significant (s), not	icant (ns), or on the borderline (s/ns), using the t-test at the 1% level of significance. 572 K, vessel B.
Table 4.—Experimental means \bar{p} /	OF THE VARIANCES ^b FOR RRKM MO	SIGNIFICANT (ns), OR (

							,				
		<u>Г</u> (р) тен /		model F			model G			model H	
u	$\bar{p}\pm$ s.e./Torr	$10^{5} S^{-1}$	ΣR		ΣV	ΣR		2V	ΣR		ΣV
19	9.0 ± 0.08	0.92 ± 0.03	-4.61	s	1.62	-2.20	s/ns	0.76	-0.65	su	0.53
18	22.8 ± 0.33	2.04 ± 0.05	-1.92	s/ns	1.10	0.48	su	0.75	2.14	s/ns	0.99
19	36.5 ± 0.29	2.82 ± 0.03	-1.55	s/us	1.47	0.89	su	1.38	2.45	s	1.63
24	63.4 ± 0.61	4.03 ± 0.08	0.02	us	2.97	2.09	su	2.87	4.30	s/ns	3.85
23	101.2 ± 0.58	5.30 ± 0.09	1.96	su	3.79	1.96	su	3.79	1.96	su	3.79
11	134.6 ± 0.90	6.13 ± 0.13	1.37		1.97	0.86	ns	1.82	-0.66	su	1.81
		overall sums	-4.72		12.92	4.07		11.37	11.31		12.58
		a Here D	$R_1^{(p)} = \Sigma[k_2^{(q)}]$	$p(\exp)-k_2^{(1)}$	⁽⁾ (model i)]/10 ⁵ s ⁻¹ ;	^b here ΣV	$\sum_{i}^{(p)} = \Sigma(R_{i})$	p)) ² .		

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UNIMOLECULAR DECOMPOSITION $\dot{C}_2H_3Cl_2 \rightarrow C_2H_3Cl+\dot{C}l$ 686

different from the experimental results in each range, but are on the borderline for the lowest pressure range. Table 4 shows that model H, with higher $A_{2}^{(\infty)}$ and $E_{2}^{(\infty)}$ than G, has residuals that are more positive than those of G at the lower pressures, whereas model F, with lower $A_2^{(\infty)}$ and $E_2^{(\infty)}$, has residuals that are more negative. The t-tests also show that models F and H give less satisfactory fits to the experimental results at 572 K than does G.



FIG. 5.—**RRKM** calculations of $k_{\xi}^{(p)}$ for model G with mean $k_{\xi}^{(p)}$ for \diamondsuit , 572; \bigcirc , 560; \bigtriangledown , 547; \bigtriangleup 534 and □, 521 K.

To investigate how G and other models behave at other temperatures, E_0 for each model was kept constant and $E_2^{(\infty)}$, $A_2^{(\infty)}$ were calculated using the equations in the footnote, page 684. The calculations for model G are compared in fig. 5 with the experimental means (shown with the number of contributory runs). At 572 K, the model gives an excellent fit at all except the lowest point. At 560 and 534 K it gives good fits, although a model with slightly lower parameters (but not as low as those of F) gives better fits. At 547 K model F is better than G, and a model with even lower $E_0, A^{(\infty)}$ would fit still better; at 521 K a model with slightly higher $E_0, A_2^{(\infty)}$ is better than G. In view of the minor scale of these differences, the choice of a single representative model would fall on G, admitting that a small range of values around $E_0(G)$ (say 16.6±0.3 kcal mol⁻¹) and a correlated (compensating) range of its $\log_{10}[A^{(\infty)}(G)/s^{-1}]$ (say 14.0±0.2) would give very similar fits.

Having decided the preferred model without allowance for the centrifugal effect, it remains to match with its predictions a model allowing for centrifugal effects. This is more important than with the Forst calculations, as the larger A-factor suggests that the activated complex is 'looser' than had appeared from the Forst value of the A-factor. Simple models for the radical and activated complex suggested that I^{\neq}/I would probably be ca. 2. A range of I^{\neq}/I values from 1 to 4 was examined using the approach of Waage and Rabinovitch.⁵ The factor F_{WR} was calculated for the radical from [for symbols, see ref. (13), p. 91]

$$F_{\rm WR} = \left(1 + \frac{(s-1)(I^{\neq}/I - 1)kT}{E_0 + aE_z}\right)^{-1}$$

to give the values:

I≠/I	1	1.5	2.0	3.0	4.0
E WB	1.00	0.72	0.56	0.39	0.29.

The computed fall-off curve for a given $A_2^{(\infty)}$, $E_2^{(\infty)}$ with no centrifugal effects was then treated as follows: (a) $k_2^{(p)}$ was multiplied by I^{\neq}/I , (b) the pressure p was divided by F_{WR} and (c) $A_2^{(\infty)}$ correspondingly became $A_2^{(\infty)} \times I^{\neq}/I$, with $E_2^{(\infty)}$ unchanged. For some of the calculations, the starting data were generated by interpolation between models F, G and H rather than by explicit RRKM computations. After trial comparisons with the experimental results for 572 K, attention was focused on the models $X_1 \dots Z_3$ listed in table 2 with $I^{\neq}/I = 2.0$. Note that the final line gives the final $A_2^{(\infty)}$, *i.e.* the initial $A_2^{(\infty)} \times I^{\neq}/I$.

The predicted curves at 572 K for the nine models are shown with the experimental means in fig. 6. In each triplet the centre curves pass very close to the experimental



FIG. 6.—Fall-off curves at 572 K for models X, Y and Z which allow for centrifugal effect with $I^{\neq}/I = 2.0$. Parameters of the models are given in table 2.

UNIMOLECULAR DECOMPOSITION $\dot{C}_{2}H_{3}Cl_{2} \rightarrow C_{2}H_{3}Cl + \dot{C}l$

means at $\bar{p} = 101$ Torr $(k_2^{(p)} = 5.30 \times 10^5 \text{ s}^{-1})$. However, closer inspection shows that curve Y_2 is a close fit to all the experimental means; curve Z_2 passes very close to the experimental mean at $\bar{p} = 101$ Torr but lies well below the experimental means at p < 100 Torr and above them at p > 100 Torr; curve X₂ lies above the experimental means at p < 80 Torr, and below them at p > 80 Torr. This is shown more quantitatively in table 5, which lists the residuals $[\bar{k}_2^{(p)}(\exp) - k_2^{(p)}(\mod i)]$ for each mean pressure. The residuals for Y₂ are in all cases very much smaller than the standard errors of the experimental means; for Z_2 , the residuals are very much larger than the standard errors of the mean; for X₂, they are comparable or larger and there is a systematic change in sign along the curve. Application of the t-test to the lower pressure ranges gives the significance results at the 1% level shown in table 5, and these confirm that model Y_2 is to be preferred to models X_2 and Z_2 for representing the experimental results.

TABLE 5.—EXPERIMENTAL MEANS $\bar{\rho}$ and $\bar{k}_2^{(p)}$ with the residuals of the means $\{[\bar{k}_2^{(p)}(\exp)$ $k_2^{(p)}$ (model i)]/10³ s⁻¹} for RRKM models X₂, Y₂ and Z₂ which allow for centrifugal EFFECTS. THE RESIDUAL ARE INDICATED AS SIGNIFICANT (S) OR NOT SIGNIFICANT (NS) USING THE t-tests at the 1% level of significance. 572 K, vessel B.

			residu	als of means/1	0^3 s^{-1}
n	<i>₱</i> /Torr	$\bar{k}_{2}^{(p)}(\exp)/10^{5} \text{ s}^{-1}$	\mathbf{X}_2	Y ₂	Z ₂
19	9.0 ± 0.08	0.92 ± 0.03	-12.0 s	0.0 ns	+14.0 s
18	22.8 ± 0.33	2.04 ± 0.05	-1.4 ns	+1.4 ns	+18.3 s
19	36.5 ± 0.29	2.82 ± 0.03	-9.8 s	0.0 ns	+10.5 s
24	63.4 ± 0.61	4.03 ± 0.08	-4.2 ns	0.0 ns	+11.2 ns
23	101.2 ± 0.58	5.30 ± 0.09	+2.8 ns	0.0 ns	+1.4 ns
11	134.6±0.90	6.13 ± 0.13	+4.9 ns	-4.9 ns	-14.8 ns

We conclude that the preferred model after allowing for centrifugal effects is Y₂ with $E_2^{(\infty)} = 20.0$ kcal mol⁻¹ and $A_2^{(\infty)} = 1.8 \times 10^{14}$ s⁻¹; other models with parameters close to these, but with $A_{2}^{(\infty)}$ and $E_{2}^{(\infty)}$ compensating, would give similar fits.

Rather surprisingly, a similar study of models with $I^{\neq}/I = 4.0$ pointed to parameters close to those of Y₂, with $E_2^{(\infty)} = 20.0$ kcal mol⁻¹ and $A_2^{(\infty)} = 1.7 \times 10^{14}$ s⁻¹.

The Arrhenius parameters for Y_2 lead to the prediction

$$\log_{10}(k_2^{(\infty)}/s^{-1}) = 14.26 - \frac{20\,000}{4.576\,T/K}$$
(XIII)

and this is plotted as line (XIII) in fig. 4. The Arrhenius plot for model G would lie slightly below line (XIII).

DISCUSSION OF THE RRKM RESULTS

Line (XIII) in fig. 4, and that for model G, lie well above line (XII) for the results of Huybrechts et al.⁹ Their results were obtained in the pressure range of p_{DCE} between 150 to 450 Torr. The general position of their points and of line (XII) are very satisfactory in relation to the RRKM plot (XIII) - much more so than with line (XI) from the Forst calculations. They did not report any fall-off, but the predicted fall-off is, of course, much smaller at the lower temperatures of their work, e.g. at 454 K $k_{2}^{(p)}$ (calc) falls by ca. 25% when p changes from 450 to 150 Torr; at 572 K, $k_{2}^{(p)}$ (calc)

changes by a factor of nearly two. There is slight evidence for a fall from the spread of their results at 490 K, and rather stronger evidence from their (few) results at 510 K. It is also possible that photolytically generated Cl atoms, comprising ${}^{2}P_{\frac{1}{2}}$ and ${}^{2}P_{\frac{3}{2}}$ states, produce excited \dot{R} in reaction (1), which results in a k_{2} value rather larger than the thermal $k_{2}^{(p)}$.

It therefore appears that the RRKM calculations not only fit our own experimental observations¹ at five temperatures, but can also resolve the apparent major conflict between our early results and those of Huybrechts *et al.*⁹ What appeared to be systematic errors in one or both of the experimental determinations of k_2/k_3 from the thermal- or the photo-sensitised decompositions are now seen to be a natural consequence of the unimolecular behaviour of k_2 at different pressures.

Our evaluation of $A_2^{(\infty)}$ and $E_2^{(\infty)}$, and the statistical treatment of our experimental data, have of necessity ignored possible systematic errors, for example in the experimental evaluation² of k_3 or in the parameters quoted in table 2. The direct experimental investigation of $k_2^{(p)}$ at high pressures, in the absence of competitive chlorination, is very difficult as evidenced by earlier work referenced in Part 1. The thermal decomposition of 1,2-C₂H₄Cl₂ in the absence of chlorine shows complicated rate relationships (as referenced in Part 1) and cannot provide a check on $k_2^{(p)}$ at high pressures. A further check on our evaluation of $A_2^{(\infty)}$ and $E_2^{(\infty)}$ may be provided by applying the methods advocated by Troe¹⁵ and this will be set in motion. In the meantime the satisfactory explanation based on RRKM theory of experimental results from different laboratories over a wide range of temperatures would seem to justify our evaluation of $E_2^{(\infty)}$ within a few kJ mol⁻¹, with corresponding limits on $A_2^{(\infty)}$, and the resulting eqn (XIII). Some further support comes from consideration of the rate constant $k_2^{(p)}$ for the reverse reaction (-2).

ARRHENIUS PARAMETERS FOR THE REACTION (-2)

Our experimental investigations¹ of k_{-2} through the inhibitory effects of VC on the decomposition of DCE clearly showed that k_{-2} is pressure-dependent and increases with increase in temperature. These results did not allow accurate determinations of $A_{-2}^{(p)}$ and $E_{-2}^{(p)}$, but by combining them with data from studies of reaction (-2) at lower temperatures, reasonably accurate values of the Arrhenius parameters of reaction (-2) and their variation with pressure can be obtained.

Reaction (-2) has been studied experimentally in the course of extensive investigations of the chlorination of ethylene and the chloroethylenes. Knox and Waugh¹⁶ found difficulties with heterogeneous reactions in studying

but evaluated k_{-2} indirectly as 3.5×10^{10} dm³ mol⁻¹ s⁻¹ at all temperatures. Ayscough *et al.*¹⁷ quoted an earlier value¹⁸ (10^{10.2} dm³ mol⁻¹ s⁻¹) but preferred their own assessments over the range 20-50 °C, with low pressures of VC around 5-30 Torr, of $\log_{10}(k_{-2}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10.3 - 1500 \text{ K}/4.576 T.$

In a theoretical study of several related reactions, BKPW⁵ calculated rate constants for the following detailed mechanism (using our nomenclature):

$$Cl + VC \xrightarrow{A} \dot{R}^{*}$$
$$\dot{R}^{*} + M \xrightarrow{k_{bi}} \dot{R} + M$$
$$\dot{R}^{*} \xrightarrow{k_{a}} VC + Cl$$
$$\frac{d[\dot{R}]}{dt} = \frac{k_{bi} A[Cl] [VC] [M]}{k_{a} + k_{bi} [M]}$$

which combine to give

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	-	equivalent pressure	$\log_{10}(k_{-1}^{(a)})$	calculated $\frac{x,b,c}{2}$ , $\frac{x,b,c}{2}$ , $\frac{x}{2}$ mc	o −1 s ^{−1} )	ò	$\exp_{g_{10}(k_{-2}^{(a,b,c)}/d}$	nental m ³ mol ⁻¹ s ⁻	(1	$E_{-2}^{(a,b,c)}$	$A^{(a,b,c)}_{-2}$
	$M/10^{-3}$ mol dm ⁻³	at 260 K - /Torr	308 K	352 K	406 K	520 K	544 K	570 K	595 K	/kcal mol ⁻¹	/dm [°] mol ⁻¹ s ⁻¹
1	8	8	9.51	9.64	9.69						
	2.87	100	9.43	9.53	9.54	9.74	9.83	9.85	9.88	1.37	1010.38
	1.60	55	9.38	9.48	9.48	9.61	9.64	9.66	9.69	0.80	10 ^{9.98}
	0.73	25	9.32	9.41	9.39	9.50	9.51	9.49	9.56	0.46	109.70

### P. G. ASHMORE, A. J. OWEN AND P. J. ROBINSON

and hence

10.5

$$k_{-2} = A k_{\rm bi}[{\rm M}]/(k_{\rm a} + k_{\rm bi}[{\rm M}]).$$
 (XIV)

From this expression it is clear that  $k_{-2}^{(\infty)} \equiv A$ , and BKPW gave the values of A at 308, 352 and 406 K shown here in the top line of table 6. They also gave  $k_{\rm bi} = 1.23 \times 10^{11} \,\mathrm{dm^3 \,mol^{-1} \, s^{-1}}$  at 352 K, from their fig. 5 it is possible to estimate  $k_{\rm a}$  at the three temperatures and at chosen pressures or concentrations, so that  $k_{-2}^{(p)}$  can be calculated for their temperatures from eqn (XIV). The results of these calculations are listed in table 6. It seemed more appropriate to consider constant concentration rather than constant pressure, in view of the wide temperature difference between those calculated and our experimental results. Accordingly,  $k_{-2}^{(a,b,c)}$  was calculated for three concentrations which are equivalent to pressures of (a) 100, (b) 55 and (c) 25 Torr at 560 K, the mid-temperature of A.J.O.'s experimental values which are given in the right half of table 6.

Before comparing the calculated and experimental results, a fundamental difficulty must be mentioned. It arises from the complex relations between the reversible reactions (2, -2) and the function of DCE and VC as collision partners (M). In studies of the photochlorination of VC, VC itself is usually the effective collision parameter (chlorine is less effective); in studies of the thermal decomposition of DCE, DCE is the effective collision partner. Our experiments summarised in fig. 9 of Part 1 show that VC and DCE are of very similar but not identical efficiency as M. Unfortunately we can see no rigorous way of allowing for this difference in the data at present available for reaction (2) and for reaction (-2), so that our comparisons that follow are limited by that consideration.

When the results in table 6 are plotted as an Arrhenius diagram (fig. 7) the points for each concentration are reasonable fits to straight lines. The activation energy  $E_{-2}$ 

(d)



FIG. 7.—Arrhenius plots of  $k^{(\underline{n})}$  for concentrations that are equivalent to (a) 100 Torr at 560 K with  $\triangle$  (this work) and  $\triangle$  etc. from BKPW;⁵ (b) 55 Torr at 560 K with  $\bigcirc$  (this work) and  $\bigcirc$  from BKPW;⁵ (c) 25 Torr at 560 K with  $\square$  (this work) and  $\square$  from BKPW;⁵ (d) very high pressures, estimated from this work, with + from BKPW⁵ table 3.

692 UNIMOLECULAR DECOMPOSITION 
$$\dot{C}_2H_3Cl_2 \rightarrow C_2H_3Cl+\dot{C}l$$

falls as the concentration falls, and so does the pre-exponential factor  $A_{-2}$ . These changes would be expected from the corresponding falls in  $E_2$  and  $A_2$  as the pressure is lowered, by the requirements of microscopic reversibility. As a result eqn (XV) and (XVI) bear the same relation to each other as do eqn (VIA) and (VIIA) [derived from the eqn (VI) and (VII) of Part 1 using the Arrhenius expression² for  $k_3$ ]

$$\log_{10}(k_{-2}/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 10.38 - \frac{1370}{4.576\ T/\mathrm{K}} \quad (100\ \mathrm{Torr}) \tag{XV}$$

$$\log_{10}(k_{-2}/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 9.70 - \frac{460}{4.576\ T/\mathrm{K}} \quad (25\ \mathrm{Torr}) \tag{XVI}$$

$$\log_{10}(k_2/s^{-1}) = 12.40 - \frac{17420}{4.576 T/K} \quad (100 \text{ Torr}) \qquad (VIA)$$

$$\log_{10}(k_2/s^{-1}) = 11.61 - \frac{16470}{4.576 T/K}$$
 (25 Torr). (VIIA)

These equations for  $k_{-2}^{(p)}$  and  $k_{2}^{(p)}$  have been derived from quite separate experiments and separate calculations. They correspond within very close limits to an equilibrium constant for reactions (2, -2) given by eqn (VXII), where  $K_{eq} = k_2/k_{-2}$  for  $\dot{\mathbf{R}} \rightleftharpoons \mathbf{VC} + \dot{\mathbf{C}}\mathbf{I}$ 

$$\log_{10}(K_{\rm eq}/{\rm mol}\ {\rm dm}^{-3}) = 2.00 - \frac{16\,000}{4.576\,T/{\rm K}}.$$
 (XVII)

If the concept of microscopic reversibility can be extended to  $k_2^{(\infty)}$  and  $k_{-2}^{(\infty)}$  then by combining eqn (XVII) with the Arrhenius equation for  $k_2^{(\infty)}$  there emerges eqn (XVIII)

$$\log \left(k_{-2}^{\infty}/\mathrm{dm^3\,mol^{-1}\,s^{-1}}\right) = 12.26 - \frac{4000}{4.576\,T/\mathrm{K}}.$$
 (XVIII)

This equation gives the line (d) in fig. 7. It passes close to Knox's calculated  $k_{-2}^{(\infty)}$  at the lower temperatures (+).

The large changes in  $A_{-2}$ ,  $E_{-2}$  with increasing pressure are of course, reflections of the correspondingly large changes in  $A_2$ ,  $E_2$  over the same pressure range. It may be recalled that the values of  $E_2^{(100)}$  and  $E_2^{(25)}$  were derived from RRKM calculations that fit the experimental results at these pressures; however, they are substantially independent of whether one chooses model G, or the model  $Y_2$  with centrifugal effects. On the other hand,  $E_2^{(\infty)}$  does depend on which model one uses, but the difference  $E_2^{(\infty)}(Y_2) - E_2^{(\infty)}$ (model G) is only 400 cal mol⁻¹, and if the Arrhenius equation for  $k_2^{(\infty)}$ for model G were used in place of eqn (XVIII) the plot would be only very slightly displaced from the line (d) in fig. 7.

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(PAPER 0/1987)