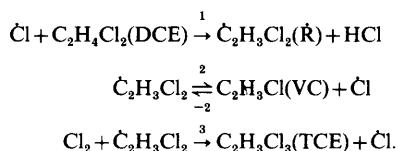# Chlorine-catalysed Pyrolysis of 1,2-Dichloroethane

## Part 1.—Experimental Results and Proposed Mechanism

By Philip G. Ashmore,* John W. Gardner, Anthony J. Owen,
Barbara Smith and Philip R. Sutton

Department of Chemistry, University of Manchester Institute of Science and
Technology, P.O. Box 88, Manchester M60 1QD

Experimental studies of the pyrolysis and chlorination of $1,2\text{-}C_2H_4Cl_2$ in the presence of small proportions of chlorine, or of chlorine plus nitric oxide, confirm that the main propagating steps between 520 and 620 K are

$$\dot{C}l + C_2H_4Cl_2(DCE) \xrightarrow{1} \dot{C}_2H_3Cl_2(\dot{R}) + HCl$$

$$\dot{C}_2H_3Cl_2 \underset{-2}{\overset{2}{\rightleftharpoons}} C_2H_3Cl(VC) + \dot{C}l$$

$$Cl_2 + \dot{C}_2H_3Cl_2 \xrightarrow{3} C_2H_3Cl_3(TCE) + \dot{C}l.$$

The initial rates $(d[VC]/dt)_0$ and $(d[TCE]/dt)_0$ decrease together as the vessels age, but $k_2/k_3 = \gamma$ remains constant at constant $p_{DCE}$. $\gamma$ increases as $p_{DCE}$ is increased, or if inert gases are added, as expected from unimolecular behaviour of $k_2$, and the Arrhenius parameters of $\gamma$ increase together as $p_{DCE}$ is increased. $\gamma^{(p)}$ is evaluated for several ranges of $p_{DCE}$ at five temperatures to allow study of $k_2^{(p)}$ by unimolecular theory in Part 2. The addition of VC lowers $(d[VC]/dt)_0$ through reaction $(-2)$, and the results are used to evaluate $k_{-2}/k_1$; $k_{-2}$ is also pressure-dependent.

In vessels with fresh surfaces, $d[VC]/dt$ is proportional to $p_{DCE} \times p_{Cl_2}^{0.5}$ for low $p_{Cl_2}$, and is independent of added inert gases; in aged vessels, the order in $p_{DCE}$ becomes 0.62, very close to the dependence of $\gamma^{(p)}$ on $p_{DCE}$. Calculations of $[\dot{R}]_0$ and $[\dot{C}l]_0$ from the observed rates and rate constants point to an initiation step

$$Cl_2 + S \rightarrow ClS + \dot{C}l$$
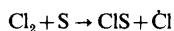
and termination by the reverse reaction in fresh-surfaced vessels, where S is a surface site; with aged surfaces, the results point to the same initiation step combined with termination by
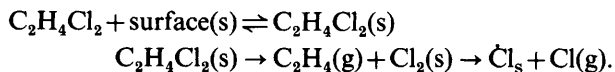
$$\dot{R} + SCl \rightarrow C_2H_3Cl_3 + S$$
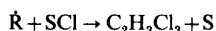
especially at lower temperatures.

---

The pyrolysis of 1,2-dichloroethane (DCE) to hydrogen chloride and vinyl chloride (VC) at temperatures between 670 and 770 K is thought to proceed by a radical chain mechanism with the propagation steps

$$\dot{C}l + C_2H_4Cl_2 \rightarrow \dot{C}_2H_3Cl_2 + HCl \tag{1}$$

$$\dot{C}_2H_3Cl_2 \rightarrow C_2H_3Cl + \dot{C}l. \tag{2}$$
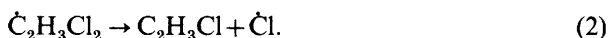
The early investigations[1,2] were interpreted in terms of homogeneous initiation and termination steps, but there are many difficulties with such an interpretation. The reaction rate generally increases in a run to a maximum rate, and widely different Arrhenius parameters have been reported for the overall rate constant. The differences seem to arise in part from changes to the vessel surface, suggesting that initiation

and/or termination may occur on the surfaces.[3, 4] Holbrook *et al.*[5] also pointed out that the autocatalysis of the thermal decomposition might be caused by chlorine formed by surface reactions

$$C_2H_4Cl_2 + surface(s) \rightleftharpoons C_2H_4Cl_2(s)$$
$$C_2H_4Cl_2(s) \rightarrow C_2H_4(g) + Cl_2(s) \rightarrow \dot{C}l_s + Cl(g).$$

Catalysis by *ca.* 1% of chlorine had been reported by Barton,[1] using a Pyrex flow system at 623 K, and by Takahashi *et al.*[6] who used a stainless-steel reactor and proposed that the chlorine initiated the chains by the reaction

$$metal + Cl_2 \rightarrow metal—Cl + \dot{C}l(g).$$
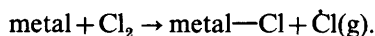
Huybrechts *et al.*[7] investigated the chlorine-sensitised photo-decomposition, and from the relative rates of formation of VC by reaction (2) and of 1,1,2-trichloroethane (TCE) by reaction (3)

$$Cl_2 + \dot{C}_2H_3Cl_2 \rightarrow C_2H_3Cl_3 + \dot{C}l \qquad (3)$$
$$k_2/k_3 = (d[VC]/dt) [Cl_2]/(d[TCE]/dt)$$
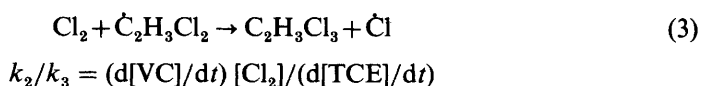
they determined the ratio $k_2/k_3$ at five temperatures between 433 and 510 K. From the published[8] Arrhenius parameters for $k_3$ they found

$$\log_{10} k_2/s^{-1} = 14.33 \pm 0.47 - (10710 \pm 630) \, K/4.576 \, T. \qquad (I)$$

However, a contemporary investigation by Gardner (J.W.G.) of the chlorine-catalysed *thermal* decomposition, at temperatures between 525 and 630 K, showed much lower values of $k_2$ than predicted by eqn (I), and also smaller Arrhenius parameters.[9] In a short extension of J.W.G.'s work, Sutton (P.S.) showed that $k_2$ falls with total pressure as expected for a unimolecular rate constant at appropriate pressures,[10] a possibility not considered in the photolysis studies. The effects of different pressures of DCE and of added inert gases upon $k_2$ have later been investigated in more detail by Smith (B.S.) and Owen (A.J.O.), who also investigated the inhibitory effects of VC through reaction (−2)

$$\dot{C}l + C_2H_3Cl \rightarrow \dot{C}_2H_3Cl_2. \qquad (-2)$$

This paper summarises the essential features of the dependence of the rates d[VC]/dt, d[TCE]/dt and −d[DCE]/dt on reaction conditions, and our evaluations of $k_2^{(p)}/k_3 = \gamma^{(p)}$ and $k_{-2}^{(p)}$ at different temperatures and pressures. These results, and published data on $k_1$ and $k_3$, are used to evaluate [$\dot{C}l$] and [$\dot{C}_2H_3Cl_2$] for different reaction conditions, and hence to provide information about the initiation and termination steps in fresh- and aged-surface vessels. In the following paper[11] the predictions of various theories of unimolecular fall-off are tested against A.J.O.'s extensive observations on the variations of $k_2^{(p)}$ and $k_{-2}^{(p)}$ with $p_{DCE}$ in order to obtain the best model for reaction (2).

## EXPERIMENTAL

The cylindrical vessels were maintained at temperatures controlled by a Sirect controller and measured by a Pt/13% Rh-Pt thermocouple, in a tubular electric furnace (J.W.G., P.S.) or an air-thermostat with forced circulation (B.S., A.J.O.). Mixtures were made up in heated, blackened vessels and fed to the reaction vessel through heated tubing and greaseless stopcocks (Young's). Vessels A and B were of quartz with plane ends and s/v ratios 1.4 and 6.6 cm$^{-1}$, respectively.[9] Pyrex vessel C, of dimensions similar to A, was used uncoated and then with coatings of KCl, AgCl and Teflon to investigate the effects of different surfaces. Pressures were

measured (J.W.G., P.S.) by an all-glass transducer, developed and kindly supplied by Dr P. J. Thomas of I.C.I. Mond Division, or by an S.E. transducer (B.S., A.J.O.), and recorded on a Servoscribe chart recorder.

The reactants and samples of products were purified as described elsewhere.[9] To check our 1,2-$C_2H_4Cl_2$, Dr G. Martens kindly supplied some unstabilised material; both samples gave the same results.

The organic compounds were identified and determined quantitatively by gas chromatography, using a Pye Unicam model 104 dual-column instrument, flame ionisation detector and a temperature programming unit. The columns used and the calibrations are detailed elsewhere.[9] The product HCl was determined by titrating samples from the reaction vessel and also by determining the pH of a solution prepared by a standard routine from the gas-chromatography sample.

Pressures of chlorine were determined with a single-beam photometer, using a monochromator (J.W.G.) or a Carl-Zeiss filter (B.S., A.J.O.) passing wavelengths close to 330 nm. The exit beam was monitored using an RCA 1P28 photomultiplier (J.W.G.) or an EMI photomultiplier (B.S., A.J.O.), the output being fed to a Servoscribe recorder. Frequent calibration checks against chlorine pressures were carried out with both systems.

In experiments using chlorine plus nitric oxide to catalyse the decomposition by the reaction

$$NO + Cl_2 \rightarrow NOCl + \dot{C}l$$
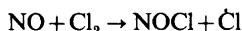
the nitrosyl chloride formed (in small amounts, *ca.* 10-15% of the initial nitric oxide) was monitored[9] using 250 nm radiation from the monochromator.

## RESULTS

### OVERALL REACTIONS AND RATES

Early work by J.W.G., confirmed by later checks, established that the primary products of the decomposition catalysed by chlorine were hydrogen chloride, vinyl chloride (VC) and 1,1,2-trichloroethane (TCE). The secondary products 1,1-dichloroethylene and *cis*- and *trans*-1,2-dichloroethylene are formed by pyrolysis of the TCE. Typical results are shown in fig. 1 (*a*). A careful search was made for other $C_1$ and $C_2$ chloroalkanes and chloroalkenes, ethane, ethylene and methane; it can be asserted that none were present in concentrations $> 10^{-5}$ of typical initial DCE concentrations. It was also established by gas-chromatographic analysis that no detectable amounts of organic derivatives of NO were formed during the experiments with NO and $Cl_2$ present. High-molecular-weight products would not have been detected, but sample mass balances of observed reactants and products agreed within $\pm 1\%$ at all extents of reaction in both vessels.

Initial mixtures of DCE, $Cl_2$ and NOCl gave much slower initial rates than with chlorine alone; initial mixtures of DCE, $Cl_2$ and NO gave much faster rates, but these fell off rapidly as NOCl was formed. Later in each run with NO plus $Cl_2$, however, the pressure increases were closely equal to the pressure of VC formed, as shown in fig. 1(*b*). The amount of chlorine that disappeared was again closely equal to the amount of TCE formed.[9] The changes were the same in the fresh vessels A and B, as shown, and were found to be the same for pressures of NO between 0.5 and 5.0 Torr.[9]* The absence of surface effects clearly indicates homogeneous initiation and homogeneous termination, probably by the reactions

$$NO + Cl_2 \rightleftharpoons NOCl + \dot{C}l.$$
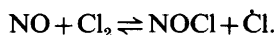
At suitable points during various runs, determinations were made of $k_2/k_3$ from $(d[VC]/dt) [Cl_2]/(d[TCE]/dt)$ and these are discussed in a later section.

* 1 Torr = 101 325/760 N m$^{-2}$.

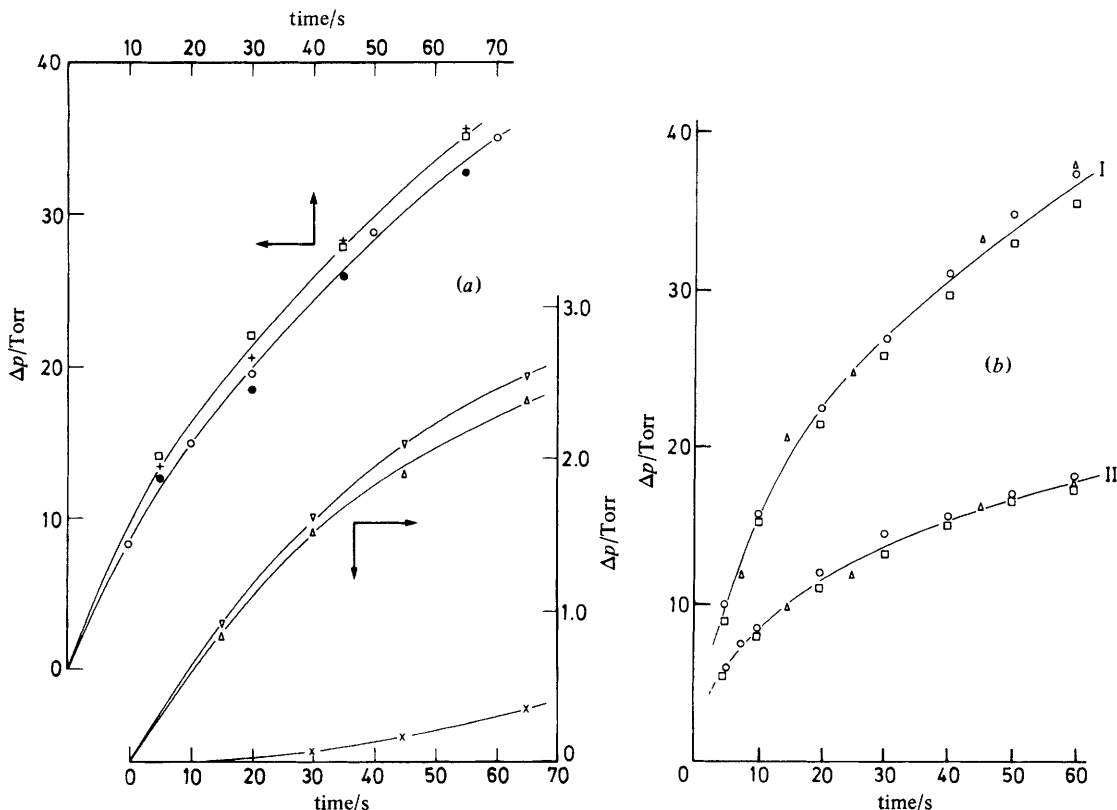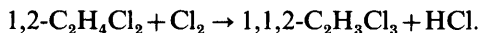FIG. 1.—(a) Correlations between pressure change ($\bigcirc$) and VC formed ($\bullet$) and between HCl formed ($\square$) and VC plus TCE plus dichloroethylenes formed ($+$). Relationships between $Cl_2$ lost ($\triangledown$), TCE formed ($\triangle$) and total dichloroethylenes formed ($\times$). $p_{DCE,0} = 82.5$ Torr at 584 K. Vessel B. (b) Correlations of pressure changes in vessel B ($\bigcirc$) and in vessel A ($\square$) with $p_{VC}$ formed ($\triangle$) for initial pressures $p_{Cl_2} = 10.8$ Torr, $p_{NO} = 2.0$ Torr and $p_{DCE} = 120.5$ Torr (curve I) or 73.5 Torr (curve II). 544 K. The curves are independent of $p_{NO}$ between 0.5 and 5.0 Torr.

In the chlorine-catalysed reaction the overall initial reactions are

$$1,2\text{-}C_2H_4Cl_2 \rightarrow CH_2\!=\!CHCl + HCl$$

and

$$1,2\text{-}C_2H_4Cl_2 + Cl_2 \rightarrow 1,1,2\text{-}C_2H_3Cl_3 + HCl.$$

We have repeatedly confirmed by comparison between pressure increase, photometry of $Cl_2$ and analyses of reactants and products, as illustrated in fig. 1(a), that $(dp_{total}/dt)_0 = (dp_{VC}/dt)_0$ and $-(dp_{Cl_2}/dt)_0 = (dp_{TCE}/dt)_0$, and hence that the *initial* rates could be determined satisfactorily from the continuous recording of total pressure (transducer) and chlorine partial pressure (photometer). The rates were corrected for the dead space;[12] this is very important, because the corrections for $dp_{total}/dt$ and $-dp_{Cl_2}/dt$ are in opposite senses.

### INITIAL RATES $(dp_{VC}/dt)_0$

After *ca.* 100 successive runs J.W.G. found the initial rates settled to nearly constant values for fixed initial pressures of DCE and $Cl_2$ at fixed $T$. These rates, in the still-fresh vessels A (quartz, $s/v = 1.4$ cm$^{-1}$) and B (quartz, $s/v = 6.6$ cm$^{-1}$) were strictly proportional[9] to $p_{DCE,0}$ with fixed $p_{Cl_2,0}$. Defining $k'$ by

$$(dp_{VC}/dt)_0 = k'p_{DCE,0}$$

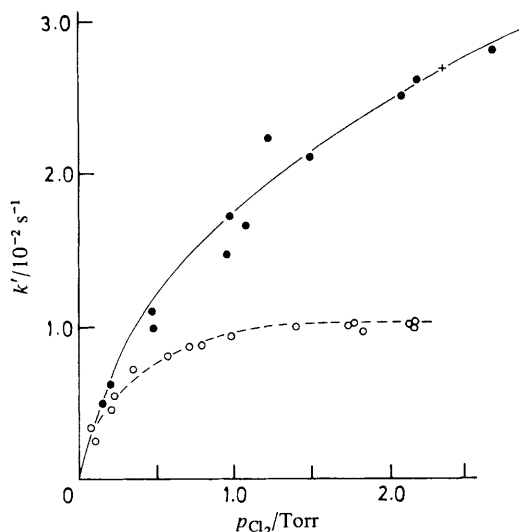$k'$ was found to vary with $p_{Cl_2,0}$ as shown in fig. 2 for the fresh vessels A and B at



FIG. 2.—The experimental rate constants $k'_{1.4}$ (○) in fresh vessel A ($s/v = 1.4$ cm$^{-1}$) and $k'_{6.6}$ (●) in fresh vessel B ($s/v = 6.6$ cm$^{-1}$) against $p_{Cl_2}$ at 584 K. The solid curves is based on point + with $k'_{6.6}$ proportional to $p_{Cl_2}^{0.5}$.

584 K. In vessel A, $k'_{1.4}$ appeared to reach a limiting value as $p_{Cl_2,0}$ increased to moderate values. In vessel B, however, a limiting rate was not achieved even at much higher values of $p_{Cl_2,0}$. Indeed, in the lower range of $p_{Cl_2,0}$, the rates were proportional to $p_{Cl_2,0}^{0.5}$. This is illustrated in fig. 2, where the line for $k'_{6.6}$ is based on point + with

$$k'_{6.6} \propto p_{Cl_2,0}^{0.5}.$$

In the aged vessel B (*i.e.* after *ca.* 500 runs) the initial rates remained proportional to $p_{Cl_2,0}^{0.5}$ over a wide range, as shown in fig. 3 for three pressures of DCE. Moreover, in other vessels with different surface coatings the rates with fixed $p_{DCE}$ were found by A.J.O. to be proportional to $p_{Cl_2,0}^{0.5}$ or to a slightly higher order. Thus the behaviour of fresh vessel A seems in retrospect to be anomalous.

As vessel B aged (*i.e.* during the experiments of J.W.G. and B.S.) several significant changes in the kinetics of the decomposition occurred. In the first place the rates for chosen conditions of $T$, $p_{DCE}$ and $p_{Cl_2}$ decreased significantly as shown in table 1. Secondly, the order of reaction in $p_{DCE}$ decreased significantly, falling well below unity in later experiments by B.S.; from the slopes in fig. 3 it was deduced that in the aged vessel B

$$(dp_{VC}/dt)_0 = \beta(p_{Cl_2,0}/\text{Torr})^{0.5} \, (p_{DCE,0}/\text{Torr})^{0.62}$$
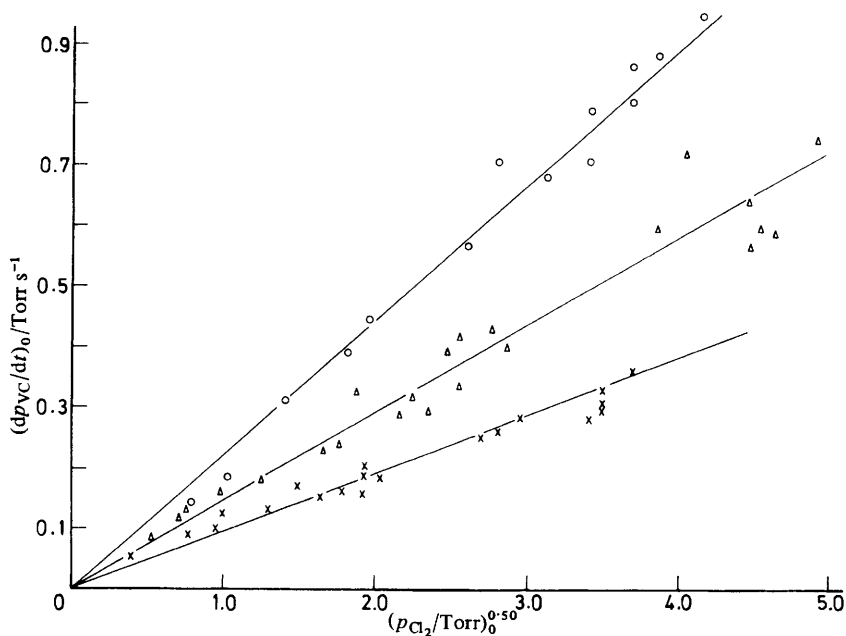
FIG. 3.—Plots of $(dp_{VC}/dt)_0$ against $(p_{Cl_2})_0^{0.5}$ in aged vessel B with $p_{DCE,0}$ equal to ×, 35; △, 65 and ○, 135 Torr. 572 K.

TABLE 1.—$(dp_{VC}/dt)_0$/Torr s$^{-1}$ IN FRESH AND AGED VESSEL B AT 572 K

| $p_{Cl_2,0}$/Torr | state of B | $p_{DCE,0}$/Torr | | |
| --- | --- | --- | --- | --- |
| | | 35 | 65 | 135 |
| 1.0 | fresh | 0.37 | 0.70 | 1.43 |
| | aged | 0.10 | 0.13 | 0.19 |
| 2.0 | fresh | 0.53 | 0.98 | 2.02 |
| | aged | 0.14 | 0.19 | 0.29 |

where $\beta$ is a specific rate. Thirdly, at a fixed chlorine pressure (1.0 Torr) the activation energies for $k'_{1.4}$ (vessel A, fresh), $k'_{6.6}$ (vessel B, fresh) and for $\beta$ (vessel B, aged) were found to be 27, 32 and 47 kcal mol$^{-1}$, respectively. Fourthly, while investigating the effect of adding inert gases J.W.G. found that large pressures of added argon had no effect on $(dp_{VC}/dt)_0$, whereas B.S. found that adding inert gases such as $CO_2$, $CCl_4$, cyclo-$C_4F_8$ and $C_5F_{12}$ all increased $(dp_{VC}/dt)_0$, the increases being larger for the gases with larger molecules. Table 2 illustrates the change for adding $CO_2$ to 41 Torr of DCE at 532 K (the significance of $\gamma_{exp}$ is explained in the next section of this paper). Fifthly, the order in chlorine in fresh vessel A was not simple, as the rates reached limiting values at moderate $p_{Cl_2,0}$; in the fresh vessel B it was 0.5 at low values of $p_{Cl_2,0}$, but not simple at higher pressures; in aged vessel B, it was 0.5 over a wide range of pressures; in other vessels, with different surface coatings, it was 0.5 or (at some temperatures) slightly higher.

TABLE 2.—RELATIVE MAGNITUDE OF $(dp_{VC}/dt)_0$ ON ADDING $CO_2$ TO 41 TORR OF DCE (VESSEL B, 532 K)

| $p_{CO_2}/p_{DCE}$ | relative magnitude $dp_{VC}/dt$ | relative magnitude $\gamma_{exp}$ |
|---|---|---|
| 0 | 1.00 | 1.00 |
| 1.00 | 1.39 | 1.41 |
| 1.80 | 1.63 | 1.61 |
| 2.60 | 1.80 | 1.74 |

In summary, it appears that the rate $(dp_{VC}/dt)_0$ depends on the state of the vessel as well as on $T$, $p_{DCE,0}$ and $p_{Cl_2,0}$.

### STUDIES OF THE PROPAGATING STEPS (2) AND (3) IN THE CHLORINE-CATALYSED DECOMPOSITION

If VC and TCE are formed predominantly by steps (1)-(3), where $\dot{R} = CH_2Cl\dot{C}HCl$,

$$\dot{C}l + DCE \rightarrow \dot{R} + HCl \tag{1}$$

$$\dot{R} \rightarrow VC + \dot{C}l \tag{2}$$

$$\dot{R} + Cl_2 \rightarrow TCE + \dot{C}l \tag{3}$$

and the reverse of reaction (2) is ignored while [VC] is small then

$$\frac{k_2}{k_3} = \frac{dp_{total}/dt}{-dp_{Cl_2}/dt} \times p_{Cl_2} = \gamma_{exp} \tag{II}$$

where $\gamma_{exp}$ is calculated from the rates and $p_{Cl_2}$.

J.W.G. measured the rates $(dp_{total}/dt)$ and $-(dp_{Cl_2}/dt)$ and $p_{Cl_2}$ at various points during each of many runs. On plotting $(dp_{total}/dt) \times p_{Cl_2}$ against $-(dp_{Cl_2}/dt)$ it was found that points for runs in fresh vessels A and B at the same temperature and the same $p_{DCE,0}$ fitted the same straight line, as exemplified in fig. 4 for $p_{DCE,0} = 24$ Torr. These results suggested that $\gamma_{exp}$ was independent of the vessel and of the percentage of chlorine, and did represent the ratio $k_2/k_3$ of the rate constants of two homogeneous reactions. It was thought at that time that $\gamma_{exp}$ was also independent of $p_{DCE}$ (which was usually in the range 40-90 Torr) so the values were averaged at each temperature. The averages for five temperatures are shown on an Arrhenius plot in fig. 5, with the weightings of the averages in brackets, together with four values derived from the experiments[9] on the homogeneous catalysis of the decomposition by chlorine + nitric oxide. Line III in fig. 5 was fitted by a least-squares procedure to the chlorine-catalysed results. Regression analysis of the individual experimental variances shows the 95% confidence limits on $E_2 - E_3$ and on $\log[(A_2/A_3)/dm^3 mol^{-1}]$ are as shown in eqn (III)

$$\log_{10} \frac{k_2/s^{-1}}{k_3/dm^3 mol^{-1} s^{-1}} = (3.57 \pm 0.13) - \frac{17100 \pm 350}{4.576 \, T/K}. \tag{III}$$

These results seem to confirm that the principal reactions forming VC and TCE in the chlorine-catalysed pyrolysis are the homogeneous reactions (2) and (3). However, doubt was cast on these results or their interpretation when it became known that Huybrechts et al.[7] had studied the apparently similar chlorine-sensitised photo-
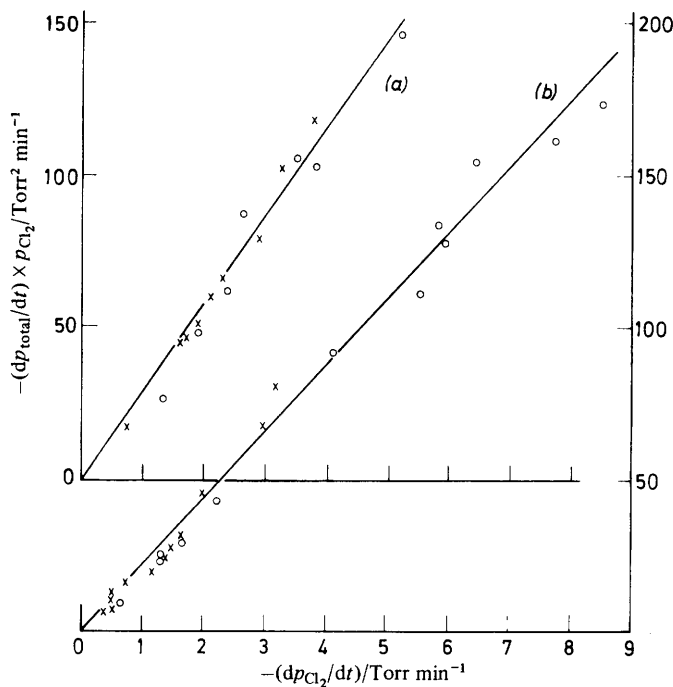
FIG. 4.—Plots for 578 and 561 K which show $(dp_{total}/dt)\,p_{Cl_2}$ is proportional to $-(dp_{Cl_2}/dt)$, independently of the vessel. Vessel A, $s/v = 1.4$ cm$^{-1}$ ($\times$); vessel B, $s/v = 6.6$ cm$^{-1}$ (○); $p_{DCE,0} = 24$ Torr.
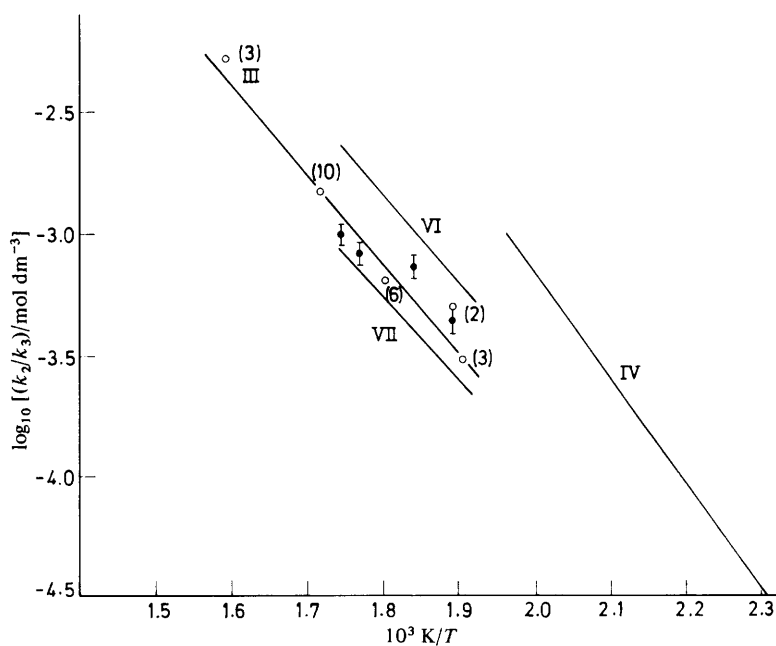


FIG. 5.—Arrhenius plots of log $(k_2/k_3)$ for chlorine catalysed (○ with weightings in brackets) and nitric oxide + chlorine catalysed (●) decompositions (line III) and for eqn (IV), (VI) and (VII).

decomposition of 1,2-dichloroethane over the temperature range 433-510 K and found

$$\log_{10}\frac{k_2/s^{-1}}{k_3/dm^3\ mol^{-1}\ s^{-1}} = 5.58\pm0.27-\frac{19970\pm580}{4.576\ T/K}.\qquad(IV)$$

Eqn (IV) gave considerably higher values of $k_2/k_3$ than eqn (III) as shown in fig. 5.

In searching for reasons for the discrepancies, it was considered that they could not be attributed to the onset of reactions other than (2) or (3) at our higher temperatures, nor to other effects of the photolysing beam such as enhanced decomposition of $\dot{R}$. In view of the unimolecular nature of reaction (2), the most likely explanation of our lower results at lower total pressures than those of Huybrechts et al. was the unimolecular fall-off of $k_2$ at pressures around 10-100 Torr. The apparently similar reaction

$$\dot{C}_2H_5 \rightarrow C_2H_4+\dot{H}$$
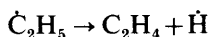
shows fall-off in that (total) pressure range.[13]

In a short project, P.S. found a clear dependence of $k_2$ on pressure of DCE by exploring a wider pressure range and lower temperatures than used by J.W.G., as reported in ref. (10). Those experiments were extended by B.S., who found further evidence for unimolecular behaviour of reaction (2) in experiments with selected pressures of DCE at temperatures between 520 and 575 K in vessel B. Typical fall-off curves were found for $\gamma_{exp}$, illustrated by curve (1) through the points ○ in fig. 6
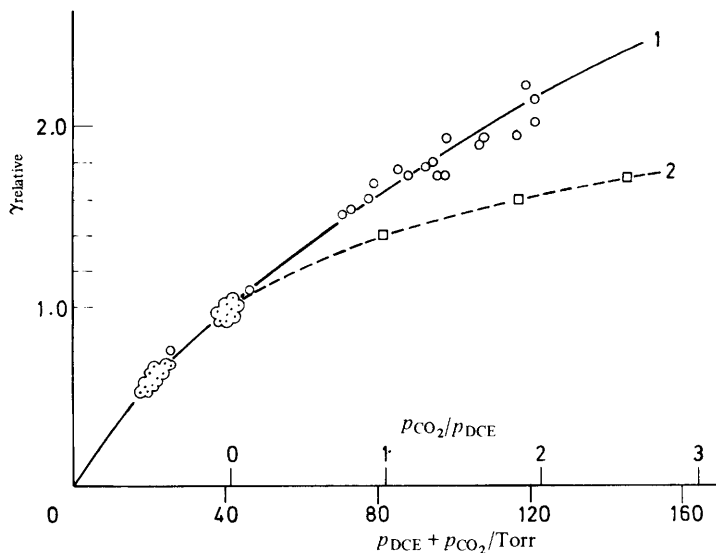


FIG. 6.—Relative values of $\gamma$ as $p_{DCE,0}$ is increased (○, curve 1) and as $CO_2$ is added to 41 Torr of DCE (□, mean of 9 runs, curve 2). 532 K. Vessel B, intermediate age.

which shows $\gamma_{exp}$ relative to the value for $p_{DCE} = 41$ Torr. Fig. 6 also shows the effects on $\gamma_{relative}$ of adding $CO_2$ to 41 Torr of DCE at 532 K as points □, each being the mean of 9 runs. The increases in $\gamma_{relative}$ as $CO_2$ was added are shown in table 2, together with relative changes in $(dp_{VC}/dt)$. The increases in $\gamma_{relative}$ closely parallel the increases in $dp_{VC}/dt$; there was very little increase in $dp_{TCE}/dt$. Inspection of the rate equations for reactions (2) and (3) shows that these results can only be explained

by changes in $k_2$, and not by changes in [$\dot{R}$], as $CO_2$ is added. B.S. also observed that adding inert gases such as cyclo-$C_4F_8$ and $C_5F_{12}$ increased $\gamma_{exp}$ to a greater extent than did $CO_2$, bringing the fall-off curves close to that of DCE itself. These 'inert gas' effects are in keeping with unimolecular rate theory. Chlorine itself would be expected to have less effect than $CO_2$; in addition, the proportion of chlorine used was rarely $> 10\%$ of the total pressure, and all later experiments (A.J.O.) at fixed $p_{DCE}$ showed that $\gamma_{exp}$ was independent of $p_{Cl_2}$ in those proportions.

A.J.O. obtained extensive results with aged vessel B and also with a Pyrex vessel C, of dimensions close to those of A, when uncoated (CP) and when coated with Teflon (CT). While running-in the vessels CP and CT, A.J.O. observed that the overall rates fell but $\gamma_{exp}$ remained constant as shown in fig. 7. Table 3 summarises data at 572 K
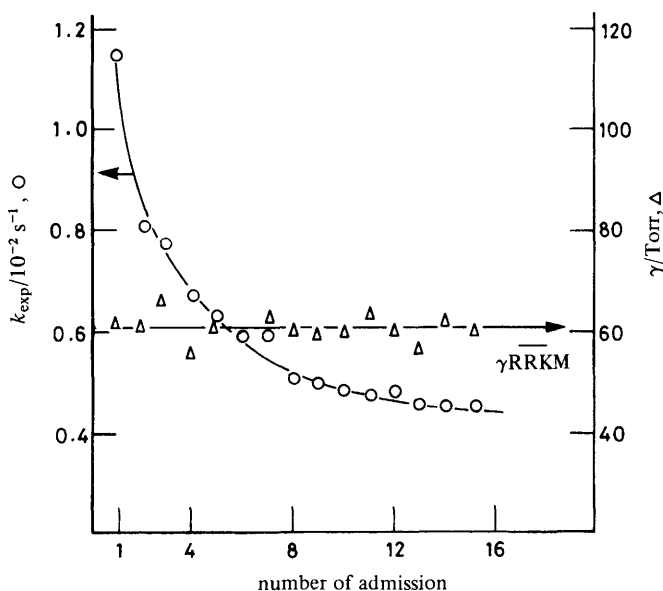


FIG. 7.—Changes in $k_{exp} = (d \ln p_{DCE}/dt)_0$ (○) and constancy of $\gamma_{exp}$ (△) with successive admissions in a fresh Teflon-coated vessel, s/v $= 1.4$ cm$^{-1}$, 572 K. $p_{DCE,0} \approx 62 \pm 2$ Torr, 7.8-8.1% $Cl_2$.

for the three vessels after running-in, and shows that $\gamma_{exp}$ is substantially independent of the particular vessel. Over the higher pressure range the results are a reasonable fit to the empirical equation

$$\log_{10}(\gamma/\text{Torr}) = 0.64 + 0.61 \log_{10}(p_{DCE}/\text{Torr}). \quad \text{(V)}$$

The last line of table 3 gives the predicted values of $\gamma$ for the mean pressures in vessel B. The dependence of $\gamma$ upon $p_{DCE}$ can only be attributed to changes in $k_2$ with $p_{DCE}$, so

$$k_2 \propto (p_{DCE}/\text{Torr})^{0.61}.$$

It is significant that this proportionality correlates very closely with the equation established for $(dp_{VC}/dt)_0$ in aged vessel B, viz.

$$(dp_{VC}/dt)_0 = k_2[\dot{R}]_0 = \beta(p_{Cl_2}/\text{Torr})_0^{0.5}(p_{DCE}/\text{Torr})_0^{0.62}.$$

TABLE 3.—MEAN VALUES $\bar{p}$, $\bar{\gamma}$ (WITH STANDARD ERRORS OF MEANS AND NUMBER OF RUNS) OF $p_{DCE}$, $\gamma^p_{exp}$ FOR DIFFERENT VESSELS AT 572 K

| | | | | | | |
|---|---|---|---|---|---|---|
| quartz B<br>s/v = 6.6 cm⁻¹ | $\bar{p}\pm$S.E./Torr | 9.02±0.08 | 22.8±0.33 | 36.5±0.29 | 63.4±0.61 | 101.2±0.58 |
| | $\bar{\gamma}\pm$S.E./Torr | 13.1±0.49 | 29.1±0.78 | 40.1±0.48 | 57.4±1.12 | 75.4±1.29 |
| | no. of runs | 19 | 19 | 19 | 24 | 23 |
| Pyrex C (CP)<br>s/v = 1.4 cm⁻¹ | $\bar{p}\pm$S.E./Torr | 9.05±0.13 | 23.4±0.35 | 36.4±0.58 | 65.0±0.47 | 103.0±2.23 |
| | $\bar{\gamma}\pm$S.E./Torr | 12.6±1.20 | 32.8±1.20 | 41.0±1.07 | 63.1±1.76 | 73.0±3.58 |
| | no. of runs | 4 | 4 | 3 | 8 | 4 |
| Teflon C (CT)<br>s/v = 1.4 cm⁻¹ | $\bar{p}\pm$S.E./Torr | 8.97±0.16 | 23.3±0.25 | 36.7±0.31 | 64.3±0.31 | 104.0±1.11 |
| | $\bar{\gamma}\pm$S.E./Torr | 12.3±0.89 | 32.6±2.93 | 44.7±1.80 | 60.0±0.63 | 70.0±3.12 |
| | no. of runs | 6 | 8 | 9 | 27 | 8 |
| prediction from eqn (V) of $\gamma$ for $\bar{p}$ values in aged vessel B | | — | 30.1 | 40.2 | 56.4 | 75.2 |

TABLE 4.—MEAN VALUES $\bar{p}$, $\bar{\gamma}$ (WITH STANDARD ERRORS OF MEANS AND NUMBERS OF RUNS) OF $p_{DCE}$, $\gamma^p_{exp}$ IN VESSEL B AT THE TEMPERATURES INDICATED

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 572 K | $\bar{p}\pm$S.E./Torr | 9.0±0.08 | 22.8±0.33 | 36.5±0.29 | 63.4±0.61 | 101.2±0.58 | 134.6±0.90 |
| | $\bar{\gamma}\pm$S.E./Torr | 13.1±0.49 | 29.1±0.78 | 40.1±0.48 | 57.4±1.12 | 75.4±1.29 | 87.2±1.80 |
| | no. of runs | 19 | 19 | 24 | 23 | | 11 |
| 560 K | $\bar{p}\pm$S.E./Torr | 9.2±0.13 | 24.5±0.66 | 36.8±0.48 | 64.3±0.96 | 100.4±1.51 | 138.3±1.82 |
| | $\bar{\gamma}\pm$S.E./Torr | 12.5±0.54 | 26.1±0.92 | 31.4±1.40 | 44.1±1.73 | 54.0±2.00 | 63.8±1.55 |
| | no. of runs | 8 | 7 | 6 | 6 | 6 | 4 |
| 547 K | $\bar{p}\pm$S.E./Torr | 9.3±0.33 | 22.5±0.38 | 36.8±0.76 | 65.0±1.26 | 97.3±0.90 | — |
| | $\bar{\gamma}\pm$S.E./Torr | 8.9±0.89 | 18.4±0.83 | 24.7±1.13 | 32.4±1.74 | 38.3±1.58 | — |
| | no. of runs | 4 | 4 | 5 | 4 | 6 | — |
| 534 K | $\bar{p}\pm$S.E./Torr | 9.4±0.12 | 23.0±0.26 | 35.6±0.78 | 65.2±1.35 | 100.2±1.35 | 131.7±2.35 |
| | $\bar{\gamma}\pm$S.E./Torr | 5.3±0.16 | 11.9±0.41 | 16.0±0.37 | 23.1±0.33 | 27.7±0.92 | 30.4±1.05 |
| | no. of runs | 6 | 6 | 6 | 6 | 6 | 4 |
| 521 K | $\bar{p}\pm$S.E./Torr | 9.6±0.46 | 18.6±0.25 | 27.3±0.46 | 55.0±0.38 | 91.8±0.77 | 134.8±1.57 |
| | $\bar{\gamma}\pm$S.E./Torr | 3.6±0.36 | 5.2±0.18 | 8.1±0.40 | 11.6±0.25 | 16.8±0.62 | 18.9±0.24 |
| | no. of runs | 5 | 9 | 11 | 11 | 11 | 4 |

The correlation means that $[\dot{R}]_0$ is independent of $p_{DCE,0}$ in aged vessel B; this point is discussed in detail in a later section of this paper.

Table 4 summarises the results from many runs in the aged vessel B, and shows the mean values $\bar{\gamma}$ of $\gamma_{exp}^{(p)}$ for groups of pressures at five different temperatures. In Part $2^{11}$ of this series RRKM calculations are described that identify the model of unimolecular fall-off that best fits these mean $\bar{\gamma}$, $\bar{p}$ values, and the appropriate fall-off
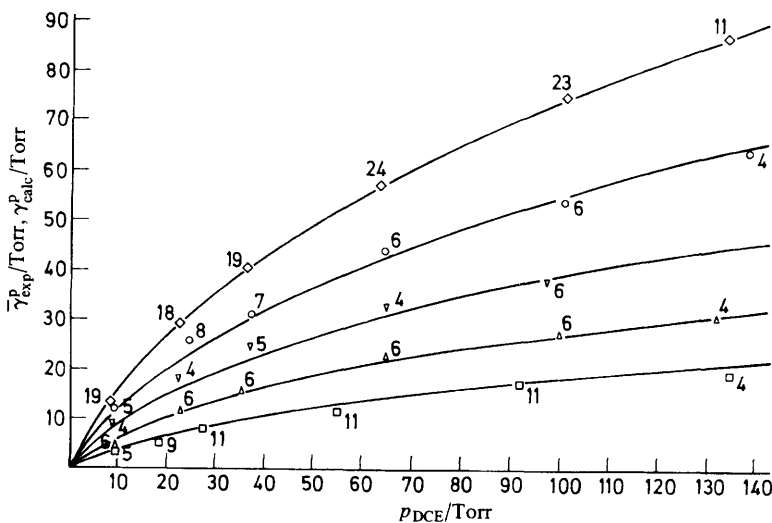


FIG. 8.—Mean-values $\bar{\gamma}$ of $\gamma_{exp}^{(p)}$ at $\diamond$, 572; $\bigcirc$, 560; $\triangle$, 547; $\triangle$, 534 and $\square$, 521 K with the number of runs which determined each mean. The curves show the RRKM predictions for model G (see Part $2^{11}$ of this series).

curves are shown in fig. 8. From these curves the variations of $k_2/k_3$ with temperature was found to depend on the pressure range according to eqn (VI) and (VII)

$$\log_{10}\left(\frac{k_2/s^{-1}}{k_3/dm^3\ mol^{-1}\ s^{-1}}\right) = 3.65 - \frac{16\,500}{4.58\ T/K}\ (100\ Torr) \qquad (VI)$$

$$= 2.86 - \frac{15\,550}{4.58\ T/K}\ (25\ Torr). \qquad (VII)$$

These equations are plotted in fig. 5, and fit very satisfactorily around line III which represents J.W.G.'s mean values for the range 40–90 Torr. It therefore appears certain that the experimental results shown by lines III and IV are in keeping with predictions from RRKM theory illustrated by lines VI and VII. In Part $2^{11}$ the high-pressure parameters $A_2^\infty$ and $E_2^\infty$ of $k_2^\infty$ are evaluated.

### EFFECTS OF THE PRODUCT VC ON THE RATE OF THE CATALYSED DECOMPOSITIONS

J.W.G. showed[9] that the addition of VC to mixtures of DCE and $Cl_2$ reduced the initial rate of decomposition, because reaction $(-2)$ is then important. A full stationary-state treatment of reactions (1), (2), $(-2)$ and (3) shows that expression (II)

for $\gamma_{exp}$ is modified to give $\gamma^{VC}$ in the presence of VC:

$$\gamma^{VC} = \left( \frac{dp_{total}/dt}{-dp_{Cl_2}/dt} \right)^{VC} \times p_{Cl_2}$$

$$= \left( \frac{k_2}{k_3} - \alpha p_{Cl_2} \right) (1 + \alpha) \qquad \text{(VIII)}$$

where $\alpha = k_{-2}[VC]/k_1[DCE]$. Thus if values of $k_2/k_3$ are known it is possible to calculate $k_{-2}/k_1$ for selected points in any run. Using this method J.W.G. found $k_{-2}/k_1 = 0.75$ at 630 K.

A.J.O. investigated this effect in greater detail in order to study the temperature variation of $k_{-2}/k_1$ and to see whether $k_{-2}$ was pressure-dependent, as would be
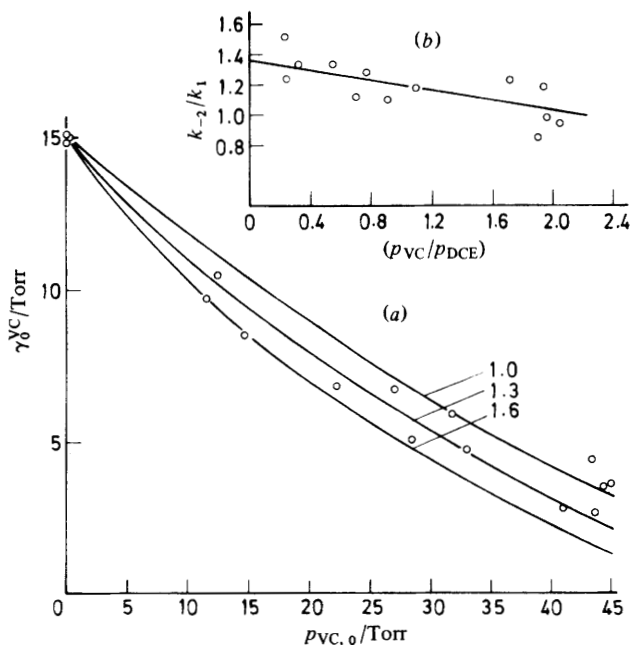


FIG. 9.—(a) Experimental values (○) of $\gamma_0^{VC}$ dotted against $p_{VC,0}$ with $(p_{DCE} + p_{VC})_0 = 65$ Torr, at 520 K. The curves are calculated from eqn (VIII) for $k_{-2}/k_1 = 1.0$, 1.3 or 1.6. (b) Plots of $k_{-2}/k_1$ at 520 K calculated from eqn (VIII) assuming $\gamma^{VC} = 15.0$ Torr for $p_{DCE,0} = 65$ Torr, $p_{VC,0} = 0$. The line is the least-mean-squares fit. Vessel B.

expected by analogy with the pressure dependence of $k_2$. Fig. 9(a) shows the experimental values of $\gamma_0^{VC}$ determined from

$$\gamma_0^{VC} = p_{Cl_2} \left( \frac{dp_{total}/dt}{-dp_{Cl_2}/dt} \right)_0$$

plotted against $p_{VC,0}$ for runs at 520 K with $p_{DCE,0} + p_{VC,0}$ kept constant at 65 Torr. The three lines show $\gamma_0^{VC}$ calculated from eqn (VIII) assuming (a) $k_{-2}/k_1$ has values 1.0, 1.3 or 1.6 and calculating $\alpha$ from appropriate values of $p_{VC}$, $p_{DCE}$ and $p_{Cl_2}$, and (b) $k_2/k_3$ is constant and has the value for $p_{VC} = 0$, which would only be true if DCE

and VC have equal efficiencies in energising or de-energising the radical $\dot{C}_2H_3Cl_2$. The best fit is for $k_{-2}/k_1 \approx 1.3$, but the lines do not curve sufficiently. This may be because $k_2/k_3$ changes as $p_{VC,0}/p_{DCE,0}$ changes.

A practical way round the difficulty is to use the same basic data and eqn (VIII) to calculate $\alpha$ and hence $k_{-2}/k_1$ point by point, and to investigate whether the ratio changes systematically with $p_{VC,0}/p_{DCE,0}$. Fig. 9(b) shows the plot of $k_{-2}/k_1$ against $p_{VC,0}/p_{DCE,0}$ (with $p_{DCE,0}+p_{VC,0} = 65$ Torr) with the line fitted by least-mean-squares procedures. Similar systematic variation was found at other pressures (100, 35 and 25 Torr) at 520 K, and also from experiments at 544, 570 and 590 K. For comparison of results we take the intercept values of $k_{-2}/k_1$, so that the only energising/de-energising species is DCE.

TABLE 5.—VALUES OF $k_{-2}/k_1$ AND $\varnothing = \log_{10} (k_{-2}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$. $\varnothing_m$ IS THE MEAN OF THE $\varnothing$ AT EACH TEMPERATURE.

|  |  | $\approx 25$ | $\approx 35$ | $\approx 65$ | $\approx 100$ | $\varnothing_m$ |
|---|---|---|---|---|---|---|
|  | $p_{DCE}/\text{Torr}$ |  |  |  |  |  |
| 595 K | $k_{-2}/k_1$ | 0.79 | 0.87 | 1.12 | 1.66 | — |
|  | $\varnothing$ | 9.56 | 9.60 | 9.71 | 9.88 | 9.69 |
| 570 K | $k_{-2}/k_1$ | 0.76 | 0.81 | 1.45 | 1.74 | — |
|  | $\varnothing$ | 9.49 | 9.52 | 9.77 | 9.85 | 9.66 |
| 544 K | $k_{-2}/k_1$ | 0.91 | 0.89 | 1.41 | 1.90 | — |
|  | $\varnothing$ | 9.51 | 9.50 | 9.70 | 9.83 | 9.64 |
| 520 K | $k_{-2}/k_1$ | 1.00 | 1.15 | 1.35 | 1.75 | — |
|  | $\varnothing$ | 9.50 | 9.56 | 9.63 | 9.74 | 9.61 |

Table 5 shows the intercept ($p_{VC} = 0$) values of $k_{-2}/k_1$, and the corresponding values of $\varnothing = \log_{10} (k_{-2}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$, using the published data[14] for $k_1$.

At all four temperatures the values of $k_{-2}/k_1$ fall with decrease in pressure, showing that $k_{-2}$ is in a fall-off region, just as $k_2$ is, in the pressure range investigated. These results are examined in more detail in Part 2.[11]

## DISCUSSION

### OVERALL MECHANISMS OF THE CATALYSED DECOMPOSITIONS

The experimental results confirm that the propagating steps in the early stages of the catalysed decompositions are (1)-(3), with reaction (−2) affecting the rates later in each run or when VC is added to initial mixtures.

The changes in rates and rate laws in vessel B as it aged, and differences from vessel to vessel, point to changes and differences in the control of the chain-centre concentrations by the initiation and termination steps. Many overall rate laws, derived from different combinations of heterogeneous and homogeneous initiation and termination steps, were tested against the experimental results but did not prove very discriminating. Examination of chain-centre concentrations calculated from measured rates and the rate constants $k_1$, $k_2^{(p)}$ and $k_3$ has revealed much more about the nature of the initiation and termination steps under different reaction conditions.

## CHAIN-CENTRE CONCENTRATIONS BASED ON RATE MEASUREMENTS

### THE RELATIVE CONCENTRATIONS $[\dot{R}]_0/[\dot{C}l]_0$

These depend solely on the propagating reactions (1)-(3) in the initial stages when VC is low and reaction (−2) can be neglected. For steady rates they will adjust to give

$$\frac{[\dot{R}]_0}{[\dot{C}l]_0} = \frac{k_1[DCE]_0}{k_2^{(p)} + k_3[Cl_2]_0} \tag{IX}$$

irrespective of the initiation and termination reactions. Taking the published date for $k_1$ and $k_3$ and using the data for $k_2^{(p)}$ reported in Part 2,[11] the ratio takes the value shown in table 6.

TABLE 6.—THE RATIO $[\dot{R}]_0/[\dot{C}l]_0$ FOR VARIOUS REACTION CONDITIONS

| $T/K$ | 520 | | 572 | | 629 | |
|---|---|---|---|---|---|---|
| $p_{Cl_2, 0}/Torr$ | 2 | 5 | 2 | 5 | 2 | 5 |
| $P_{DCE, 0}/Torr$ | | | | | | |
| 35 | 43 | 34 | 14 | 13 | 4.7 | 4.6 |
| 65 | 57 | 48 | 18 | 17 | 5.8 | 5.7 |
| 135 | 88 | 77 | 25 | 24 | 7.6 | 7.5 |

shown in table 6. It is therefore likely that termination reactions involving R will be more important at lower temperatures, lower $p_{Cl_2}$ and higher $p_{DCE}$; and those involving Cl will be relatively more important at higher temperatures and lower $p_{DCE}$.

### ABSOLUTE VALUES OF $[\dot{C}l]_0$ AND $[\dot{R}]_0$ IN VESSEL B

$[\dot{C}l]_0$ was calculated from $-(d[DCE]/dt)_0/k_1[DCE]_0$ with[14]

$$\log_{10}(k_1/dm^3\ mol^{-1}\ s^{-1}) = 10.80 - (3100\ K/4.576\ T).$$

Fig. 10 shows how $[\dot{C}l]_0$ depends on $[Cl_2]_0$ at 572 K. In the fresh vessel $[\dot{C}l]_0$ is proportional to $[Cl_2]_0^{0.5}$, is independent of $[DCE]_0$, and lies very close to $[\dot{C}l]_{eq} = (K_D[Cl_2]_0)^{0.5}$. In the aged vessel $[\dot{C}l]_0$ depends on a power $> 0.5$, and is smaller with higher values of $[DCE]_0$. Similar differences were found at other temperatures.
$[\dot{R}]_0$ was calculated from $(d[TCE]/dt)_0/k_3[Cl_2]_0$ with[8]

$$\log_{10}(k_3/dm^3\ mol^{-1}\ s^{-1}) = 8.76 - (920\ K/4.576\ T);$$

check calculations from $(d[VC]/dt)_0/k_2^{(p)}$ confirmed the values. The left-hand lines in fig. 11 show that in the fresh vessel at 572 K $[\dot{R}]_0$ is proportional to $[Cl_2]_0^{0.5}$ but is larger for higher values of $[DCE]_0$. The points show experimental results in the aged vessel at 572 K; $[\dot{R}]_0$ is then closely proportional to $[Cl_2]_0^{0.5}$ (more accurately it fits a slightly higher power) and is clearly independent of $[DCE]_0$ and the values are much lower than in the fresh vessel. Similar results were found at other temperatures.

### DEDUCTIONS ABOUT INITIATION AND TERMINATION REACTIONS IN VESSEL B

#### FRESH VESSEL B

The simplest explanation of the observations summarised in fig. 10 and 11 is that the initiation and termination reactions in fresh vessel B controlled $[\dot{C}l]_0$, especially at higher temperatures where $[\dot{C}l]/[\dot{R}]$ is higher.
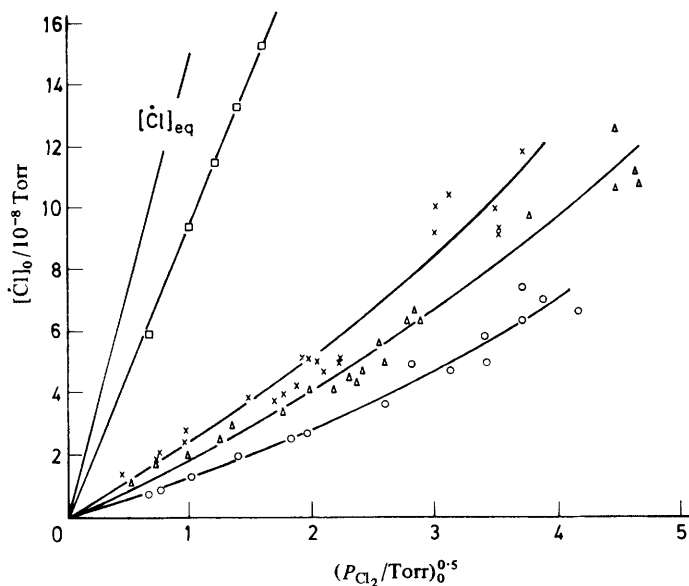
FIG. 10.—Plots of $[\dot{C}l]_{eq}$ and $[\dot{C}l]_0$ against $(p_{Cl_2}/\text{Torr})_0^{0.5}$ for the fresh vessel B ($\square$) at all $p_{DCE,0}$ and for the aged vessel B at $p_{DCE,0}$ equal to $\times$, 35; $\triangle$, 65 and $\bigcirc$, 135 Torr, 572 K.
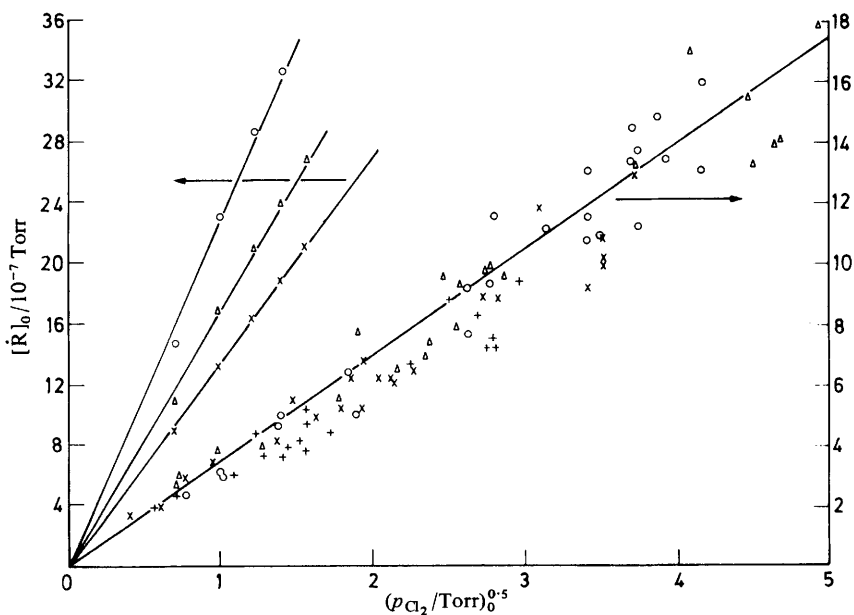


FIG. 11.—Plots of $[\dot{R}]_0$ against $(p_{Cl_2}/\text{Torr})_0^{0.5}$ at 572 K for the fresh vessel with $p_{DCE,0} \approx \times$, 35; $\triangle$, 65 and $\bigcirc$, 135 Torr (left-hand axis); and for the aged vessel B with $p_{DCE,0} \approx +$, 25; $\times$, 35; $\triangle$, 65 and $\bigcirc$, 135 Torr (right-hand axis).

Since $[\dot{C}l]_0$ is proportional to $[Cl_2]_0^{0.5}$ and close to $[\dot{C}l]_{eq} = \sqrt{(K_D[Cl_2]_0)}$, the gas-phase dissociation and recombination steps (d) and (r) must be examined as candidates for the initiation and termination reactions

$$Cl_2 + M \underset{r}{\overset{d}{\rightleftharpoons}} 2\dot{C}l + M, \qquad (d,r)$$

There are several objections to this assignment. It has been shown[15] previously that the attainment of 90% of $[\dot{C}l]_{eq}$ when $Cl_2$ is admitted to vessels at 650 K would take more than 100 s by homogeneous dissociation of $Cl_2(p_{Cl_2} = 20$ Torr, $p_{total} = 760$ Torr). It would take longer with $p_{total} \approx 100$ Torr, especially at lower temperatures, but no induction periods were observed in the catalysed pyrolysis. Reaction (r) is much slower than the termination step (t)

$$\dot{C}l + \dot{R} \overset{t}{\rightarrow} RCl \qquad (t)$$

for which the rate constant has been estimated[16] as $10^{11.3}$ dm$^3$ mol$^{-1}$ s$^{-1}$; experimentally measured values for $\dot{C}l +$ other chloroethylene radicals are lower ($10^{10.9}$ dm$^3$ mol$^{-1}$ s$^{-1}$ for $CHCl_2CCl_3$ and $10^{11.0}$ dm$^3$ mol$^{-1}$ s$^{-1}$ for $C_2Cl_5$). A recent experimental measurement[17] of the rate constant for path (r) suggests a maximum value of $5 \times 10^9$ dm$^6$ mol$^{-2}$ s$^{-1}$ at 572 K. Combining these rate constants with typical values of $[\dot{C}l]_0$ and $[\dot{R}]_0$ for fresh-surfaced vessels at 572 K shows that reaction (t) is $> 10^4$ times as effective as reaction (r) for all reactant pressures used. Similarly, calculations from published data[18] on reaction (d) show that it produces chlorine atoms at a much slower rate than they would be removed by reaction (t) were it operative under those conditions. We therefore reject reactions (d) and (r) as effective initiation and termination reactions.

Another pair of reactions that could result in $[\dot{C}l]_0 \approx [\dot{C}l]_{eq}$ are reactions of chlorine molecules and atoms with surface sites S such as the pair (i, s) that would be balanced at true equilibrium (from the principle of microscopic reversibility)

$$Cl_2 + S \underset{s}{\overset{i}{\rightleftharpoons}} SCl + \dot{C}l. \qquad (i,s)$$

Collision theory shows that surface removal of $\dot{C}l$ in vessel B would have to have an efficiency $\varepsilon(\dot{C}l) > 10^{-4}$ to compete with reaction (t) at the calculated levels of $[\dot{C}l]$ and of $[\dot{R}]$. The lowest measured[19] limit of $\varepsilon(\dot{C}l)$ is $ca.$ $10^{-5}$ on freshly acid-washed walls (conventionally described as 'poisoned' for the removal of $\dot{C}l$). After heating to 100 °C, the efficiency rises to $ca.$ $3 \times 10^{-4}$, and is higher ($> 10^{-3}$) on salt-coated or flamed Pyrex surfaces. It therefore seems likely that the surface removal can compete successfully with gas-termination steps in the vessel B under the conditions used by J.W.G., although it is unlikely that it completely overwhelms step (t).

There is a good deal of evidence from previous studies of temperature distribution in vessels where thermal chlorinations are taking place that the reaction takes place close to the walls,[20] with chains initiated and terminated on the walls.

If we assume that $[\dot{C}l]_0 \approx (K_D[Cl_2]_0)^{0.5}$ through the reversible pair (i, s) then for low $[Cl_2]_0$ in fresh B

$$\left(\frac{d[VC]}{dt}\right)_0 \approx \left(\frac{d[DCE]}{dt}\right)_0 = k_1 [DCE]_0 [\dot{C}l]_0 \approx k_1 K_D^{0.5}[DCE]_0 [Cl_2]_0^{0.5}.$$

This describes the observed kinetics. It also suggests the overall activation energy

should be close to $E_1 + \Delta H/2$ where $\Delta H$ is the enthalpy change of the reaction

$$Cl_2 \text{ (g)} \rightleftharpoons 2\dot{C}l \text{ (g)}.$$
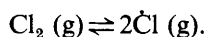
As $E_1 = 3 \text{ kcal mol}^{-1}$ and $\Delta H = 58 \text{ kcal mol}^{-1}$, the predicted overall activation energy is $3 + 29 = 32 \text{ kcal mol}^{-1}$. J.W.G.'s results[9] gave $33 \text{ kcal mol}^{-1}$ for the fresh vessel B.

Stationary-state treatment also gives

$$[\dot{R}]_0 = \frac{k_1[DCE]_0 \, [\dot{C}l]_0}{k_2 + k_3[Cl_2]_0} \approx \frac{k_1[DCE]_0 \, (K_D[Cl_2]_0)^{0.50}}{k_2}$$

because $k_2 \gg k_3[Cl_2]_0$ under the experimental conditions.

If this is correct, $[\dot{R}]_0/[Cl_2]_0^{0.50}$ should be proportional to $[DCE]_0^{0.38}$ because experimentally over this pressure range it was found that $k_2$ was proportional to $[DCE]_0^{0.62}$. The slopes of the left-hand lines in fig. 11 should then be proportional to $[DCE]_0^{0.38}$. They are closely so, as shown in table 7.

TABLE 7.—DEPENDENCE OF $[\dot{R}]_0$ ON $p_{DCE}$ (aged vessel B, 572 K)

| $p_{DCE,0}$/Torr | slope of lines (fig. 3) | slope/$(p_{DCE,0}$/Torr$)^{0.38}$ |
| --- | --- | --- |
| 135 | 22.5 | 3.49 |
| 65 | 16.8 | 3.44 |
| 35 | 13.2 | 3.42 |

Adding inert gases would increase $k_2$, but if $[\dot{C}l]_0$ is fixed $[\dot{R}]_0$ must fall proportionately from the above equation. Hence $(d[VC]/dt) = k_2[\dot{R}]_0$ remains constant, as found[9] experimentally for the fresh vessel B.
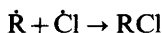
### AGED VESSEL B

In the aged vessel B, the experimental evidence shows that at the same temperature the rates are lower than in the fresh vessel and centre concentrations are correspondingly lower by factors of 4-8. This further favours a first-order surface termination against a second-order gas-phase termination.

In the aged vessel the addition of inert gases increases $(d[VC]/dt)_0$ (table 2) but not $(d[TCE]/dt)_0$. The increase in $(d[VC]/dt)_0 = k_2[\dot{R}]_0$ is entirely attributable to the increase in $k_2$, as $[\dot{R}]_0 = (d[TCE]/dt)_0/k_3[Cl_2]_0$ remains constant. This points to control of $[\dot{R}]$ by the initiating and terminating steps in the aged vessel B.

Calculations of the rates of the gas-phase termination reactions[16]

$$\dot{R} + \dot{R} \rightarrow R_2$$

and

$$\dot{R} + \dot{C}l \rightarrow RCl$$
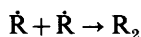
show that in the aged vessel B surface removal of $\dot{R}$ should be more effective provided $\varepsilon(\dot{R}) \geqslant 2 \times 10^{-5}$, which is very likely.

The surface removal of $\dot{R}$ by the reaction

$$SCl + \dot{R} \rightarrow RCl + S \tag{s$'$}$$

combined with the initiation step (i) and the equation

$$\theta = K[Cl_2]^{0.5}/(1 + K[Cl_2]^{0.5})$$

where $K$ is the Langmuir coefficient, for the fraction $\theta$ of sites occupied by Cl leads to the prediction

$$[\dot{R}]_0 = k_i[Cl_2]_0^{0.5}/k_{s'}K.$$

Thus $[\dot{R}]_0$ is proportional to $[Cl_2]_0^{0.5}$ and is independent of $[DCE]_0$ as required by the experimental results in fig. 11.

If $[\dot{R}]_0$ is controlled, then by eqn (IX) $[\dot{Cl}]_0$ has to follow

$$[\dot{Cl}]_0 = \frac{k_i[Cl_2]_0^{0.5}}{k_{s'}K} \times \frac{k_2+k_3[Cl_2]_0}{k_1[DCE]_0}.$$

Recalling that $k_2 \propto [DCE]^{0.62}$ and that $k_3[Cl_2]_0 < k_2$ when $[Cl_2]_0$ is low, the expression for $[\dot{Cl}]_0$ correctly describes the shape of the curves through the experimental points $\times$, $\triangle$, and $\bigcirc$ in fig. 10, and their slopes at fixed $[Cl_2]_0$ are closely proportional to $[DCE]^{-0.38}$.

Other assumptions about surface termination reactions, such as removal of R by empty sites S, do not lead to the correct relationships for $[\dot{R}]_0$ and $[\dot{Cl}]_0$.
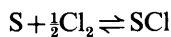
Accepting path (i) as the initiating step and path (s′) as the terminating step,

$$(d[VC]/dt)_0^{(p)} = k_2^{(p)}k_i[Cl_2]_0^{0.5}/k_{s'}K$$

and the overall activation energy is given by

$$E_{overall} = E_2^{(p)} + E_i - E_{s'} - \Delta H'$$

where $\Delta H'$, the enthalpy change of the reaction

$$S + \tfrac{1}{2}Cl_2 \rightleftharpoons SCl$$

is equal to $\tfrac{1}{2}D_{(Cl-Cl)} - D_{(S-Cl)}$. $E_i$ is not less than the enthalpy change of the reaction (i) which is $D_{(Cl-Cl)} - D_{(S-Cl)}$. $E_s$ is probably small.

Therefore

$$E_{overall} \approx E_2^{(p)} + D_{(Cl-Cl)} - D_{(S-Cl)} - \tfrac{1}{2}D_{(Cl-Cl)} + D_{(S-Cl)} \approx E_2^{(p)} + \tfrac{1}{2}D_{(Cl-Cl)}.$$

Now $D_{(Cl-Cl)} \approx 58$ kcal mol$^{-1}$ and $E_2^{(p)} \approx 17$ kcal mol$^{-1}$ at $p \approx 100$ Torr (see eqn (VI), with $E_3 \approx 0.9$ kcal mol$^{-1}$]. Therefore

$$E_{overall} \approx 46 \text{ kcal mol}^{-1}.$$

This predicted value compares very favourably with the experimental value for the aged vessel B of 47 kcal mol$^{-1}$ (A.J.O.).

### CONCLUSIONS FOR VESSEL B

We therefore have self-consistent and reasonably quantitative interpretations of the experimental results for the chlorine-catalysed pyrolysis in the fresh-surface vessel B and in the aged vessel B, on the basis that the chain-termination reaction in the fresh vessel is essentially removal of $\dot{Cl}$ on the surface, while in aged B it is removal of $\dot{R}$ on the surface. This change-over is helped, undoubtedly, by the relatively higher values of $[\dot{R}]/[\dot{Cl}]$ at the lower temperatures used for many of the experiments in the aged vessel.

Unfortunately, we lack information about the ageing process that might point to chemical reasons for the aged quartz surface to favour reaction (s′) with $\dot{R}$ rather than (s) with $\dot{Cl}$, and the fresh quartz surface to favour reaction with $\dot{Cl}$ rather than with $\dot{R}$.

## INITIATION AND TERMINATION REACTIONS IN OTHER VESSELS

It is not possible to provide a satisfactory explanation of the limiting rate shown in fig. 2 for the quartz vessel A, $s/v = 1.4$ cm$^{-1}$, as $p_{Cl_2}$ is increased. Inclusion of the gas-phase termination step (t) as well as the surface termination, which would be reduced at the lower $s/v$, makes the rate *less* dependent on $p_{Cl_2}$ than one-half order, and this effect increases as $p_{Cl_2}$ and the radical concentrations increase. However, detailed analysis shows that including (t) makes the order in $p_{DCE}$ lower than the observed unity.

In the uncoated Pyrex vessel C, with $s/v = 1.4$ cm$^{-1}$, [$\dot{C}l$] and [$\dot{R}$] behaved like the results found for fresh vessel B, with some evidence for gas-phase as well as surface termination. After coating with Teflon the concentrations fell to even lower levels than in aged vessel B. This suggests that coating with Teflon, and to a less extent ageing in B, might reduce the rate of initiation through blocking chemisorption sites for $Cl_2$, while retaining the ability of the walls to adsorb or remove $\dot{R}$.

[1] D. H. R. Barton, *J. Chem. Soc.*, 1949, 148. D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 1949, 155.

[2] K. E. Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25.

[3] G. A. Kapralova and N. N. Semenov, *Russ. J. Phys. Chem. (Engl. Transl.)*, 1963, **37**, 35, 156, 258.

[4] K. A. Holbrook, R. W. Walker and W. R. Watson, *J. Chem. Soc. B*, 1968, 1089.

[5] K. A. Holbrook, R. W. Walker and W. R. Watson, *J. Chem. Soc. B*, 1971, 577.

[6] T. Takahashi, T. Abe, Y. Migkoshi and S. Asano, *Kogyo Kagaka Zasshi*, 1968, **71**, 504.

[7] G. Huybrechts, J. Katihabwa, G. Martens, M. Nejszaten and J. Olbregts, *Bull. Soc. Chim. Belg.*, 1972, **81**, 65.

[8] F. S. Dainton, D. A. Lomax and M. Weston, *Trans. Faraday Soc.*, 1962, **58**, 308.

[9] J. W. Gardner, *Thesis* (University of Manchester, 1975). (This includes a full summary of earlier work on the catalysed and uncatalysed decompositions).

[10] P. G. Ashmore, J. W. Gardner and P. Sutton, *Chem. Wetenschap, Belgische Chemische Industrie, June 1973*, p. 11 (abstract of paper, Third International Symposium on Gas Kinetics, Brussels, 1973).

[11] P. G. Ashmore, A. J. Owen and P. J. Robinson, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 677.

[12] P. J. Robinson, *Trans. Faraday Soc.*, 1965, **61**, 1655.

[13] P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley Interscience, New York, 1972), pp. 262-263.

[14] C. Cillien, P. Goldfinger, G. Huybrechts and G. Martens, *Trans. Faraday Soc.*, 1967, **63**, 1631.

[15] S. W. Benson and J. H. Buss, *J. Chem Phys.*, 1957, **27**, 301.

[16] G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens and G. Verbeke, *Chem. Rev.*, 1963, **63**, 355.

[17] M. A. A. Clyne and D. H. Stedman, *Trans. Faraday Soc.*, 1968, **64**, 2698.

[18] R. A. Carabetta and H. N. Palmer, *J. Chem. Phys.*, 1967, **46**, 1333.

[19] P. G. Ashmore, A. J. Parker and D. E. Stearne, *Trans. Faraday Soc.*, 1971, **67**, 3081.

[20] G. A. Kapralova and N. N. Semenov, *Russ. J. Phys. Chem. (Engl. Transl.)*, 1963, **37**, 35, 156, 258.