

520. *The Pyrolysis of Chloroalkenes. Part III.* The Molecular Mode of Decomposition of the 1 : 2-Dichloroethylenes.*

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Gas-phase pyrolyses of both the *cis*- and the *trans*-isomer of 1 : 2-dichloroethylene have been studied. These compounds decompose to give hydrogen chloride and monochloroacetylene, the kinetics of both dehydrochlorinations being identical. Free-radical chains play an important part in the overall reaction, but in the presence of the inhibitors, propene, *n*-hexane, and *n*-pentane, there is a residual reaction which has been identified as a unimolecular process. The reaction has been studied over the temperature range 360—475° and over the initial pressure range 31—478 mm. Variations of the parameters of the Arrhenius equation with initial concentration have been observed, and the effect of "inert" gases has been investigated. The findings are discussed in connection with current theories of unimolecular reactions.

IN Part II,¹ the molecular and chain modes of decomposition of trichloroethylene were described. The molecular part of this dehydrochlorination was of second order at a pressure of 40 mm., but owing to experimental difficulties it was impossible to investigate the process over a wide pressure range. Sufficient information could not, therefore, be obtained for a quantitative application of any of the mathematical treatments of unimolecular reactions. The decomposition of a hexatomic molecule such as trichloroethylene is of considerable interest in view of the prediction² that only molecules containing six or more atoms will show fully developed first-order kinetics for their unimolecular decompositions at reasonable working pressures. We have therefore studied the thermal dehydrochlorination of the 1 : 2-dichloroethylenes in the hope that the experimental pressure range could be widened and a quantitative treatment of the results attempted.

EXPERIMENTAL

Apparatus and Materials.—The kinetic measurements were performed in a static apparatus, and larger-scale product analyses were made by using a flow apparatus (cf. Part I³). Pure specimens of the 1 : 2-dichloroethylenes were prepared from the commercial mixture. This was shaken successively with concentrated sulphuric acid (four times), water, aqueous sodium hydrogen carbonate, and water. After drying (MgSO₄), the isomers were separated by repeated fractional distillation until separate components having boiling ranges of less than 0.1° were obtained. We believe our compounds to be of good purity and we have therefore characterised them rather fully. The *trans*-1 : 2-dichloroethylene had b. p. 47.36° (corr.), n_D^{20} 1.4462, d_4^{20} 1.2551 g. cm.⁻³, $10^6\chi$ -0.533 c.g.s. unit, $\log_{10} p_{(\text{mm.})}$ (-6° to 50°) = 16.289 - 1932/*T* - 2.946 log₁₀*T*; *cis*-1 : 2-dichloroethylene had b. p. 60.25° (corr.), n_D^{20} 1.4495, d_4^{20} 1.2830 g. cm.⁻³, $10^6\chi$ -0.542 c.g.s. unit, $\log_{10} p_{(\text{mm.})}$ (-6° to 60°) = 22.807 - 2314/*T* - 5.147 log₁₀ *T*.

All experiments were carried out in seasoned reaction vessels whose walls were covered with a carbonaceous film. The kinetics of the reactions were followed by analysis for hydrogen chloride in the reaction products, since, with this type of decomposition, pressure measurements have been shown to be unsatisfactory.^{1,3} The results refer therefore to dehydrochlorination processes only.

Argument and Results.—Before carrying out a detailed examination of the kinetics of the thermal decompositions of the 1 : 2-dichloroethylenes it was important to determine, first, whether the isomers reacted at the same or different rates, and second, whether or not the reactions had reached completion when one molecular proportion of hydrogen chloride had been eliminated. There are good reasons for believing that the isomers undergo molecular elimination of hydrogen chloride at equal speeds. The transition state for unimolecular

* Part II, *J.*, 1954, 2599.

¹ Goodall and Howlett, *J.*, 1954, 2599.

² Slater, *Phil. Trans.*, 1953, 246, A, 57.

³ Goodall and Howlett, *J.*, 1954, 2596; see also Goodall, Thesis, London, 1955.

decomposition from either isomer must be akin to the *trans*-compound. Now the rates of interconversion⁴ of the 1:2-dichloroethylenes, without decomposition, in the region of 290—330°, suggest that the rate of equilibration, starting from the *trans*-isomer, is rapid in the temperature range in which the pyrolytic work has been performed. Since the reverse reaction (*cis* → *trans*) is of similar velocity,⁵ our reactant should be virtually an equilibrium mixture of the geometrical isomers, regardless of which one is admitted to the reaction vessel. Therefore the measured kinetics of the pyrolysis should be independent of which compound is used.

A direct confirmation of this disparity between the rates of isomerisation and dehydrochlorination was made at 428° by static experiments similar to those used by Jones and Taylor.⁴ About 200 mm. of *trans*-1:2-dichloroethylene were admitted to the reaction vessel, and then condensed after a short, known length of time into a trap surrounded by liquid air. The refractive index of the product was found, and the extent of isomerisation calculated by assuming that the relation between refractive index and composition of the product mixture was linear. These results were not very precise but the mean first-order rate constant for isomerisation found from some 20 runs was 2×10^{-2} sec.⁻¹. Extrapolation of Jones and Taylor's Arrhenius plot indicates an even greater rate constant at 428°. Our result for this rate constant will be seen later to be more than 100 times the constants for molecular dehydrochlorination at this temperature. The latter therefore always refer to pyrolysis of the equilibrium mixture of isomers. It was found later that rate constants for molecular decomposition from either isomer could be fitted to the same Arrhenius plot, so that, in fact, even for the slowest observed mode of decomposition, the velocity constants for pyrolysis of *cis*- and *trans*-1:2-dichloroethylene are indistinguishable.

It has been reported⁶ that one of the products, monochloroacetylene, unlike dichloroacetylene,¹ is fairly stable, and we have confirmed this in various ways. In long-term kinetic experiments, of duration about 40 half-lives of the uninhibited decomposition, or about 4 half-lives for the maximally inhibited reaction, approximately 1 mol. of hydrogen chloride was produced per mol. of reactant except at the highest temperatures. This is illustrated in Table 1, and was confirmed by flow experiments (see Table 2) in which there was reasonable agreement between the yields of hydrogen chloride and monochloroacetylene* at moderate flow speeds.

TABLE 1.

Temperature	428°	444.5°	460°
Pressure range investigated (mm.)	23—123	39	17—42
Mean yield (%) of HCl	93	116	125

TABLE 2.

Temperature	430°	430°	430°	452°	452°	493°	493°
Estimated hot contact time (sec.) ...	30	60	120	20	60	60	120
C ₂ HCl/HCl (found)	0.81	0.59	0.57	1.03	0.68	1.02	0.32

In the latter experiments the preponderance of hydrogen chloride at low temperatures and slow rates of flow can be attributed to partial polymerisation of monochloroacetylene. (The low increases in pressure in the static experiments are consistent with a certain degree of polymerisation of monochloroacetylene.) Cracking of monochloroacetylene must also occur at high temperatures. These experiments prove that the initial products are equimolecular proportions of hydrogen chloride and monochloroacetylene.

The evidence suggests that in kinetic studies of the early stages of pyrolysis there are not likely to be complications due to further reactions of the initial products or to an approach to a measurable position of equilibrium. The rate constants quoted in Tables 3, 7, and 8 are either obtained from initial rates or measured over the first 20% of reaction.

The kinetic measurements showed that the reaction was complex, since curves co-ordinating the yield of hydrogen chloride with time were sigmoid, the length of the induction periods being dependent on both temperature and concentration of reactant. The effect of propene on the course of the decomposition was therefore studied. The reaction was strongly inhibited by small amounts, and the rate constant was reduced to a limiting value which was practically insensitive to variations in the pressure of propene over the range 5—20 mm. The maximally

* See ref. 1 for method of analysis for monochloroacetylene.

⁴ Jones and Taylor, *J. Amer. Chem. Soc.*, 1940, **62**, 3480.

⁵ Cf. Pitzer and Hollenberg, *ibid.*, 1954, **76**, 1493.

⁶ Bashford, Emeléus, and Briscoe, *J.*, 1938, 1358.

inhibited reaction showed a marked variation of order with initial pressure of dichloroethylene. The order was approaching 2 at 30 mm. and was almost unity above 200 mm. although k_{∞} had not been attained at 500 mm.

More extensive inhibition studies were made by using *n*-hexane as inhibitor. In this case the rate of dehydrochlorination was reduced to a limiting value slightly higher than that found with propene as the inhibitor. Also the rate was found to be sensitive to quite small changes in the inhibitor concentration. This point receives attention below. The mechanism of inhibition of dehydrochlorination reactions by paraffins, which has been noted before,¹ has not been investigated. It is possible that the competing reaction is one of attack by a chlorine atom on the inhibitor molecule. Such processes are known to be fast.⁷

The least possible amount of *n*-hexane necessary for complete suppression of radical activity being used, the initial rates of dehydrochlorination of 1 : 2-dichloroethylene were found over wide ranges of temperature and pressure. Since no simple order could be used to express the results, arbitrary first-order velocity constants were calculated from the initial rates. Kinetic experiments were also carried out in a packed reaction vessel. No appreciable difference in the speed of reaction was observed on increasing the surface/volume ratio from 1.7 to 22 cm.⁻¹, and the actual surface available from 300 to 2700 cm.². Therefore the pyrolysis of 1 : 2-dichloroethylene is a homogeneous reaction. The temperatures, initial pressures of reactant, and mean velocity constants for all experiments on the maximally inhibited reaction are given in Table 3.

TABLE 3. Mean values of 10^5k (sec.⁻¹).

Temp.	With propene as the inhibitor.							
	p_0 (mm.)							
444.5°	39.5	69	123	152	188	239	332	478
461	2.74	3.10	5.10	6.17	6.68	7.51	8.26	9.79
		5.07	8.75			12.5		

Temp.	With hexane as the inhibitor.					
	p_0 (mm.)					
395°	31	31 *	69	123	239	321
407			1.35	0.722	1.20	1.41
410				1.58	2.28	2.82
428	2.74	2.28	3.01	4.26	6.63	8.34
444.5°	5.36	5.36	7.39	7.24	13.4	
461			12.9	15.3	24.2	
462	9.54	9.54				
475	19.8	20.1				

* Denotes packed reaction vessel used.

For each initial pressure the results have been summarised by the method of least squares. It is observed that both the energy of activation and the non-exponential term fall with decreasing initial concentration of dichloroethylene. The values of the Arrhenius parameters are given in Table 4.

TABLE 4.

p_0 (mm.)	∞	321	239	123	69	31
E (kcal. mole ⁻¹)	52.7	50.2	45.6	44.7	42.5	42.5
$\log_{10} A$	12.56	11.57	9.99	9.50	8.77	8.66

The only simple mechanism which accounts for these results is that the residual reaction is unimolecular. A criterion for this kind of mechanism is the influence of "chemically inert" gases on the speed of reaction. The maximally inhibited reaction in the presence of other gases was therefore studied. The first gas to be tried was diethyl ether which had been purified over sodium and stored *in vacuo* over quinol. In a series of experiments at 428°, a few mm. of *n*-hexane were admitted to the reaction vessel, and this was followed rapidly by 123 mm. of dichloroethylene and a known pressure of ether. The yield of hydrogen chloride was found in the usual way. Calculated first-order constants were found to increase steadily with increasing

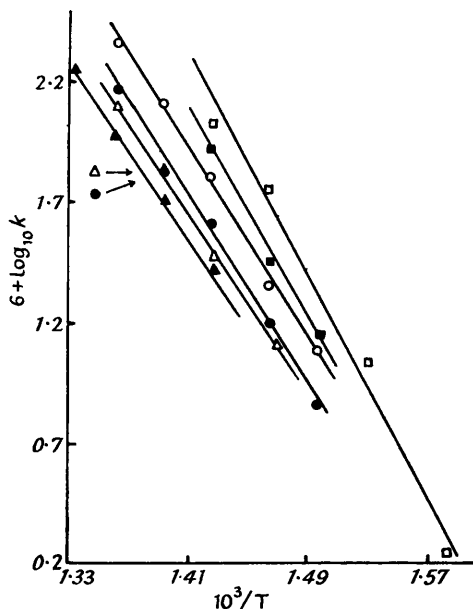
⁷ Pritchard, Pyke, and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629.

pressure of ether. The mean results, given in Table 5, show that diethyl ether does appear to act as a physical accelerator for the molecular decomposition of 1 : 2-dichloroethylene.

TABLE 5.

Pressure of ether (mm.)	0	25	50	99	176
Mean $10^6 k$ (sec. ⁻¹)	(4.26)	5.80	7.40	9.02	9.40

First-order constants for runs in which propene was the inhibitor showed that true first-order kinetics were being approached above an initial reactant pressure of 500 mm. This range was inconveniently high with the present apparatus and thus an indirect method of reaching k_∞ was sought. Diethyl ether was an unsatisfactory physical accelerator at high pressures because it decomposed to give products which were not readily condensable in liquid air.⁸ It has already been remarked that the maximally inhibited rate observed with *n*-hexane as inhibitor was invariably higher than the corresponding rate in presence of propene. It is difficult to think of any chemical effect which would produce this result. It is more probable that it is due to an energy-transfer phenomenon, because hexane should be a more efficient accelerator than propene by virtue of its greater number of degrees of freedom. This explanation is also consistent with the variation of rate constant with partial pressure of *n*-hexane. For various reasons, however, it was impracticable to investigate the effect of a wide range of pressures of hexane on the rate of dehydrochlorination. In order, therefore, to determine k_∞ and to obtain information regarding energy transfer, the effect of *n*-pentane on the pyrolysis of 1 : 2-dichloroethylene was investigated. *n*-Pentane proved to combine the properties of an efficient radical-chain suppressor and a molecular accelerator. This is probably the first deliberate attempt to use one compound as a simultaneous inhibitor and physical accelerator. In Table 6 it is shown that at 456° the rate in the presence of pentane passes through a minimum as the hydrocarbon concentration is increased. These experiments consisted of allowing 46 mm. of dichloroethylene to decompose for 18 min. in the presence of various amounts of *n*-pentane. The volume of 0.01N-sodium hydroxide solution required to neutralise the products is tabulated. It is clear that minute amounts of pentane are required for complete inhibition, because in the experiments marked with an asterisk the rate constants are similar to those obtained when



Values of p_0 (mm.): □, ∞; ■, 321; ○, 239; ●, 123; △, 69; ▲, 31.

TABLE 6.

$p(\text{C}_5\text{H}_{12})$ (mm.)	0	—*	—*	0.6	1.4	3.0
Titre, 0.01N-NaOH (c.c.)	5.24	0.70	0.62	0.91	0.97	1.00

* In these experiments the vessel was flushed out with pentane and quickly evacuated before admission of reactant.

using propene as inhibitor. The inert-gas accelerating effect, however, is also intense and is apparent at quite low pressures.

Most of the experiments with *n*-pentane were therefore aimed at finding the true value of k_∞ . Various proportions of substrate and additive were used, and provided that a sufficiently large quantity of pentane was employed, the velocity constant was independent of the initial pressure of dichloroethylene. This limit was near the approximate limit reached in experiments using ether as accelerator, and was also in harmony with the maximally inhibited rate constants using high partial pressures of reactant. This is good evidence for assuming that the rate constants

⁸ Cf. Hinshelwood, *Proc. Roy. Soc.*, 1927, **114**, A, 84.

found at high pressures of pentane were those corresponding to the fully developed first-order region of the reaction. The results found at 428° when using a constant initial pressure of 123 mm. of dichloroethylene are given in Table 7.

TABLE 7.

$p(\text{C}_2\text{H}_4)$ (mm.) ...	6	7.5	11	18	28	48	62	>70
Mean 10^5k (sec. ⁻¹)	7.40	8.88	9.42	10.7	10.3	9.9	10.8	10.9

The experiments were repeated at other temperatures, and the values of k_∞ are given in Table 8. The Arrhenius parameters obtained from these results are incorporated in Table 4. It may be noted that, whereas the rate constants given in Table 3 fall quite close to straight Arrhenius plots, the k_∞ values are more liable to error. The logarithms of all the rate constants given in Tables 3 and 8 are plotted against $1/T$ in the Figure, and it is seen that the values of $\log_{10} k_\infty$ may be up to 0.1 unit off the line.

TABLE 8.

Temperature	359°	380°	410°	428°
Mean 10^5k (sec. ⁻¹)	0.173	1.10	5.90	10.9

DISCUSSION

The three compounds propene, *n*-hexane, and *n*-pentane are all strong inhibitors of the free-radical decomposition of 1 : 2-dichloroethylene. It is probable that all the reported kinetic results refer to reactions in which chain processes are completely suppressed but different degrees of physical acceleration occur. This is supported by the fact that, with very small quantities of propene and pentane, the same maximally inhibited rate constants are obtained for the dehydrochlorination. Although the rate constants found by using the poor physical accelerator propene are slightly lower than those obtained with hexane, the latter experiments are the more extensive and the discussion centres mainly on them. These results do not quite refer to the unassisted molecular reaction but will be treated as such. The inhibited reaction is almost certainly unimolecular because the reaction order varies with pressure between 1 and 2. Some novel features, however, are presented.

Experiments with ether as an inert gas showed that it is 2—3 times as efficient as 1 : 2-dichloroethylene for transferring energy in collision. With pentane, however, this efficiency factor is about 25. Such a high value is most unusual—few values exceeding unity are recorded, but it is obviously connected with the deliberate choice of the small, hexatomic reactant and the more structurally complex inert gas. By using this efficiency, k_∞ results were obtained, and the critical pressure region for the unaided unimolecular decomposition estimated to be about 1000 mm. This is supported by the trend of the rate constants obtained with high pressures of reactant. The value of 25 for the efficiency factor has important consequences. If the effective collision diameter for the transfer of large amounts of energy by pentane is taken as the kinetic-theory diameter, then the corresponding diameter involving 1 : 2-dichloroethylene is $1/\sqrt{25}$ of the kinetic-theory diameter (*i.e.*, effectively $\sigma \approx 0.8 \times 10^{-8}$ cm.). This diameter and the effective number of classical oscillators ($\frac{1}{2}n$) storing energy in the molecule are required for the application of the unimolecular reaction theory of Rice and Ramsperger.⁹ It is desirable to estimate σ and n independently of the actual "fit" of the theory to the experimental results.¹⁰ At least 4 methods are available for the determination of n . These are :

(a) The specific heat C_p° of either dichloroethylene in the relevant temperature range is 23—24 cal.;⁵ n would be expected to be about two-thirds of this, *i.e.*, ~ 16 .

(b) If the Rice-Ramsperger model is used, then the difference in activation energy between the fully developed first- and second-order regions is $(n - 3)RT/2$.¹¹ k_∞ has been reached by using pentane, whilst at 31 mm. the reaction order in the presence of small quantities of hexane is approaching 2. The observed activation energy difference between these extremes is 10,200 cal. mole⁻¹. This corresponds to $n = 17$.

⁹ Rice and Ramsperger, *J. Amer. Chem. Soc.*, 1927, **49**, 1617.

¹⁰ Cf. Howlett, *J.*, 1952, 3695.

¹¹ Ramsperger, *Chem. Rev.*, 1932, **10**, 27.

(c) The critical pressure region has been estimated to be at 1000 mm. This may be used in conjunction with $\sigma = 0.8 \times 10^{-8}$ cm. in Hinshelwood's method¹² of estimating n . The result is 14.

(d) Slater² suggests that for constant values of k/k_{∞} , $pT^{-m/2}$ is constant, if m is the effective number of vibrational modes of the molecule. Our results are insufficiently precise to obtain constant values for this function, but at the middle of the pressure range the value derived for m is 15. The same figure is obtained by applying formulæ (53)—(55) of Slater's paper to the activation-energy difference between the first- and second-order decompositions. Since $m \approx n$ this result supports the other estimates for n and shows that the treatments are consistent.

The variation of the unimolecular rate constant of the reaction with pressure has been calculated by the method of Rice and Ramsperger.⁹ Computations were made, by applying equation 19 of Rice and Ramsperger's paper, for $T = 701^{\circ}$ K, and using $k_{\infty} = 0.000109$, $\sigma = 0.8 \times 10^{-8}$ cm., and $n = 15$. Table 9 compares the results with the experimental results. Since the variables have not been adjusted in order to obtain correspondence, the agreement is reasonable.

TABLE 9.

p (mm.)	∞	321	239	123	69	31
$10^5 k^1$, calc. (sec. ⁻¹)	(10.9)	7.7	7.2	6.1	5.1	4.0
$10^5 k^1$, expt. (sec. ⁻¹)	10.9	8.3	6.6	4.3	3.0	2.7

One of the main objectives in this work was to obtain a value for the critical-pressure region for unimolecular dissociation of a hexatomic molecule. The estimate of 1000 mm. compares favourably with Slater's prediction² of about 2 atm. Although a full application of Slater's theory presents difficulties, some aspects may be considered. The non-exponential term of the Arrhenius equation for k_{∞} is $10^{12.56}$. Slater's model requires this quantity to be a weighted mean of the vibration frequencies. For *trans*-1 : 2-dichloroethylene the frequencies range^{5,13} from $10^{13.96}$ to $10^{12.87}$, or possibly¹⁴ to $10^{12.65}$. It is significant that the lowest frequency, the B_u type ν_{12} , is the one most closely allied to the formation of the activated complex. A heavy weighting of this frequency would mean that the experimental non-exponential factor does not differ markedly from the theoretical figure.

It was shown in Part II¹ that at 40 mm. the molecular decomposition of trichloroethylene is in the second-order unimolecular region. The fact that the low-pressure rate constants obtained with 1 : 2-dichloroethylene were increased in the presence of excess of pentane suggests that a similar inert-gas effect should be observable for the pyrolysis of trichloroethylene. It has now been shown that *n*-pentane also acts as a radical-chain inhibitor and a physical accelerator for this reaction. In Table 10 the maximally inhibited,

TABLE 10.

Temp. (mm.)	$p(C_2H_{12})$	$10^2 k$	Temp. (mm.)	$p(C_2H_{12})$	$10^2 k$	Temp. (mm.)	$p(C_2H_{12})$	$10^2 k$
		(sec. ⁻¹ mole ⁻¹ l.)			(sec. ⁻¹ mole ⁻¹ l.)			(sec. ⁻¹ mole ⁻¹ l.)
409°	10	4.0	409°	109	10.5	424°	37	11.7
409	20	5.6	409	182	12.7	424	69	14.5
409	34	7.1	424	10	8.2	424	100	17.6
409	65	8.7						

$p(C_2HCl_3) = 42.5$ mm. throughout.

The rate constants for the maximally inhibited decomposition of trichloroethylene are calculated from Part II to be $k_{409} = 4.2 \times 10^{-2}$, $k_{424} = 8.1 \times 10^{-2}$.

second-order rate constants, calculated from the results given in Part II,¹ are compared with the apparent second-order constants obtained when trichloroethylene is pyrolysed in the presence of *n*-pentane at 409° and 424°. This result confirms the conclusions of Part II. Another satisfactory point concerns the non-exponential factors for the molecular decompositions of the di- and tri-chloroethylenes. On Slater's model these terms should

¹² Hinshelwood, "The Kinetics of Chemical Change," Oxford, 1940, p. 80.

¹³ Bernstein and Ramsay, *J. Chem. Phys.*, 1949, **17**, 556.

¹⁴ Luft, *J. Phys. Chem.*, 1955, **59**, 573.

be similar. For this comparison we took the calculated first-order constants of dichloroethylene decomposition for the lowest pressure range where the order is approaching 2 and divided them by the concentrations to obtain true second-order constants. The resulting non-exponential term ($10^{11.81}$) is close to the corresponding figure for trichloroethylene ($10^{12.08}$).

It may be concluded that the molecular dehydrochlorinations of chloroethylenes may be broadly explained in terms of the older statistical theories of unimolecular reactions, but that Slater's powerful treatment is capable of giving a more detailed physical significance to the Arrhenius parameter.

We thank Dr. V. C. G. Trew for the determinations of the magnetic susceptibilities of the 1 : 2-dichloroethylenes. Part of the work described in this paper was carried out while one of us (A. M. G.) was in receipt of a D.S.I.R. maintenance award.

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[Received, February 3rd, 1956.]
