452. *The Kinetics of the Dehydrochlorination of Substituted Hydrocarbons. Part VIII.* The Mechanisms of the Thermal Decompositions of* n-*Propyl and* n-*Butyl Chloride and 2 : 2′-Dichlorodiethyl Ether.*

By D. H. R. Barton, A. J. Head, and R. J. Williams.

n-Propyl chloride decomposes in the temperature range 693—751° K. by a homogeneous, first-order reaction to give, stoicheiometrically, propylene and hydrogen chloride. *n*-Butyl chloride decomposes in the temperature range 700—744° K. by a similar homogeneous, first-order reaction to furnish butene and hydrogen chloride; neither with the former over the pressure range 50—155 mm., nor with the latter over the range 10—135 mm., is there any falling off in rate constant with lowering of initial pressure. The rate constant equation for propyl chloride is given by $k = 10^{13\cdot45 \pm 0\cdot35}e^{(-55,000 \pm 1,200)/\boldsymbol{RT}}$ sec.$^{-1}$, and that for butyl chloride by $k = 10^{14\cdot0 \pm 0\cdot1}e^{(-57,000 \pm 400)/\boldsymbol{RT}}$ sec.$^{-1}$. Neither decomposition is subject to the slightest inhibition on addition of propylene, and neither gives any indication of temperature-dependent induction periods. The reactions are regarded as unambiguous examples of unimolecular decompositions.

2 : 2′-Dichlorodiethyl ether decomposes in the temperature range 646—702° K. by a first-order reaction. The reaction products are a complex mixture. The rate-constant equation can be approximately represented by $k = 10^{15}e^{-54,500/\boldsymbol{RT}}$ sec.$^{-1}$ at 30 mm. initial pressure. The rate constant fell over the pressure range 65·8—16·7 mm. In all experiments moderately reproducible induction periods were observed. These were inversely dependent on the temperature and on the initial pressure. They could be prolonged indefinitely by the addition of propylene, the increase in the length of the induction period being proportional to the amount of propylene added. The rate of decomposition was reduced by packing the reactor, the induction periods being thereby lengthened. The decomposition of 2 : 2′-dichlorodiethyl ether must be exclusively of the radical-chain type. The termination step proceeds, at least in part, on the walls of the reactor. The chain length, estimated from inhibition experiments in the packed reactor, was about 23 at 686° K. for 30 mm. initial pressure of reactant.

This paper reports a continuation of our studies on the thermal decomposition of saturated chlorinated hydrocarbons. Previously we had suggested (Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725) that *n*-propyl and *n*-butyl chloride would decompose by homogeneous first-order reactions, the mechanisms of which would be unimolecular. This suggestion was based on the fact that propylene (and doubtless also butene) is a powerful inhibitor for the chain type of decomposition shown by 1 : 2-dichloroethane (Barton and Howlett, *J.*, 1949, 155), 1 : 1 : 1-trichloroethane (Barton and Onyon, *J. Amer. Chem. Soc.*, 1950, **72**, 988), and the two tetrachloroethanes (Barton and Howlett, preceding paper), and therefore, if it were a reaction product, it could not be produced by a chain mechanism. The decomposition would thus proceed by an alternative mechanism which, if homogeneous, would be of the unimolecular type (compare Barton and Onyon, *loc. cit.*, 1949). This view now receives confirmation.

We have also investigated the thermal decomposition of 2 : 2′-dichlorodiethyl ether. Here it was not possible to make a firm prediction as to the mode of decomposition because if the attack of chloride atoms were preferentially at a 2-(C–H) bond, as in (*A*), then a reaction chain could not be propagated, whereas if the attack were at a 1-(C–H) bond, as in (*B*), then chain propagation (cf. Ash and H. C. Brown, *Records of Chemical Progress*, 1948, p. 81) would be facilitated. As shown below, the chlorinated ether actually decomposes by the chain mechanism, although the reaction is a complex one and not suited for detailed quantitative study.

(*A*) $Cl + Cl{\cdot}C_2H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl \longrightarrow HCl + Cl{\cdot}C_2H_4{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}$
$Cl{\cdot}C_2H_4{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}$ (no ready loss of a chlorine atom)

(*B*) $Cl + Cl{\cdot}C_2H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl \longrightarrow HCl + Cl{\cdot}C_2H_4{\cdot}O{\cdot}\dot{C}H{\cdot}CH_2Cl{\cdot}$
$Cl{\cdot}C_2H_4{\cdot}O{\cdot}\dot{C}H{\cdot}CH_2Cl \longrightarrow Cl{\cdot}C_2H_4{\cdot}O{\cdot}CH{:}CH_2 + Cl$ (ready loss of β-chlorine atom)

No physicochemical investigation of these decompositions has hitherto been reported.

---

* Part VII, preceding paper.

EXPERIMENTAL.

Materials.—Difficulty was found in the purification of *n*-propyl chloride. The commercial material, purified by the general method described by Barton and Howlett (*J.*, 1949, 155) and crystallised twice, gave kinetic runs characterised by a fast start. When the partly decomposed propyl chloride was frozen out of the reactor, and the undecomposed propyl chloride vapour then re-admitted, the fast start was no longer apparent and the kinetics were of first order from zero time. This behaviour indicated that a readily decomposed contaminant had resisted the purification procedure. The impure propyl chloride was then refluxed with concentrated sulphuric acid for 30 minutes and worked up again by the usual procedure. Two low-temperature crystallisations afforded material which showed no fast start and gave satisfactory first-order kinetics (see p. 2042). The following constants were recorded for the purified material and are compared with the means of the best literature values (in parentheses): b. p. 46·9° (corr.)/760 mm. (mean 46·6°, corr.: from 46·8°, Berthoud, *J. Chim. physique*, 1917, **15**, 3; 46·6°, Timmermans and Hennault-Roland, *ibid.*, 1930, **27**, 401; 46·5°, Mumford and Phillips, *J.*, 1950, 75); $d_4^{21\cdot1}$ 0·8900 (mean 0·8900: interpolated from d_4^{15} 0·8985, d_4^{30} 0·8799, Timmermans and Hennault-Roland, *loc. cit.*; d_4^{20} 0·8890, d_4^{25} 0·8830, Mumford and Phillips, *loc. cit.*); $n_D^{23\cdot5}$ 1·3863 (cf. n_D^{20} 1·3900, Mumford and Phillips, *loc. cit.*).

Difficulty was also experienced in the purification of *n*-butyl chloride. Treatment of the commercial material in the usual way (Barton and Howlett, *loc. cit.*), including two low-temperature crystallisations, gave material which also exhibited fast starts. Further purification, involving refluxing with concentrated sulphuric acid for 35 minutes, furnished a preparation of b. p. 77·8—78·4°/760 mm. The last and main fraction, b. p. 78·4° (corr.)/760 mm., gave satisfactory first-order kinetics. It was further fractionated by one low-temperature crystallisation without alteration of the kinetic behaviour. The following constants were recorded for the purified material and are compared with the means of the best literature values (in parentheses): b. p. 78·4°/760 mm. (mean 78·4° corr.: from 78·6°, Timmermans, *Bull. Soc. chim. Belg.*, 1921, **30**, 65; 78·5°, Timmermans and Hennault-Roland, *loc. cit.*; 78·5°, Smyth and McAlpine, *J. Chem. Physics*, 1935, **3**, 347; 77·9°, Vogel, *J.*, 1943, 636; 78·4°, Mumford and Phillips, *loc. cit.*); $d_4^{23\cdot5}$ 0·8829 (mean 0·8827; interpolated from d_4^{15} 0·89197, d_4^{30} 0·87549, Timmermans and Hennault-Roland, *loc. cit.*; d_4^{20} 0·8866, Vogel, *loc. cit.*; d_4^{20} 0·8866, and d_4^{25} 0·8811, Mumford and Phillips, *loc. cit.*); n_D^{22} 1·4010 (compare n_D^{20} 1·4023, Smyth and McAlpine, *loc. cit.*; n_D^{20} 1·4023, Wiswall and Smyth, *J. Chem. Physics*, 1941, **9**, 356; n_D^{20} 1·4022, Vogel, *loc. cit.*; n_D^{20} 1·4021, Mumford and Phillips, *loc. cit.*).

Commercial 2 : 2′-dichlorodiethyl ether was washed several times with concentrated hydrochloric acid and then fractionally distilled under reduced pressure. The following constants were recorded for the purified material and are compared with the means of the best literature values (in parentheses): b. p. 178·7—178·9° (corr.)/760 mm. (mean 178·4°: from 178·75°, Gallaugher and Hibbert, *J. Amer. Chem. Soc.*, 1937, **59**, 2521; 178·6°, Tschamler, *Monatsh.*, 1948, **78**, 297; 177·9°, Mumford and Phillips, *loc. cit.*); d_4^{26} 1·2121 (1·2118: extrapolated from d_4^{20} 1·2192, d_4^{25} 1·2130, Mumford and Phillips, *loc. cit.*); n_D^{20} 1·4568 (mean 1·4572: from n_D^{20} 1·4570, Gallaugher and Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 813; n_D^{20} 1·4573, Mumford and Phillips, *loc. cit.*; n_D^{20} 1·4574, Tschamler, *loc. cit.*).

Apparatus.—The apparatus and experimental technique were those detailed by Barton and Howlett (*J.*, 1949, 155). Because of the low vapour pressure of 2 : 2′-dichlorodiethyl ether the same precautions with regard to the heating of the dead space were adopted as for the two tetrachloroethanes (see preceding paper). All the results recorded below were obtained in reaction vessels the walls of which had been coated with a carbonaceous film (cf. Barton and Howlett, *loc. cit.*; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725). The kinetics of the reactions were elucidated by following the increase in pressure at constant volume as in all the previous papers of this series.

RESULTS.

Stoicheiometry.—By analogy with work in previous Parts of this series (see especially Barton, *J.*, 1949, 148; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725; Barton and Head, *ibid.*, 1950, **46**, 114) it was expected that *n*-propyl and *n*-butyl chloride would decompose according to (*C*) and (*D*) respectively. This was confirmed by the fact that the final pressure in the reactor after a long run was

$$(C)\quad \mathrm{CH_3{\cdot}CH_2{\cdot}CH_2Cl \longrightarrow CH_3{\cdot}CH{:}CH_2 + HCl}$$

$$(D)\quad \mathrm{CH_3{\cdot}[CH_2]_2{\cdot}CH_2Cl \longrightarrow CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + HCl}$$

close to twice the initial pressure (Table I). However for butyl chloride the ratio increased above the theoretical value in the higher part of the temperature range investigated.

The decomposition of 2 : 2′-dichlorodiethyl ether furnished a mixture of products. We assume that

$$(E)\quad \mathrm{(CH_2Cl{\cdot}CH_2)_2O \longrightarrow (CH_2{:}CH)_2O + 2HCl}$$

the stoicheiometry of the initially occurring reaction is represented by (*E*), and that this is followed by the (slower) decomposition of divinyl ether, a reaction known to furnish a complicated mixture of products (H. A. Taylor *J. Chem. Physics*, 1936, **4**, 116). In agreement, the ratio of the final to the initial pressure, p_f/p_0, for long-term experiments (Table I) exceeded 4·0, and the ratio p/p_0 at times equal to several half-lives of the decomposing dichloro-ether approached 3·0, the final approach to 4·0 and higher ratios being much slower. It is of interest to compare these values of p_f/p_0 with those obtained by Taylor (*loc. cit.*) for divinyl ether at 723—773° K. Taylor's data being accepted, a value of 4·05—4·24 can be computed for the decomposition of 2 : 2′-dichlorodiethyl ether in this temperature range. In presenting the results for this ether the stoicheiometry (*E*) has been assumed throughout.

Kinetics.—All three decompositions exhibited first-order kinetics as illustrated by Fig. 1 (*n*-propyl chloride), Fig. 2 (*n*-butyl chloride), and Fig. 3 (2 : 2′-dichlorodiethyl ether). In all experiments with the monochloro-compounds there were no indications of induction periods even at the lowest temperatures studied (compare Figs. 1 and 2). In contrast, the decomposition of 2 : 2′-dichlorodiethyl ether (see Fig. 3) exhibited temperature-dependent induction periods. The variation of velocity constant with initial pressure was insignificant over the pressure range 50—155 mm. for *n*-propyl chloride and 10—135 mm. for *n*-butyl chloride (Table II). With the dichloro-ether, both the rate constants and the

TABLE I.

Temp., °K.	p_0, mm.	Time of reaction, hrs.	p_f/p_0.	Temp., °K.	p_0, mm.	Time of reaction, hrs.	p_f/p_0.	Temp., °K.	p_0, mm.	Time of reaction, hrs.	p_f/p_0.
n-*Propyl chloride.*											
Unpacked reactor.											
693	128·4	19	1·96	729	109·7	18	2·03	744	107·9	18	2·03
695	123·3	70	1·95	729	88·3	20	2·06	745	97·1	19	2·08
705	93·3	18	1·98			44	2·09	746	48·7	18	2·10
713	88·1	70	2·04	734	68·2	18	2·09	746	50·3	18	2·08
716	110·2	18	2·03	734	97	18	2·02	746	51·7	19	2·06
724	47·7	18	2·06	734	104·2	18	2·03	746	80·6	18	2·06
724	103·1	18	1·97	739	91·8	19	2·03	746	80·8	18	2·07
728	43·3	19	2·06	739	102·1	18	2·06				
Packed reactor.											
719	103·5	18	1·98	732	103·6	18	2·04	738	100·7	18	2·01
719	95·8	18	1·98	735	101·1	18	2·04	740	91·6	22	2·08
732	64·1	22	2·12	735	105·9	18	2·00	740	105·8	18	2·02
732	82·9	21	2·07	738	98·4	19	2·06	741	110·1	19	2·05
n-*Butyl chloride.*											
Unpacked reactor.											
700	102·1	16	2·01	723	74·5	16	2·14	730	70·3	16	2·18
700	113·9	16	2·03	723	69·0	16	2·10	738	68·2	16	2·24
700	90·2	39	2·08	723	76·9	16	2·14	744	66·2	16	2·35
712	116·2	17	2·08	723	75·0	46	2·30	744	63·7	19	2·36
712	89·2	16	2·08	730	91·0	18	2·20	744	55·6	68	2·56
716	107·5	17	2·09								
Packed reactor.											
712	71·5	42	2·19	729	60·2	20	2·18	729	70·6	16	2·24
712	63·5	16	2·08	729	71·0	16	2·22	729	74·0	16	2·24
729	61·0	16	2·18								
2 : 2′-*Dichlorodiethyl ether.*											
Unpacked reactor.											
647	30·2	16	3·55	684	31·5	16	4·10	684	27·9	16	4·06
671	29·6	46	4·21	684	29·0	66	4·38	684	33·0	16	4·06
673	26·2	16	4·01								
Packed reactor.											
683	30·7	16	4·14	683	30·4	46	4·19	689	30·0	16	4·00
683	30·5	16	4·08	689	31·1	16	4·11				

TABLE II.

p_0, mm.	10^4k, sec.$^{-1}$.	p_0, mm.	10^4k, sec.$^{-1}$.	p_0, mm.	10^4k, sec.$^{-1}$.	p_0, mm.	10^4k, sec.$^{-1}$.
n-*Propyl chloride at* 736° K. (unpacked reactor).							
53·2	9·04	98·7	8·93	105·6	8·92	132·1	9·02
69·9	8·92	100·2	9·10	111·2	8·94	154·4	8·83
91·2	8·82	103·1	8·95				
n-*Butyl chloride at* 737·6° K. (unpacked reactor).							
31·1	14·0	70·1	13·7	94·8	13·7	134·6	13·4
46·4	12·9	80·3	13·0	110·2	13·8		
n-*Butyl chloride at* 712·1° K. (packed reactor).							
10·4	3·27	17·5	3·39	29·4	3·48	52·4	3·46
16·7	3·68	19·4	3·43	40·6	3·42	*ca.* 70	3·39

FIG. 1.

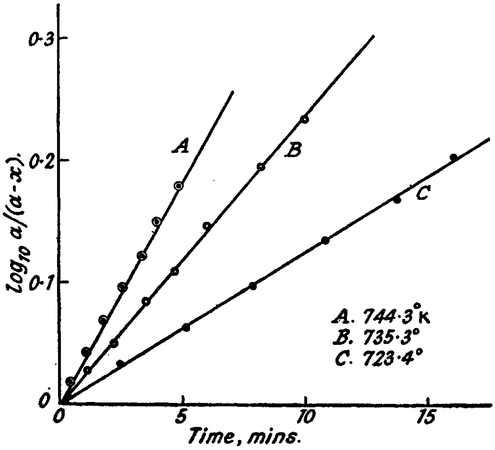


FIG. 2.

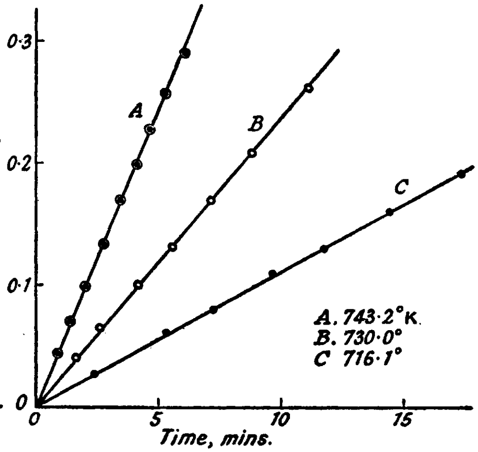


FIG. 3.

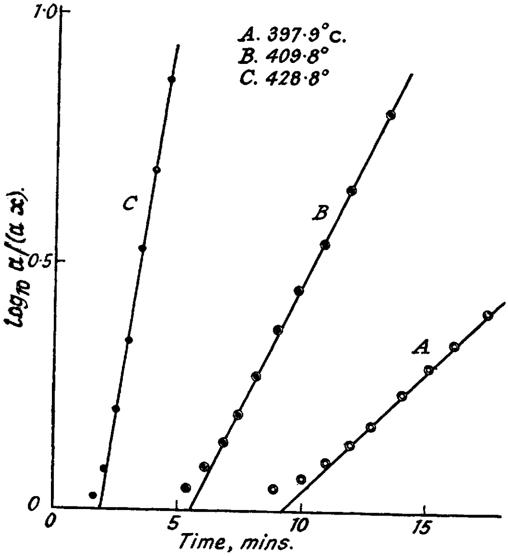
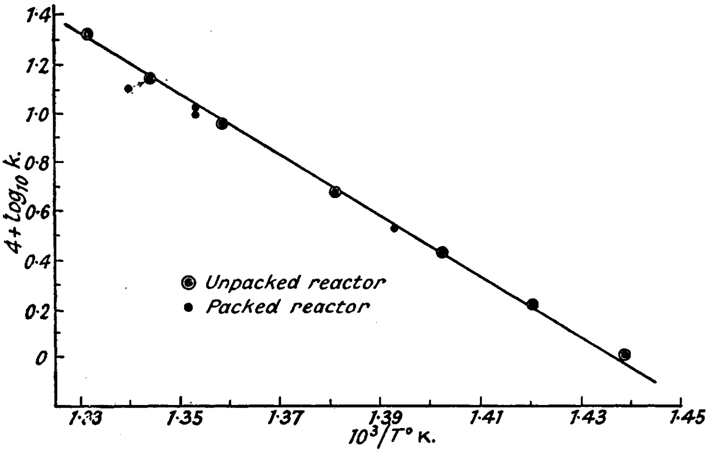


FIG. 4.



induction periods varied with the initial pressure of reactant over the range 16·7—65·8 mm. (Table III). It was of interest that the induction periods observed were inversely proportional to the initial pressures (Table III).

TABLE III.

p_0, mm.	16·7	23·5	32·2	65·8
10^4k, sec.$^{-1}$ *	9·3	17·5	25·9	30·4
Induction period, I, min.	16·0	10·6	7·7	3·3
$p_0 \times I \times 10^{-2}$, mm. min.	2·67	2·49	2·48	2·17

* Packed reactor at 685·5° K.

The rate-constant equations over the pressure ranges studied (see above) were given by $k = 10^{13 \cdot 45 \pm 0 \cdot 35}e^{(-55{,}500 \pm 1200)/\boldsymbol{R}\boldsymbol{T}}$ sec.$^{-1}$ for *n*-propyl chloride and by $k = 10^{14 \cdot 0 \pm 0 \cdot 1}e^{(-57{,}000 \pm 400)/\boldsymbol{R}\boldsymbol{T}}$ sec.$^{-1}$ for *n*-butyl chloride. The rate data are summarised in Table IV and illustrated further in Fig. 4 (*n*-propyl chloride) and Fig. 5 (*n*-butyl chloride). The straight lines in these figures have been drawn by the least-squares method, the same statistical weight being given to every observation of k. The error limits have been computed by the procedure detailed by Barton and Onyon (*loc. cit.*, 1949). Packing the reactor (see Table IV and Figs. 4 and 5) with glass tubing to give an approximately 6-fold increase in the surface area : volume ratio had a negligible effect on the rates of decomposition of *n*-propyl and *n*-butyl chloride and therefore the reactions must be homogeneous.

TABLE IV.

Temp., °K.	No. of runs.	Mean $k \times 10^4$, sec.$^{-1}$.	% Standard deviation of mean k.*	Temp., °K.	No. of runs.	Mean $k \times 10^4$, sec.$^{-1}$.	% Standard deviation of mean k.*
n-*Propyl chloride.*							
Unpacked reactor.							
695·0	7	1·02	0·6	736·0	10	8·95	0·3
704·0	6	1·65	0·4	744·0	19	13·85	0·4
713·0	5	2·68	0·5	751·0	7	21·0	0·9
724·0	7	4·76	0·6				
Packed reactor.							
718·0	7	3·34	0·8	744·0	12	13·88	0·5
739·0	29	9·89	0·4				
n-*Butyl chloride.*							
Unpacked reactor.							
700·0	23	1·70	0·4	723·0	25	6·26	0·4
708·7	7	2·72	0·7	730·2	11	9·09	0·5
712·4	13	3·42	0·7	737·6	9	13·52	0·7
715·7	10	4·09	0·7	743·6	18	18·75	0·5
Packed reactor.							
712·1	11	3·58	0·5	729·2	18	8·75	0·4

* Given by $100 \times \sqrt{\dfrac{\Sigma(x - \bar{x})^2}{n(n - 1)}} \Big/ \bar{x}$, where the symbols have the usual significance.

The rate-constant equation for 2 : 2′-dichlorodiethyl ether at initial pressures close to 30 mm. was given by $k = 10^{15}e^{-54{,}500/\boldsymbol{R}\boldsymbol{T}}$ sec.$^{-1}$ (experiments in the unpacked reactor). The rate-constant data, together with the appropriate induction periods, which decreased with increasing temperature, are summarised in Table V. We do not attach a high degree of accuracy to the data. Packing the reactor as for *n*-propyl and *n*-butyl chloride (see above) caused an approximate halving of the rate of decomposition and an approximate doubling of the induction periods (see Table V).

TABLE V.

Temp., °K.	No. of runs.	Mean 10^4k, sec.$^{-1}$.	% Standard deviation of mean k.*	Mean I, min.	Based on no. of runs.	% Standard deviation of mean I.*
Unpacked reactor.						
646·2	4	4·19	1·6	36·4	2	—
671·1	11	20·1	2·0	9·1	8	2·9
683·6	11	40·8	1·1	5·5	9	5·9
702·0	10	123·0	1·2	1·7	9	2·5
Packed reactor.						
686·2	36	21·0	1·5	9·0	30	2·0

* Calculated as in Table IV.

FIG. 5.

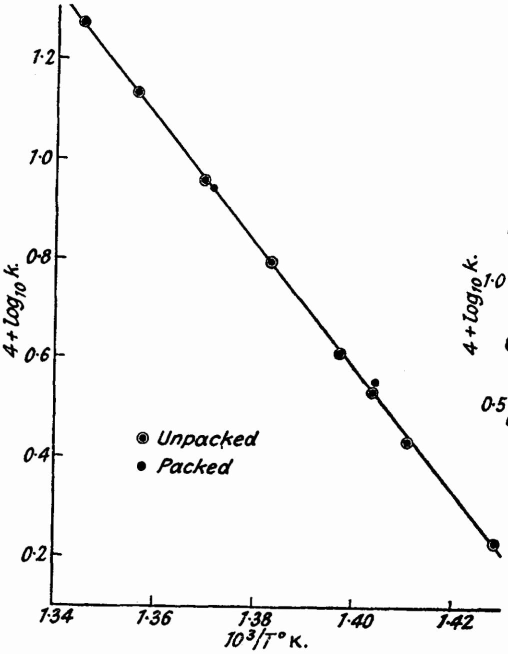


FIG. 6.

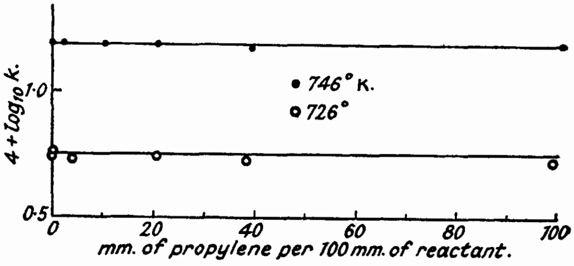


FIG. 7.

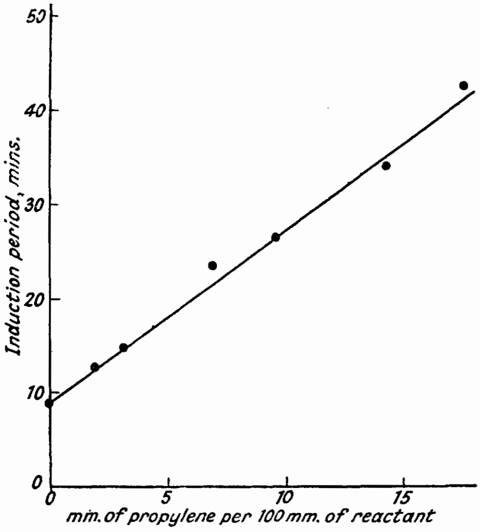
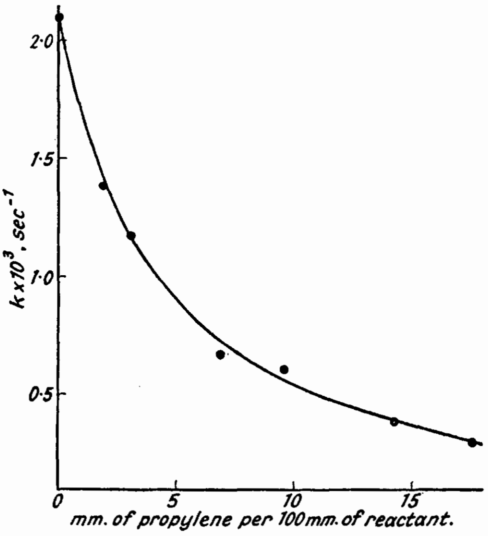


FIG. 8.



The addition of propylene to decomposing *n*-propyl and *n*-butyl chloride had no effect. This is illustrated by Fig. 6 for *n*-propyl chloride (initial pressures close to 50 mm.) and by Table VI for *n*-butyl chloride. In all cases the kinetics remained of the first order.

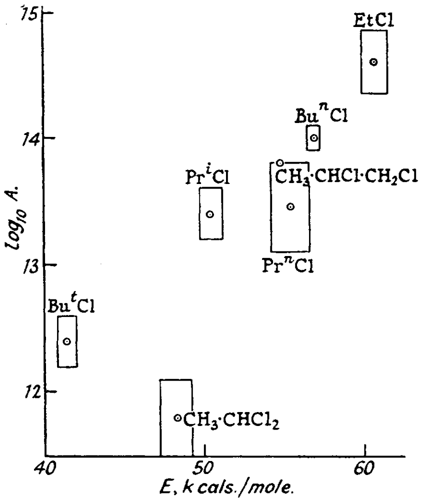
TABLE VI.

n-Butyl chloride, mm.	10—135	107·6	112·8	105·9	104·2
Propylene, mm.	0	0·4	0·8	1·5	3·7
10^4k, sec.$^{-1}$ *	3·40	3·55	3·51	3·39	3·42

* All experiments at 712·4° K. in the unpacked reactor.

The effect of adding propylene to decomposing 2 : 2′-dichlorodiethyl ether was quite different. First, the already present induction periods were prolonged in proportion to the amount of propylene added, as shown in Fig. 7, which refers to runs in the packed reactor at 686·2° K. with initial pressures close to 30 mm. Secondly, whilst the reaction continued to exhibit first-order kinetics, the rate of decomposition of the 2 : 2′-dichlorodiethyl ether, after the induction period was over, was reduced, the reduction in rate increasing with the concentration of added propylene. Fig. 8, which refers to experiments under the same conditions as for Fig. 7, is illustrative.

FIG. 9.



DISCUSSION.

The thermal decompositions of *n*-propyl and *n*-butyl chloride follow first-order kinetics, the rate constants *not* varying with the initial pressure. The reactions are homogeneous, exhibit no induction periods even at the lowest temperatures studied, and are totally unaffected by the addition of propylene. All these experimental features are identical with those established previously for ethyl chloride, 1 : 1-dichloroethane, *tert.*-butyl chloride, *iso*propyl chloride, and 1 : 2-dichloropropane (Barton and Howlett, *J.*, 1949, 165; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725; Barton and Head, *ibid.*, 1950, **46**, 114), and, without repeating the arguments in detail, we regard them as adequate to prove that *n*-propyl and *n*-butyl chloride decompose by the unimolecular mechanism.

In a previous paper (Barton and Head, *loc. cit.*) it was shown that there was a linear relationship between $\log_{10}$ of the non-exponential terms of the rate-constant equations and the corresponding activation energies for the decompositions of ethyl chloride, *iso*propyl chloride, and *tert.*-butyl chloride, reactions which are authenticated as unimolecular. It is of interest that the data for *n*-propyl and *n*-butyl chloride (see Fig. 9) also fall on the same straight line within the error limits indicated by the rectangles. The data for 1 : 2-dichloropropane are also included, but without error limits. The data for 1 : 1-dichloroethane, however, do not fall on the line.

Although also exhibiting first-order kinetics, the decomposition of 2 : 2′-dichlorodiethyl ether shows temperature-dependent induction periods which are prolonged proportionately by the addition of small amounts of propylene. The rate of decomposition after the induction period is also reduced by addition of propylene. The reaction is *slower* in the packed than in the empty reactor, and the induction periods are longer. In contrast to the unimolecular type of decomposition (see above), the rate constant varies with the initial pressure. We regard these experimental facts as proof that decomposition of the dichloro-ether proceeds by the radical-chain mechanism (see Barton and Howlett, *J.*, 1949, 155), and further that the prolongation of the natural induction periods shows the decomposition to be 100% of the chain type (compare Barton and Howlett, preceding paper). Following the argument in the preceding paper, it is possible to calculate the kinetic chain length from the inhibition studies summarised in the Experimental Section as about 23 (packed reactor, 686·2° K., p_0 ~30 mm.). The reduction in rate constant on packing the reactor and on reducing the initial pressure of reactant implies that, as with the decomposition of 1 : 1 : 1-trichloroethane (Barton and Onyon, *loc. cit.*, 1950), the reaction chains are, at least in part, terminated at the reactor walls.

The experimental results do not furnish a complete picture of the more intimate aspects of the 2 : 2′-dichlorodiethyl ether decomposition. However, the validity of first-order kinetics suggests that the second elimination of hydrogen chloride is much more rapid than the first. The nature of the first propagation step has already been discussed (p. 2039).

Ash and H. C. Brown's important paper (*loc. cit.*) makes it desirable to discuss in somewhat greater detail the relation between molecular structure and mode of thermal decomposition which we have previously established (Barton and Onyon, *loc. cit.*, 1949). Ash and Brown have pointed out that, if allowance is made for the formation of C_2H_4 by β-elimination of a chlorine atom from the $\cdot CH_2\cdot CH_2Cl$ radical, then the predominant attack of chlorine atoms on ethyl chloride is at the β- and not at the α-position (as one would conclude from the ratio of 1 : 1- to 1 : 2-dichloroethanes formed). If this view be accepted, then it remains to explain why ethyl chloride and 1 : 1-dichloroethane should decompose by the unimolecular rather than by the radical-chain mechanism. Now, if a saturated chlorinated hydrocarbon is pyrolysed to eliminate hydrogen chloride,* the mechanism, if homogeneous, may be unimolecular or of radical-chain character (Barton and Onyon, *loc. cit.*). We can regard the two mechanisms as competitive, the relative rates being given by

$$\text{Rate (unimolecular)} = k_1[\text{A}] \quad . \qquad \text{(i)}$$

$$\text{and Rate (radical chain)} = k_2[\text{Cl}][\text{A}] \qquad \text{(ii)}$$

where [A] represents the concentration of chlorinated hydrocarbon and the other symbols have the usual significance. For 1 : 2-dichloroethane and the more highly chlorinated ethanes a β-chlorine atom can be eliminated from the 1 : 2-dichloroethyl radical intermediate and thus continue the chain :

$$\text{Cl} + \text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl} \longrightarrow \text{HCl} + \cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$$

$$\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl} \longrightarrow \text{CHCl}{:}\text{CH}_2 + \text{Cl}$$

This is also the case for β-attack on ethyl chloride and 1 : 1-dichloroethane, but α-attack on these compounds gives rise to " dead " radicals which cannot propagate the chain by β-elimination and thus act as chain terminators :

$$\text{Cl} + \text{CH}_3\cdot\text{CH}_2\text{Cl} \longrightarrow \text{HCl} + \text{CH}_3\cdot\dot{\text{C}}\text{HCl} \text{ (no β-elimination)}$$

$$\text{Cl} + \text{CH}_3\cdot\text{CHCl}_2 \longrightarrow \text{HCl} + \text{CH}_3\cdot\dot{\text{C}}\text{Cl}_2 \text{ (no β-elimination)}$$

The chain length of the radical decomposition of ethyl chloride is thus limited to the ratio of β- to α-attack in the chlorination reaction. Such a value (about 10) is negligible compared with the probable chain length (about 10^4) of the radical-chain decomposition of (say) 1 : 2-dichloroethane. The unimolecular mode of decomposition is thus greatly favoured. The same argument applies for the case of 1 : 1-dichloroethane.

Further illustrations of the relationship between molecular structure and mode of thermal decomposition will be given in later papers.

We thank the Central Research Fund of London University for a Grant in aid of this investigation, which was carried out during the tenure of a Postgraduate Studentship in the University (A. J. H.). We also thank the D.S.I.R. for a Maintenance Grant (R. J. W.).

BIRKBECK COLLEGE RESEARCH LABORATORY,
21, TORRINGTON SQ., LONDON, W.C.1.
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

[*Received, February 27th,* 1951.]

---

* We assume that the necessary stereochemical requirements for the unimolecular elimination are satisfied (Barton, *J.*, 1949, 2174; Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114; Barton, Head, and Williams, forthcoming paper).