

598. *The Pyrolysis of Chloroalkenes. Part IV.* The Radical-chain Decomposition of the 1 : 2-Dichloroethylenes.*

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In the temperature range 370—480° *cis*- and *trans*-1 : 2-dichloroethylene decompose chiefly by a radical-chain mechanism to monochloroacetylene and hydrogen chloride. No kinetic distinction can be made between the pyrolyses of the two isomers because the effective reactant is an equilibrated mixture. The rate of dehydrochlorination is considerably reduced by the addition of small amounts of propene, *n*-hexane, or *n*-pentane, but it is not appreciably influenced by the reaction products. Reproducible induction periods are observed. These are dependent on the temperature, concentration, and available surface area. The reaction order is uniformly 1.5 in a packed reaction vessel but between 1 and 1.5 in an empty vessel. A mechanism is proposed which accounts for these features. The quantitative importance of the observations on induction periods is stressed.

In two recent papers ^{1,2} we discussed the kinetics of the decompositions of some hexatomic molecules. In both radical and molecular mechanisms all unimolecular steps involving molecules or radicals of low atomicity are of order greater than one at reasonable working pressures. In the chain decomposition of trichloroethylene,¹ the initiating and the radical decomposition steps are of this type. The overall chain reaction in the case of trichloroethylene is, however, a unique type of dehydrochlorination because of the strongly inhibiting effect of the secondary product hexachlorobenzene. Since a much wider pressure range is available for the study of the pyrolysis of the 1 : 2-dichloroethylenes than for trichloroethylene, it was desirable to examine any chain mode of decomposition of the dichloroethylenes.

EXPERIMENTAL

The purification of the dichloroethylenes and the apparatus employed are described elsewhere.^{2,3}

• Part III, *J.*, 1956, 2640.

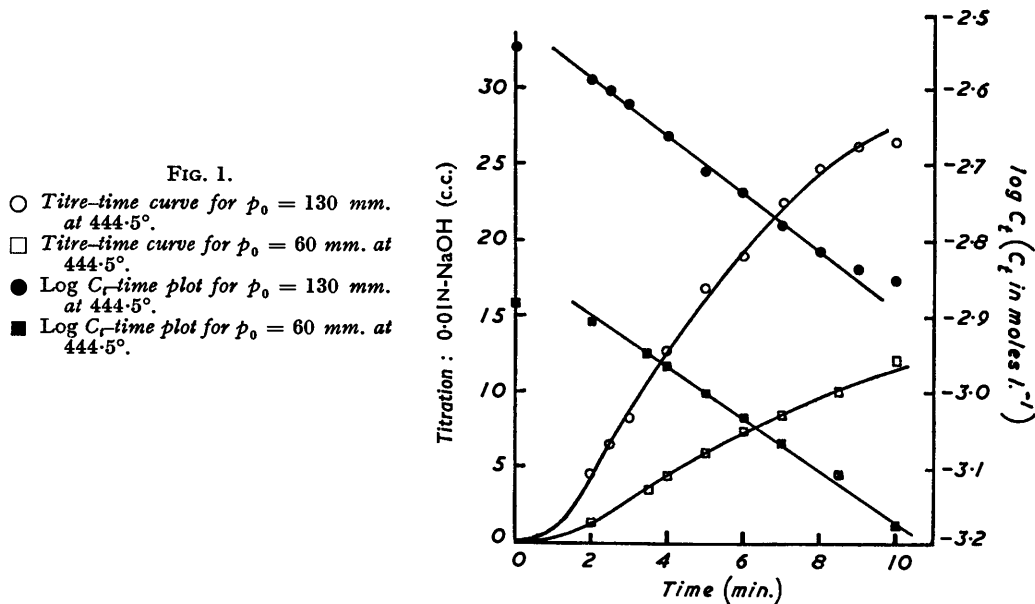
¹ Goodall and Howlett, *J.*, 1954, 2600.

² *Idem*, *J.*, 1956, 2640.

³ Goodall, Thesis, London, 1955.

Argument and Results.—As in the work detailed in other Parts of this series, the kinetics of the dehydrochlorinations were invariably studied by determining the amount of hydrogen chloride produced. It was shown in Part III² that roughly 100% yields of hydrogen chloride were produced after 4–5 half-lives of the molecular decomposition of the 1:2-dichloroethylenes. This time interval corresponds to about 40 half-lives of the chain decomposition. In the present work it has been shown that at 456° (the upper end of the observed temperature range) the mean yield of hydrogen chloride is 102% after 6 half-lives of the chain reaction. Change of mechanism does not therefore affect this result and the immediate products of the chain decomposition are hydrogen chloride and monochloroacetylene.

The pyrolysis was studied over the range 372–469°, in a seasoned reaction vessel of volume 186 c.c., and surface/volume ratio 1.7 cm.⁻¹. Curves co-ordinating yield of hydrogen chloride with time were complex because induction periods were observed under all conditions, and the order of reaction was non-integral. The work was therefore performed by using only certain



specific initial concentrations. Typical results are shown in Fig. 1. Each experimental point denotes a separate run, owing to the method of analysis.

It was necessary first to determine whether or not the induction periods are an inherent feature of the reaction. This examination, which was carried out in a packed reaction vessel, followed the method of Howlett,⁴ and of Barton and Howlett.⁵ A standard pressure (68.5 mm.) of dichloroethylene was pyrolysed for 5 min. at 456°. Table 3 shows that the induction period is about 4.5 min. under these conditions. The reaction mixture was condensed into a liquid-air trap and then 29 mm. (equivalent to 25 mm. of reactant) were returned to the reaction vessel. The subsequent decomposition of this material showed an induction period and rate appropriate to a first pyrolysis of 25 mm. of reactant (see Fig. 2). Similar experiments were repeated at 469.5° and identical conclusions obtained. This result, coupled with the reproducibility of the induction periods obtained with a number of samples of reactant over a period of 18 months of observations, shows that the induction periods are an intrinsic part of the reaction and are not caused by impurities.

Since the induction periods are long compared with the half-lives of the isomerisation reactions of *cis*- and *trans*-1:2-dichloroethylene,⁶ and since also the rates of the subsequent chain decompositions are much slower than the rates of isomerisation, the effective reactant is an equilibrium mixture of *cis*- and *trans*-isomers in all experiments reported here. This agrees with the fact that the kinetics of the radical decompositions starting from either isomer are

⁴ Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25.

⁵ Barton and Howlett, *J.*, 1951, 2033.

⁶ Jones and Taylor, *J. Amer. Chem. Soc.*, 1940, **62**, 3480; see also Part III.

practically indistinguishable (see Table 1). In the major part of our work however, the *cis*-isomer has been used, because purified *trans*-1 : 2-dichloroethylene, even when kept in the dark *in vacuo*, slowly deposits polymeric material, while the *cis*-compound does not.

In the empty reaction vessel the order of the reaction was found to vary systematically with temperature. This is shown in Table 2. Accordingly all the results obtained in this vessel are quoted as apparent first-order rate constants. Fig. 1 shows some typical first-order plots and Table 1 lists the induction periods (*I*) and rate constants found in the empty vessel for the decomposition of both *cis*- and *trans*-dichloroethylene.

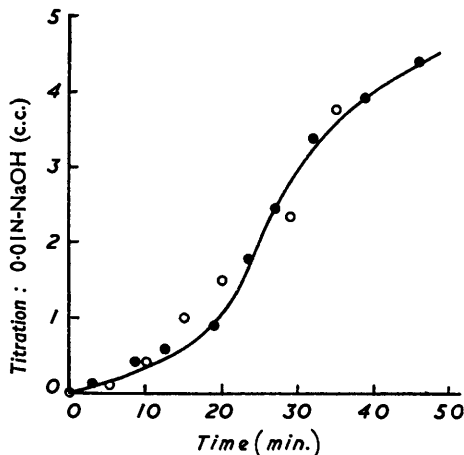


FIG. 2.
● Titre-time curve for first pyrolysis of 25 mm. of 1 : 2-dichloroethylene at 456°.
○ Results of pyrolysis of 25 mm. of 1 : 2-dichloroethylene returned from liquid-air trap.

The uninhibited reaction has also been studied extensively in a packed reaction vessel of volume 124 c.c. and surface/volume ratio 22.4 cm.⁻¹. The kinetics of the pyrolysis are substantially different in the packed vessel from those in the empty vessel. The order of reaction in the packed vessel is closely 1.5, both throughout each individual decomposition curve up to high percentages of reaction (see Fig. 3) and also over the initial pressure range

TABLE 1.

Temp.	p_0 (mm.)	<i>I</i> (min.)	10^3k (sec. ⁻¹)	Temp.	p_0 (mm.)	<i>I</i> (min.)	10^3k (sec. ⁻¹)	Temp.	p_0 (mm.)	<i>I</i> (min.)	10^3k (sec. ⁻¹)
<i>cis</i> -1 : 2-Dichloroethylene.											
372°	130	29	1.60	428°	130	2.0	54.0	456°	29.5	4.2	151
372	240	17.5	2.41	428	240	0.8	73.7	456	49.5	2.0	164
387	130	14	4.73	444.5	29.5	5.0	124	456	130	0.5	185
387	240	9	6.90	444.5	60	1.5	129	469.5	29.5	1.4	428
408.5	130	4.2	17.9	444.5	130	0.95	143	469.5	60	0.44	439
408.5	203	2.8	21.3	444.5	240	0.4	159	469.5	130	~0.2	481
428	49.5	5.7	42.4								
<i>trans</i> -1 : 2-Dichloroethylene.											
428°	130	3.8	41.5	456°	130	0.8	160°	459°	58.5	3.0	170
456	49.5	3.0	137								

TABLE 2.

Temp.	372°	387°	408.5°	428°	444.5°	456°	469.5°
Reaction order	1.6	1.6	1.4	1.2	1.1	1.1	1.1

TABLE 3.

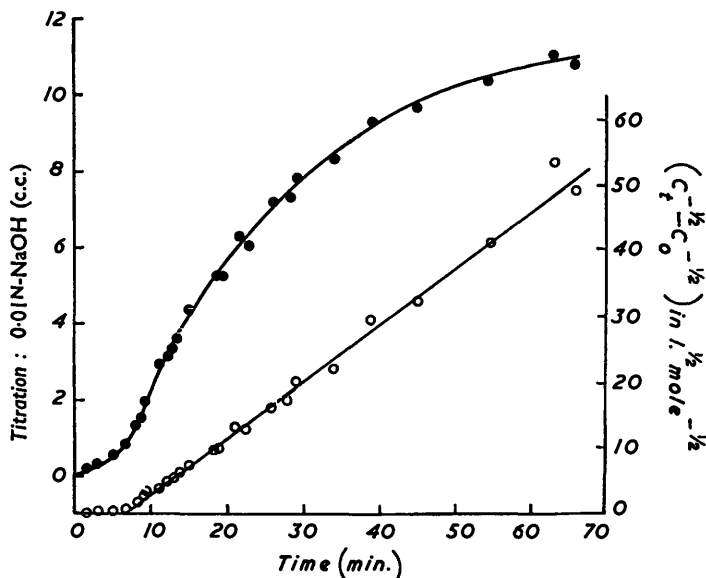
Temp.	p_0 (mm.)	<i>I</i> (min.)	10^3k *	Temp.	p_0 (mm.)	<i>I</i> (min.)	10^3k *	Temp.	p_0 (mm.)	<i>I</i> (min.)	10^3k *
398°	68.5	36	0.086	456°	29.5	13	3.18	469.5°	21.5	8.5	10.4
398	119.7	24	0.093	456	37	8.0	3.37	469.5	29.5	7.3	12.9
398	186	12.5	0.091	456	46.5	6.5	2.85	469.5	46.5	3.1	14.1
428	46.5	27	0.450	456	68.5	4.3	3.25	469.5	68.5	1.5	13.1
428	68.5	13	0.464	456	130	1.33	3.10	481	29.5	3.4	18.7
428	119.7	4.4	0.619	456	186	0.87	3.13	481	46.5	1.7	16.0
456	25	16.5	3.27								

* Mole⁻¹ l.½ sec.⁻¹.

25—186 mm. The induction periods and 1.5-order rate constants determined in the packed reaction vessel are given in Table 3.

A general point which is not brought out by superficial comparison of Tables 1 and 3 is that the rate of reaction is slower in the packed reaction vessel than in the empty vessel at the same pressure. The induction periods are longer in the packed vessel.

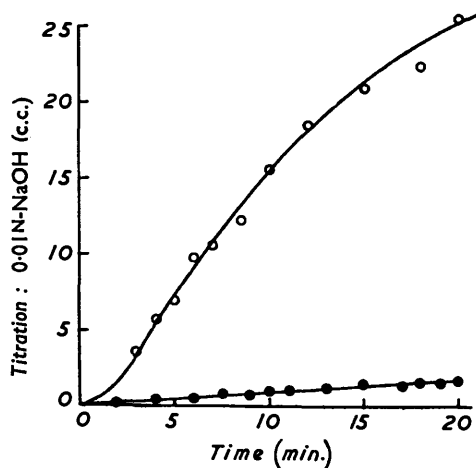
FIG. 3.



● Titre-time curve for $p_0 = 46.5$ mm. at 456° up to 85% decomposition.
○ 1.5-order plot for the same results.

FIG. 4.

○ Uninhibited decomposition from $p_0 = 130$ mm. at 428° .
● Inhibited decomposition from $p_0 = 123$ mm. at 428° .



In both vessels the pyrolysis is strongly inhibited by small quantities of propene, *n*-hexane, or *n*-pentane. Maximum inhibition is reached in each case with only about 1 mm. of additive. Most of this evidence has been given in Part III, but Fig. 4 shows a typical comparison of the course of reaction in the presence and absence of inhibitor. The extensive nature of the retardation strongly supports the idea that the normal decomposition is mainly of the radical-chain type.

It was next shown that the products of the radical-chain decomposition did not act as inhibitors for the reaction. For this purpose 46.5 mm. of reactant were pyrolysed for 60 min.

in the packed reaction vessel at 456°, and then 40 mm. of reactant were added and the pyrolysis was continued for a further 21 min. The average amount of hydrogen chloride formed after 81 min. was 0.000190 mole. The calculated yield is 0.000170 mole. There was clearly no inhibition of the second part of the reaction. The slight excess of experimental over calculated yield is probably due to physical acceleration of the unimolecular steps of the chain reaction. Abortive attempts were made to confirm this idea by using "inert" gases, such as carbon tetrachloride and tetrachloroethylene, to accelerate the chain reaction physically, *i.e.*, by using these additives as energy-transfer agents for the unimolecular steps of the mechanism. Unequivocal results were, however, not obtained.

Experiments were performed in the packed reaction vessel to examine the effect of aromatic compounds on the pyrolysis of 1 : 2-dichloroethylene, for comparison with the decomposition of trichloroethylene. Purified samples of benzene and chlorobenzene were outgassed and stored over quinol before admission to the reaction vessel. Table 4 shows the results obtained when

TABLE 4.

Additive	Titre : 0.01N-NaOH	Additive	Titre : 0.01N-NaOH
—	5.25 c.c.	1 mm. chlorobenzene	5.00 c.c.
1 mm. benzene	3.93	3 mm. chlorobenzene	3.42
3 mm. benzene	3.00	7 mm. chlorobenzene	2.25
7 mm. benzene	1.80	1 mm. pentane	1.03

46.5 mm. of 1 : 2-dichloroethylene were decomposed for a standard period of 18 min. at 456° in the presence of these additives. The titration figures are the volumes of 0.01N-sodium hydroxide required to neutralise the hydrogen chloride produced. In a subsidiary experiment it was demonstrated that opening the reaction vessel to the trap containing quinol had no effect on the rate of decomposition of dichloroethylene.

DISCUSSION

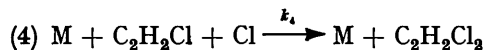
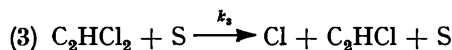
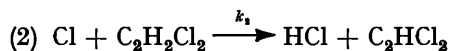
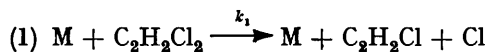
The inhibition of the pyrolysis by propene, *n*-hexane, and *n*-pentane, and the induction periods, show that the uninhibited decomposition is overwhelmingly a radical-chain reaction. In Part II¹ it was shown that the chain decomposition of trichloroethylene is, kinetically, an unusual dehydrochlorination because of the inhibiting influence of the hexachlorobenzene produced. No comparable effect has been found with 1 : 2-dichloroethylene. For example, the moderate pressure increases observed in the static experiments prove that little trimerisation of monochloroacetylene to 1 : 3 : 5-trichlorobenzene occurs. Further confirmation of the stability of monochloroacetylene was obtained from the dynamic runs described in Part III and also from a static experiment performed at 428°. In this run, 60 mm. of reactant were pyrolysed for 40 min. and the products analysed for monochloroacetylene and hydrogen chloride. The ratio C₂HCl/HCl found was 0.4. Thus, although monochloroacetylene is removed slowly from the system, it has much greater stability than dichloroacetylene since the latter is undetectable as a reaction product¹ even in dynamic experiments. It also seems probable that the mode of removal of monochloroacetylene is different from that of dichloroacetylene because no inhibition of the decomposition of dichloroethylene by its own products could be detected. Some inhibition would undoubtedly have been expected if trichlorobenzene had been produced (*cf.* Table 4, and studies on the pyrolysis of trichloroethylene in the presence of its own decomposition products¹).

In certain respects the kinetics of the decomposition of 1 : 2-dichloroethylene resemble those reported for the pyrolysis of 1 : 1 : 1-trichloroethane.⁷ Similar principles may be used in elucidating both mechanisms, but in the case of dichloroethylene there is the complication that the decomposition steps of molecules or radicals are probably not first-order unimolecular processes.

There is no unique way of accounting for a reaction which is of 1.5 order in a packed vessel and tends to first order in an empty vessel. As in Part II a decision between the various possibilities can only be made by consideration of the induction periods. If M

⁷ Barton and Onyon, *J. Amer. Chem. Soc.*, 1950, **72**, 988.

stands for any molecular species capable of transferring energy, and S for the surface area of the vessel, the mechanism suggested is :



The steady-state simultaneous equations may be set up and, since $[\text{C}_2\text{H}_2\text{Cl}] = [\text{Cl}] + [\text{C}_2\text{HCl}_2]$, may be solved to give :

$$[\text{Cl}]^2 = \frac{k_1 k_3 S [\text{C}_2\text{H}_2\text{Cl}_2]}{k_4 (k_3 S + k_2 [\text{C}_2\text{H}_2\text{Cl}_2])}$$

Two limiting conditions arise :

(a) If S is small, $k_2 [\text{C}_2\text{H}_2\text{Cl}_2] > k_3 S$

Hence, $\text{Rate} = k_2 [\text{Cl}] [\text{C}_2\text{H}_2\text{Cl}_2] = [\text{C}_2\text{H}_2\text{Cl}_2] \sqrt{\{(k_1 k_2 k_3 S)/k_4\}}$

i.e., the reaction is of the first order.

(b) If S is large, $k_2 [\text{C}_2\text{H}_2\text{Cl}_2] < k_3 S$

whence $\text{Rate} = [\text{C}_2\text{H}_2\text{Cl}_2]^{3/2} k_2 \sqrt{(k_1/k_4)}$

i.e., the reaction is of 1.5 order.

This mechanism is therefore consistent with the experimental observations on reaction order. The overall reaction order alone, however, does not require that steps 1 and 4 should be of second and third order respectively. The induction periods which would accompany a pyrolytic reaction following the suggested scheme may be computed by the approximate method of Howlett.⁴ In the steady state $[\text{C}_2\text{H}_2\text{Cl}] = k_1 [\text{C}_2\text{H}_2\text{Cl}_2] / k_4 [\text{Cl}]$, and the rate of build up to this concentration is approximately $k_1 [\text{C}_2\text{H}_2\text{Cl}_2] [\text{M}]$. At this early stage of the reaction M can only be the reactant. Hence the induction periods are calculated to be of length $(k_4 [\text{Cl}] [\text{C}_2\text{H}_2\text{Cl}_2])^{-1}$. Thus if S is small this is equal to $[\text{C}_2\text{H}_2\text{Cl}_2]^{-1} \sqrt{\{k_2 / (k_1 k_3 k_4 S)\}}$, *i.e.*, the induction periods should vary inversely as the initial concentration of reactant. Similarly if S is large the induction periods are calculated to be $[\text{C}_2\text{H}_2\text{Cl}_2]^{-3/2} \sqrt{\{1 / (k_1 k_4)\}}$, *i.e.*, they should vary inversely as the $\frac{3}{2}$ power of the initial pressure. Reductions of one each in the orders of steps 1 and 4 would make the induction periods invariant with pressure in the empty vessel (S small), and varying as $[\text{C}_2\text{H}_2\text{Cl}_2]^{-3}$ in the packed vessel (S large). The variation of the induction periods with pressure may therefore be used to determine the orders of steps 1 and 4. In Fig. 5 the logarithms of the experimental induction periods are plotted against the logarithms of the initial pressures. The full lines are drawn at the theoretical slopes of -1 and -1.5 for the results appropriate to the empty and the packed vessel respectively. It is clear that the actual variation is close to the theoretical in the packed reaction vessel, so that this experimental condition corresponds to the limiting case of S being large. In the empty vessel the experimental variation of induction periods with pressure is slightly greater than that corresponding to the limiting condition that S be small. In the empty vessel, therefore, the induction periods vary inversely with a power of the initial pressure between 1 and 1.5. The limiting condition (S small) is thus not fully reached in the empty vessel. The conclusion is in agreement with that from the variation of reaction order with pressure.

We have been unable to devise any other simple mechanism which is in agreement with

the experimental induction periods and orders of reaction in both vessels. The evidence of the induction periods therefore provides strong support for the mechanism.

Further consistency tests may be made. In the empty vessel (when the limiting condition, $S = \text{small}$, is assumed) the product of rate of reaction multiplied by induction period should be, theoretically, k_2/k_4 , *i.e.*, a constant at constant temperature. The same result may be derived for the packed vessel. Table 5 shows that this test may be applied with fair success to the experimental results. Therefore, although (a) individual rates and induction periods may be different in the two vessels and (b) they are both pressure-variant, their product is a constant within experimental error.

Further, by comparing the values of the quotients, rate/induction period for the two limiting conditions considered, the ratio of $k_2[\text{C}_2\text{H}_2\text{Cl}_2]/k_3S_1$ may be obtained, where S_1 refers to the vessel of low surface area. Clearly the mechanistic interpretation given above requires this ratio to rise with temperature and to pass through unity in the temperature range in which measurements are reported. Unfortunately the empty reaction vessel conditions only approach the limiting case where S is small, so that only approximate

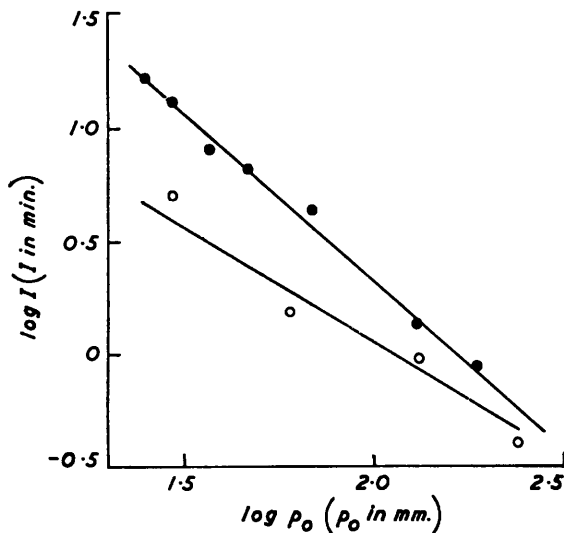


FIG. 5.

● Packed reaction vessel at 456°.
○ Empty reaction vessel at 444.5°.

estimates can be made. The figures calculated for $k_2[\text{C}_2\text{H}_2\text{Cl}_2]/k_3S_1$ are 0.1 and 0.35 at 456° and 469.5° respectively. These figures are of the correct order of magnitude for consistency between the experiments and the suggested mechanism.

It should be noted that in all the discussion, the measured rate of dehydrochlorination has been assumed to refer solely to the chain reaction. Since only about 5% of the

TABLE 5.

Packed vessel at 456°		Packed vessel at 466°		Empty vessel at 444.5°	
p_0 (mm.)	Rate $\times I \times 10^4$ *	p_0 (mm.)	Rate $\times I \times 10^4$ *	p_0 (mm.)	Rate $\times I \times 10^4$ *
25	4.17	68.5	4.90	29.5	2.94
29.5	4.12	130	3.79	60	1.54
37	3.75	186	4.27	130	2.16
46.5	3.62			240	2.05

* Mole l.⁻¹.

measured rate is due to the molecular decomposition (see Fig. 4), this assumption is justified. The kinetics of the chain decomposition in the empty vessel are complex, because the experimental conditions in this vessel do not approximate to one of the limiting conditions over the whole of the temperature range. Thus no general rate equation is satisfactory for the reaction in the empty vessel. In the packed reaction vessel, however, the decomposition shows 1.5-order kinetics throughout. The rate constants obtained

in the packed vessel (given in Table 3), together with those determined in the empty vessel at 372° and 387°, all refer to the limiting condition $k_2[\text{C}_2\text{H}_2\text{Cl}_2] < k_3\text{S}$. They have been summarised by the method of least squares to give $k = 10^{15.8} e^{-58,000/RT} \text{ l.}^\dagger \text{ mole}^{-1} \text{ sec.}^{-1}$.

It is of interest to compare the rates of dehydrochlorination of 1 : 1 : 2-trichloroethane and of 1 : 2-dichloroethylene because 1 : 2-dichloroethylene is the immediate product of the first reaction. Williams⁸ reported the somewhat unusual fact that the decomposition of 1 : 1 : 2-trichloroethane is very irreproducible. It is clear from the present work that this is due to the subsequent pyrolysis of 1 : 2-dichloroethylene, since the latter reaction shows pressure-dependent induction periods followed by a rapid rate of decomposition under the experimental conditions used by Williams. In fact, the half-lives reported for each pyrolysis separately are almost identical at 440° and 60 mm. pressure (the only figures quoted by Williams). According to the initial pressure of 1 : 1 : 2-trichloroethane employed, a variety of anomalous results would therefore be observed. Thus Williams's observations of irreproducibility are genuine and explicable.

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⁸ Williams, *J.*, 1953, 113.
