37. *The Kinetics of the Dehydrochlorination of Substituted Hydro-carbons. Part III. The Mechanisms of the Thermal Decompositions of Ethyl Chloride and of* 1 : 1-*Dichloroethane.*

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Ethyl chloride decomposes in the temperature range 398—493° by a homogeneous, first-order reaction to give, stoicheiometrically, ethylene and hydrogen chloride. 1 : 1-Dichloroethane decomposes in the temperature range 356—453° by a nearly homogeneous, first-order reaction and furnishes vinyl chloride and hydrogen chloride with negligible quantities of acetylene. The acetylene in both this reaction and the 1 : 2-dichloroethane decomposition (preceding paper) arises by the (possibly heterogeneous) decomposition of vinyl chloride, as is proved by a study of the pyrolysis of vinyl chloride alone. Neither with ethyl chloride nor with 1 : 1-dichloroethane is there any falling off in rate constant over the range 20—200 mm. initial pressure of reactant. The rate equation for ethyl chloride is given by $k = 1·6 \times 10^{14}e^{-59,500/RT}$ and that for 1 : 1-dichloroethane by $k = 1·2 \times 10^{12}e^{-49,500/RT}$, the non-exponential terms of which are close to that (10^{13}) usually accepted for unimolecular decompositions.

Neither the ethyl chloride nor the 1 : 1-dichloroethane decomposition is subject to the slightest inhibition on addition of propylene, and neither shows the temperature-variable induction periods characteristic of·1 : 2-dichloroethane (preceding paper). The reactions must proceed, therefore, by an entirely different type of mechanism from that observed with the latter. It is concluded that they constitute unambiguous examples of unimolecular decompositions. This view receives support from the fact that the activation energy for the ethyl chloride pyrolysis calculated by the semi-empirical method is in close agreement with that found experimentally.

IN Part II (preceding paper) it was shown that the thermal decomposition of 1 : 2-dichloro-ethane to vinyl chloride and hydrogen chloride proceeds by a radical-chain mechanism which, very probably, involves chlorine atoms and 1 : 2-dichloroethyl radicals. The principal evidence upon which this conclusion was based was a study of the inhibiting properties of small amounts of propylene. We have now investigated the thermal decompositions of ethyl chloride and 1 : 1-dichloroethane. No previous physicochemical investigation of significance has been made with these two substances, though Biltz and Küppers (*Ber.*, 1904, **37**, 2398) reported a few preliminary experiments with 1 : 1-dichloroethane.

EXPERIMENTAL.

Materials.—1 : 1-Dichloroethane, prepared by the addition of hydrogen chloride to vinyl chloride at −30° in the presence of aluminium chloride as catalyst, was purified in exactly the same way as that adopted with 1 : 2-dichloroethane (preceding paper). The following constants were recorded for the purified material and are compared with the means of the best literature values (in parentheses). B. p. 57·4° corr. (mean 57·3° corr.: 57·3°, Timmermans, *Chem. Zentr.*, 1911, II, 105; 57·25°, Lecat, *Rec. Trav. chim.*, 1927, **46**, 242; 57·30°, Timmermans and Martin, *J. Chim. physique*, 1926, **23**, 770; 57·1°, Henne and Hubbard, *J. Amer. Chem. Soc.*, 1936, **58**, 404).

F. p. (carbon dioxide vapour-pressure thermometer) −97·1° (mean −96·8°; −96·7°, Timmermans, *loc. cit.*; −96·6°, Timmermans and Martin, *loc. cit.*; −96·8°, Timmermans, *Bull. Soc. chim. Belg.*, 1934, **43**, 626; −97·4°, Henne and Hubbard, *loc. cit.*). $d_4^{18·5°}$ 1·177 (mean 1·178 interpolated: $d_4^{0°}$ 1·2068, Timmermans and Martin, *loc. cit.*; $d_4^{15°}$ 1·1835, *idem. ibid.*; $d_4^{20°}$ 1·1743, Brühl, *Annalen*, 1880, **203**, 11; 1·1755, Patterson and Thomson, *J.*, 1908, **93**, 371; Henne and Hubbard, *loc. cit.*; $d_4^{30°}$ 1·1601, Timmermans and Martin, *loc. cit.*). $n_D^{20°}$ 1·4169 (mean 1·4166; 1·4165, Brühl, *loc. cit.*; 1·4158, Weegmann, *Z. physikal. Chem.*, 1888, **2**, 231; 1·4164, Henne and Hubbard, *loc. cit.*).

For ethyl chloride the standard method of purification was modified in that the washed and dried liquid was simply distilled into the crystallising vessel. The following constants were recorded for the purified material and are compared with the means of the best literature values (in parentheses).

B. p. 12·9° corr. (mean 12·7° corr.: 13·1°, Timmermans, *Chem. Zentr.*, 1914, I, 618; 13·1°, von Grosse, *J. Amer. Chem. Soc.*, 1937, **59**, 2739; 13·3°, Timmermans and Hennault-Roland, *J. Chim. physique*, 1937, **34**, 693; 12·5°, Jenkin, *Trans. Faraday Soc.*, 1923, **18**, 198). F. p. (ethylene vapour-pressure thermometer) −137·5° (mean −137·5°: −138·7°, Timmermans, *loc. cit.*; −136·4°, Timmermans and Hennault-Roland, *loc. cit.*).

The purified reagents were transferred to traps attached to the apparatus (see below) by distillation in a current of oxygen-free nitrogen. Before use the liquids were very thoroughly outgassed. The reagents were kept in liquid nitrogen or solid carbon dioxide–alcohol baths when the vapours were not being admitted to the reaction vessel.

Apparatus.—Exactly the same apparatus and experimental technique were used here as detailed (preceding paper) for 1 : 2-dichloroethane. All results recorded below were determined in reaction vessels whose walls had been coated with a carbonaceous film.

Results.

In order to establish the validity of pressure measurements as indicating the course of the thermal decompositions of ethyl chloride and 1 : 1-dichloroethane, a series of analyses for hydrogen chloride and

for acetylene were carried out at various temperatures and for various percentage decompositions. The hydrogen chloride determinations indicated a close correspondence between pressure increase and hydrogen chloride formation, as will be seen from Fig. 1, where the full line is drawn at the theoretical slope of 45°. In the case of ethyl chloride these analyses were sufficient to establish that the decomposition proceeded quantitatively according to $C_2H_5Cl \longrightarrow C_2H_4 + HCl$, but it was confirmed by acetylene analyses (see Table I) that the reaction $C_2H_4 \longrightarrow C_2H_2 + H_2$, as would be expected, played no part in the observed pressure increase. The case of 1 : 1-dichloroethane is comparable with that of 1 : 2-dichloroethane. The main reaction was represented by $CH_3 \cdot CHCl_2 \longrightarrow CH_2 \cdot CHCl + HCl$, with a much smaller contribution from the process $CH_2 \cdot CHCl \longrightarrow C_2H_2 + HCl$, which could be neglected for practical purposes as is shown by the data in Table I.

It was important to establish the origin of the acetylene, particularly in the 1 : 2-dichloroethane reaction, where it might conceivably have been formed by a chain-terminating step. Both 1 : 1- and 1 : 2-dichloroethane showed the same rate of acetylene formation at comparable rates of decomposition (compare preceding paper). This suggested that the acetylene was formed by pyrolysis of vinyl chloride and experiments with the latter (Table I) confirmed this hypothesis. Although we have not made extensive experiments on this aspect of these decompositions, it seems probable that the acetylene is formed from the vinyl chloride by a heterogeneous process.
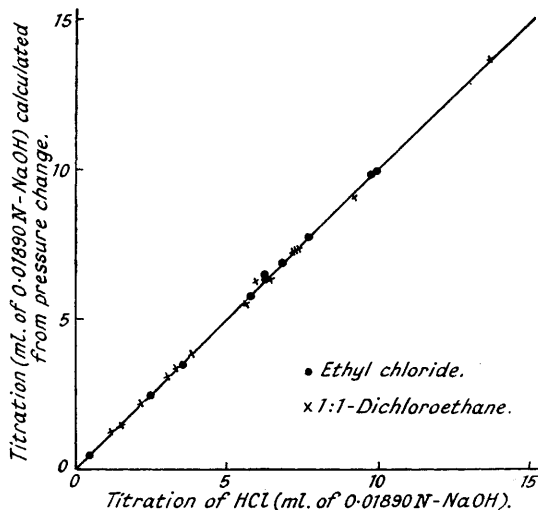
FIG. 1.

TABLE I.

| Temp.	Time of reaction, mins.	Initial compound, mols. $\times 10^{-6}$.	HCl, calc. from press. change, mols. $\times 10^{-6}$.	C_2H_2, found, mols. $\times 10^{-6}$.
		Ethyl chloride.		
438°	57	690	165	0
		1 : 1-Dichloroethane.		
444 *	10	258	121	3
444 *	12	197	105	4
444 *	16	148	96	6
444 *	27	177	145	8
		Vinyl chloride.		
444 *	10	78	4	5
444 *	12	71	4	6
444 *	14	63	3	4

* Runs in packed vessel.

A further check on the simple stoicheiometry of the reactions was provided by a series of long-term experiments (see Table II) in which the reaction was allowed to approach completion. In each case, and especially with the ethyl chloride, the pressure finally attained was close to double the initial pressure.

TABLE II.

Temp.	Initial press., p_i, mm.	Time, hrs.	Final press., p_t, mm.	p_t/p_i.	Temp.	Initial press., p_i, mm.	Time, hrs.	Final press., p_i, mm.	p_t/p_i.
		Ethyl chloride.					1 : 1-Dichloroethane.		
472°	69·5	17	136·5	1·97	420°	55	17	109	1·98
471	21	17	42·5	2·02	429	58·5	15	125	2·14
470	51	17	104·5	2·05	444	43·5	16	95	2·18
444·5	185·5	17	365	1·97	438	86	17	173	2·01
447·5	61·5	17	119·5	1·94	443	99·5	18	204	2·05
					437	74·5	20	152	2·04

FIG. 2.

- 1:1-Dichloroethane at 442°.
- Ethyl chloride at 470·5°.
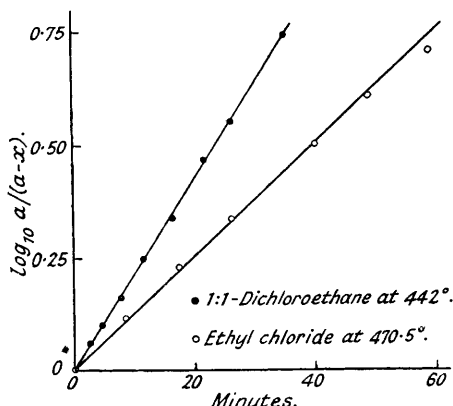
Both ethyl chloride and 1 : 1-dichloroethane conformed to a first-order equation up to at least 75% decomposition, as is illustrated by typical runs shown in Fig. 2. There was no falling off in velocity constant over the initial pressure range 20—200 mm., as is shown by the data below :

Ethyl chloride.

	At 444·5°.					At 463°.							
p_i, mm.	35	45	50	55	185	15	35	45	60	70	100	105	180
$10^5 k$, sec.$^{-1}$ ...	12·6	12·1	12·1	11·9	11·9	34·0	34·0	34·9	35·7	33·7	36·4	33·4	35·2

1 : 1-Dichloroethane.

	At 419°.			At 429°.				At 453°.				
p_i, mm.	20	75	116	30	60	65	150	40	50	55	65	80	110
$10^5 k$, sec.$^{-1}$ ...	31·8	28·9	28·2	55·0	57·0	60·0	53·5	171	159	164	174	168	164

A similar series of " double " experiments with ethyl chloride and 1 : 1-dichloroethane to those recorded in the preceding paper for 1 : 2-dichloroethane showed that the reaction products had practically no inhibiting effect on the reaction :

Temp.	p_1,* mm.	p_2,* mm.	First vel. const., $10^5 k_1$, sec.$^{-1}$.	Second vel. const., $10^5 k_2$, sec.$^{-1}$.	k_2/k_1.	Temp.	p_1,* mm.	p_2,* mm.	First vel. const., $10^5 k_1$, sec.$^{-1}$.	Second vel. const., $10^5 k_2$, sec.$^{-1}$.	k_2/k_1.
			Ethyl chloride.						1 : 1-Dichloroethane.		
444·5°	55	150	11·9	11·9	1·00	442°	20	70	81	81·5	1·01
463	45	45	34·9	33·7	0·97	442	30	70	84	82	0·98
463	60	70	35·7	36·4	1·02	437	35	60	61·5	60·5	0·98
						437	20	55	64	64	1·00

* Pressures of ethyl chloride or 1 : 1-dichloroethane admitted.

The reproducibility attained with both ethyl chloride and 1 : 1-dichloroethane was good (see Tables above)—indeed, considerably better than that with 1 : 2-dichloroethane. The accuracy of the final averages of the measurements will be seen from Table III. Ethyl chloride, studied over the temperature range 398—493°, gave an activation energy of 59·5 kcals. (see Fig. 3) and a rate equation $k = 1·6 \times 10^{14} e^{-59,500/RT}$. 1 : 1-Dichloroethane, over the temperature range 356—453°, showed similarly an activation energy of 49·5 kcals. (see Fig. 4) and a rate equation $k = 1·2 \times 10^{12} e^{-49,500/RT}$.
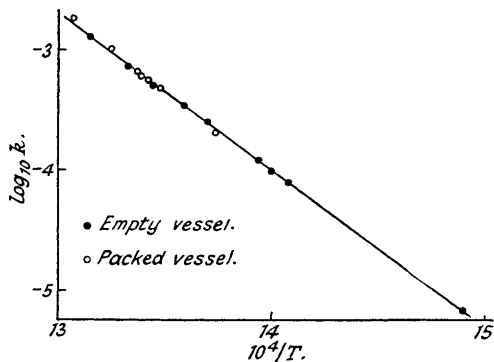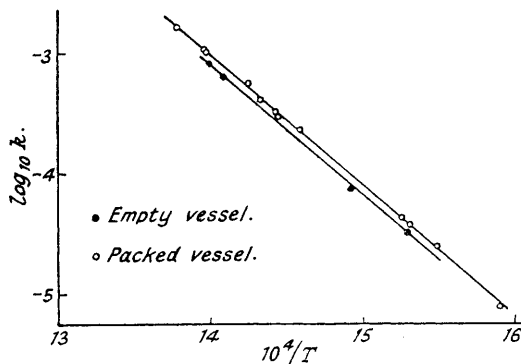
FIG. 3.

FIG. 4.

• *Empty vessel.*

○ *Packed vessel.*

TABLE III.

Temp.	No. of runs.	Mean vel. const. $\times 10^5$, sec.$^{-1}$.	Mean error of the mean vel. const. $\times 10^5$.*	Temp.	No. of runs.	Mean vel. const. $\times 10^5$, sec.$^{-1}$.	Mean error of the mean vel. const. $\times 10^5$.*
Ethyl chloride (packed vessel).				1 : 1-Dichloroethane (packed vessel).			
454·5°	5	20·1	±0·1	356°	1	0·81	—
469	7	48·5	±0·7	372·5	1	2·50	—
472	5	56·7	±0·4	380	1	3·82	—
474	1	60	—	382	1	4·22	—
475	1	66	—	382·5	1	4·40	—
481·5	3	101·3	±1·2	412	2	23·5	±0·5
491	3	182	±5	419	3	29·7	±1·0
				420	1	33·0	—
Ethyl chloride (empty vessel).				425	3	41·0	±0·9
398	1	0·69	—	429	5	56·7	±1·1
437	3	7·95	±0·3	443	2	101	±1·0
441	1	9·7	—	444	11	105	±0·9
444·5	5	12·1	±0·13	453	7	166	±2·0
463	9	34·7	±0·4				
470·5	3	51	±1·7	1 : 1-Dichloroethane (empty vessel).			
476·5	4	72·5	±0·9	381	1	3·25	—
487·5	3	129	±1·6	397	3	7·5	±0·17
				437	6	63	±0·6
				442	7	82	±1·0

* Calculated from the equation $\sigma = \sqrt{\Sigma\Delta^2/n(n-1)}$.

In marked contrast to the decomposition of 1 : 2-dichloroethane (preceding paper), that of ethyl chloride and of 1 : 1-dichloroethane showed no sign of induction periods even at the lowest temperatures

FIG. 5.

•*Ethyl chloride.*

○ *1:1-Dichloroethane.*
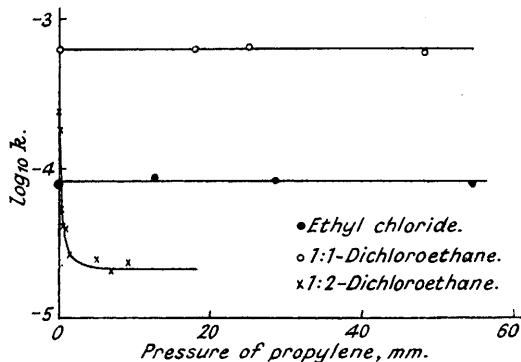
×*1:2-Dichloroethane.*

studied. The present decompositions also differed remarkably from that of 1 : 2-dichloroethane in that addition of propylene had absolutely no effect on the reaction velocity (see Fig. 5).

Packing the reaction vessel in a manner similar to that for the 1 : 2-dichloroethane reaction had no effect on the rate of ethyl chloride decomposition (Fig. 3), but slightly increased that of 1 : 1-dichloroethane

(Fig. 4). In the packed vessel the latter compound followed the rate equation $k_p = 1\cdot4 \times 10^{12}e^{-49,500/RT}$, thus indicating no change in activation energy and a 15% increase in reaction velocity. This percentage increase in rate is almost identical with that found for 1 : 2-dichloroethane under the same conditions (preceding paper).

DISCUSSION.

The complete absence of any inhibiting effect by propylene in these decompositions is well illustrated by Fig. 5 (see above). This property, together with the absence of induction periods and the excellent adherence to first-order kinetics well beyond the 50% decomposition point, proves conclusively that these reactions must have a quite different mechanism from that proposed for 1 : 2-dichloroethane (preceding paper) and that they are certainly not radical-chain reactions. Two possibilities remain to explain their mechanism. Either they are true, homogeneous, unimolecular reactions or they proceed by homogeneous non-chain-radical steps. We are strongly in favour of the former view, (a) because it is difficult to believe that the addition of propylene, which is well known to combine readily with radicals, in amounts equal to the amount of decomposing substrate would have no effect at all on the reaction rate, and (b) because all the reasonable non-chain-radical mechanisms that we have been able to devise (*e.g.*, for ethyl chloride : $C_2H_5Cl \longrightarrow C_2H_5 + Cl$, $Cl + C_2H_5Cl \longrightarrow HCl + C_2H_4Cl$, $C_2H_5 + C_2H_4Cl \longrightarrow C_2H_5Cl + C_2H_4$) should have activation energies approximately the same as the strength of the C–Cl bond (about 80 kcals.).

In the case of ethyl chloride the activation energy for the reverse reaction, addition of hydrogen chloride to ethylene, has been calculated by the semi-empirical method by Sherman, Quimby, and Sutherland (*J. Chem. Physics*, 1936, **4**, 732) to be about 45 kcals.; utilisation of modern bond energies (see Appendix of preceding paper) raises this to about 48 kcals. Since this addition reaction is exothermic to the extent of 15 ± 1 kcals. (see Conn, Kistiakowsky, and Smith, *J. Amer. Chem. Soc.*, 1938, **60**, 2764), it follows that the revised value for the unimolecular activation energy of the decomposition reaction is about 63 kcals. This is in excellent agreement with that found experimentally and supports our views as to the mechanism of the reaction. The semi-empirical method is not readily extended to the calculation of the activation energy for the decomposition of 1 : 1-dichloroethane. It is obvious, however, that it must be lower than that for ethyl chloride owing to the extra resonance energy in vinyl chloride as compared with ethylene.

Another point providing further evidence for the decompositions of ethyl chloride and 1 : 1-dichloroethane being truly unimolecular is the value of the non-exponential term in the relevant rate equations. For both substances the non-exponential terms are within a power of 10 of that (10^{13}) usually considered normal for unimolecular reactions. On the other hand, for 1 : 2-dichloroethane this term is $6\cdot4 \times 10^{10}$, which differs from the normal value by nearly 10^3-fold (see preceding paper).