36. *The Kinetics of the Dehydrochlorination of Substituted Hydrocarbons. Part II. The Mechanism of the Thermal Decomposition of 1 : 2-Dichloroethane.*

By D. H. R. BARTON and K. E. HOWLETT.

1 : 2-Dichloroethane decomposes in the temperature range 362—485° by a nearly homogeneous, first-order reaction to give vinyl chloride and hydrogen chloride. Only small quantities of acetylene are formed which, for practical purposes, may be neglected. The activation energy of the reaction is 47 kcals. and the rate equation is $k = 6{\cdot}4 \times 10^{10}e^{-47,000/RT}$ There is no falling off in rate constant over the initial pressure range of 20—200 mm.

Propylene is a powerful inhibitor for the decomposition, the inhibited reaction remaining of the first order. The inhibited rate constant is governed by the initial pressure of propylene but is independent of the 1 : 2-dichloroethane pressure. In both these respects the behaviour of the propylene is different from that observed when it is allowed to inhibit the chain decompositions of other organic substances not containing chlorine. The maximally inhibited reaction has practically the same activation energy as the uninhibited reaction and follows the rate equation $k = 6{\cdot}3 \times 10^{9}e^{-46,000/RT}$. This residual reaction is partly heterogeneous in character. *n*-Hexane resembles propylene in its inhibiting action on the decomposition, but ethylene is relatively without effect.

The 1 : 2-dichloroethane decomposition shows a fairly reproducible induction period which, when treated as a rate, gives an activation energy of 78 ± 10 kcals. This may correspond to the initial rupture of the molecule in a chain sequence.

These facts lead to a very probable radical-chain mechanism for the 1 : 2-dichloroethane decomposition involving chlorine atoms and 1 : 2-dichloroethyl radicals. The calculated activation energy (48 kcals.) is in close agreement with observation. From the postulated mechanism it is possible to compute chain lengths and to reconcile quantitatively the propylene inhibition curves with experiment. The activation energy of the chain-terminating step with propylene is about 7·5 kcals., and the non-exponential term of the rate equation for this step is close to the normal value for a bimolecular reaction.

IN Part I (preceding paper) the influence of traces of oxygen or chlorine on the rates of thermal decomposition of a number of chlorinated hydrocarbons was briefly reported. Before proceeding to a systematic study of the mechanisms involved in the induced reactions which we have discovered in the course of this work, it is clearly essential to gain some insight into the modes of thermal decomposition of chlorinated hydrocarbons without addition of any catalysing agent. In view of the industrial importance of the 1 : 2-dichloroethane pyrolysis in the manufacture of vinyl chloride, we have selected this compound before others for our first study.

The literature on the physicochemical aspects of gas-phase thermal dehydrochlorination is extremely scanty. The work of Biltz and Küppers (*Ber.*, 1904, **37**, 2398), mentioned in the preceding paper, is of no importance in this connection when judged by present-day standards. The only reliable pertinent work is that of Brearly, Kistiakowsky, and Stauffer (*J. Amer. Chem. Soc.*, 1936, **58**, 43), who studied the thermal decompositions of *tert.*-butyl and *tert.*-amyl chlorides. These reactions proved to be mainly homogeneous and of the first order. Since no tests were applied for radical chains, the American authors' conclusion that these decompositions are unimolecular, although probable, is not proven.

It should be pointed out that the results recorded below were obtained by a static method with reaction vessels whose walls had been coated with carbonaceous films. They are not strictly comparable, therefore, with the data reported in the preceding paper, which refer to dynamic experiments in clean-walled vessels.

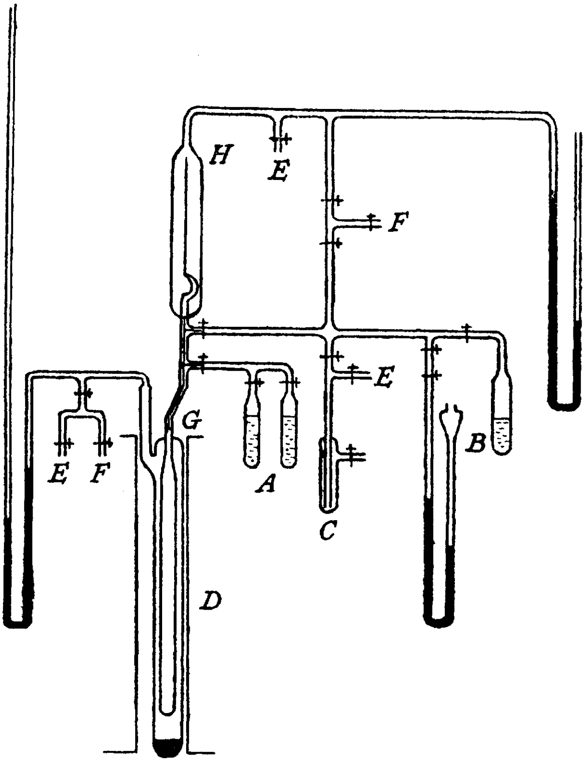
EXPERIMENTAL.

Purification of 1 : 2-Dichloroethane.—In view of the known sensitivity of a number of chlorinated hydrocarbon decompositions to trace contaminants (Barton, *Nature*, 1946, **157**, 626), special care has been taken to ensure the purity of the reagents in this and the following work. The procedure detailed below illustrates the general case. The chlorinated hydrocarbon was shaken out thoroughly with concentrated sulphuric acid until no further colour developed, washed with sodium hydrogen carbonate solution and then with water, dried ($CaCl_2$), and efficiently fractionated. The final purification was accomplished by several fractional crystallisations, the f. p. and especially the f.-p. range (finally constant to within 0·1°) indicating the purity of the compound. In each crystallisation only half the liquid was frozen, the residue being poured off. The following constants were recorded for 1 : 2-dichloroethane and are compared with the mean of the best literature values (in parentheses). B. p. 83·5° corr. (mean 83·5° corr.; 83·50°, Timmermans and Martin, *J. Chim. physique*, 1928, **25**, 420; 83·48°, Smith and Matheson, *J. Res. Nat. Bur. Stand.*, 1938, **20**, 641).

F. p. (sulphur dioxide vapour-pressure thermometer) −35·5° (mean −35·5°; −35·5°, Timmermans and Martin, *loc. cit.*; −35·5°, Michel, *Bull. Soc. chim. Belg.*, 1939, **48**, 105).

$d_{4^\circ}^{25^\circ}$ 1·2480 (mean 1·2457, interpolated; $d_{4^\circ}^{15^\circ}$ 1·2600, Timmermans and Martin, *loc. cit.*; $d_{4^\circ}^{20^\circ}$ 1·2521, Brühl, *Annalen*, 1880, **203**, 10; 1·2529, Gotz, *Z. physikal. Chem.*, 1920, **94**, 193; $d_{4^\circ}^{30^\circ}$ 1·2383, Timmermans and Martin, *loc. cit.*; 1·2383, Gotz, *loc. cit.*).

FIG. 1.



$n_D^{19^\circ}$ 1·4450 (mean 1·4453, interpolated; $n_{4^\circ}^{15^\circ}$ 1·4476, Timmermans and Martin, *loc. cit.*; $n_{4^\circ}^{20^\circ}$ 1·4443, Brühl, *loc. cit.*; 1·4444, Weegmann, *Z. physikal. Chem.*, 1888, **2**, 231; 1·4448; Smyth, Dornte, and Wilson, *J. Amer. Chem. Soc.*, 1931, **53**, 4242; $n_D^{25\cdot4^\circ}$ 1·4418, Schwers, *Bull. Acad. Belg.*, 1912, 623).

The purified 1 : 2-dichloroethane was transferred to traps attached to the apparatus (see below) by distillation in a current of oxygen-free nitrogen and also by distillation in a vacuum. Before use the 1 : 2-dichloroethane was very thoroughly out-gassed. The traps were surrounded by liquid nitrogen or solid carbon dioxide–alcohol baths except when the 1 : 2-dichloroethane vapour was being admitted to the reaction vessel.

Apparatus.—The glass apparatus used for studying the 1 : 2-dichloroethane decomposition was constructed throughout in Pyrex. It is illustrated diagrammatically in Fig. 1.

The reaction vessel, a tube approximately 75 cm. long and 1·5 cm. in diameter, was completely enclosed in an outer jacket containing the vapour of boiling mercury or sulphur. Measurement of the pressure of nitrogen admitted into the outer jacket indicated the temperature of the refluxing liquid and hence that of the reactor. The vapour-pressure curve for mercury was taken from I.C.T. (Vol. 3, p. 206) and that for sulphur from West and Menzies (*J. Physical Chem.*, 1929, **33**, 1880). Preliminary experiments with a calibrated thermometer confirmed that this method of temperature measurement was satisfactory.

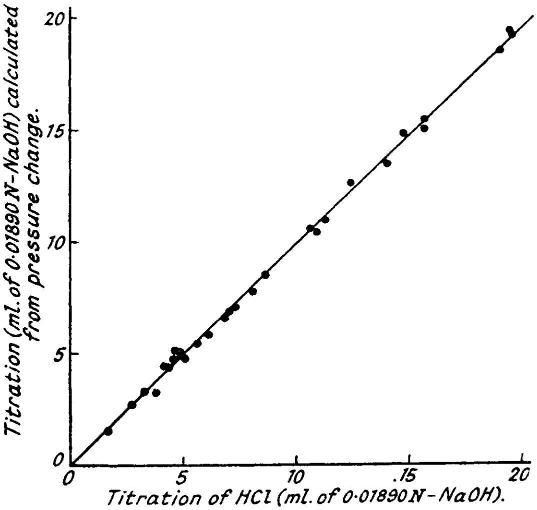
In operation, the current through the electric furnace windings was adjusted so as to maintain alone a temperature lower than that desired. Gas-heating to boil the thermostatic liquid was used as control. Initial work on the efficiency of the furnace showed that any desired temperature could be kept constant almost indefinitely to within ½°. On admission of 1 atm. of 1 : 2-dichloroethane vapour to the vessel at 350°, a thermometer suspended in it showed a fall of only 1°, and this was restored in less than a minute. Further confirmation of the almost immediate assumption of vessel temperature by entering vapour was provided by the constant pressure observed within a few seconds of closing the stopcock from reservoir to reaction vessel, the temperature being low enough for the rate of reactant decomposition to be very slow.

Pressure changes in the reaction vessel were followed in an initial apparatus by a capillary mercury manometer, but condensation difficulties and possible contamination from mercury vapour led us to modify the method of pressure measurement. An all-glass spoon-gauge manometer with external resistance wire heating (to about 100°) was found satisfactory and is illustrated in Fig. 1. The volume of the gauge and its capillary connection was less than 3% of the volume of the reaction vessel.

Traps were provided external to the vessel for storage of reactants, " catalysts ", and inhibitors and for condensation of the vessel contents before analysis. As stopcock lubricant where hot reactants or products were present, silicone high-vacuum grease was employed.

With this system, even after repeated evacuation and rinsing out, consistent results could not be obtained, the reaction rate (measured by the pressure increase) slowly falling as the experiments were repeated. This type of effect is well known in the study of organic pyrolyses (compare Daniels and Veltman, *J. Chem. Physics*, 1939, **7**, 756) and was observed by Brearly, Kistiakowsky, and Stauffer (*loc. cit.*) in their experiments. It is due to the slow deposition of a carbonaceous film on the glass surface. But whereas the latter authors report that ten experiments were sufficient to coat the vessel walls, we found that, using 1 : 2-dichloroethane at 350—400°, more than 100 runs were required before the results became reproducible. A more rapid method of coating the walls was found to be co-decomposition of 1 : 2-dichloroethane and propylene or ethylene, but after such treatment the inhibiting effects of the two gases, especially the propylene, on subsequent decompositions of 1 : 2-dichloroethane alone were noticeable for many runs. The admission of air to the coated-wall vessel, as would be expected, greatly increased the rate of decomposition of 1 : 2-dichloroethane in subsequent runs, but the effect was not permanent, being exhausted in the course of a few experiments. Brearly, Kistiakowsky, and Stauffer (*loc. cit.*) report that too thorough evacuation also destroys the usefulness of the deposited carbonaceous film. In our investigation an oil pump has been employed to evacuate to approximately 10^{-2} mm. between runs.

FIG. 2.



Results.

In order to establish the validity of pressure measurements as indicating the course of reaction, a series of analyses on condensed reaction products was carried out at various temperatures and various percentage conversions. The products were analysed for hydrogen chloride, and in some cases for acetylene, using Ilosvay's test as applied by Willstätter and Maschmann (*Ber.*, 1920, **53**, 939).

Determinations of hydrogen chloride indicated a close correspondence between pressure increase and hydrogen chloride formation. This is illustrated by Fig. 2, where the line is drawn at the theoretical slope of 45°. That the stoicheiometry of the reaction is closely represented by the equation $CH_2Cl{\cdot}CH_2Cl \longrightarrow CH_2{:}CHCl + HCl$ was proved by the above experiments combined with determinations (see Table I) which showed that the amount of acetylene formed was, for practical purposes, negligible within the temperature range employed. This shows that the further reaction $CH_2{:}CHCl \longrightarrow CH{:}CH + HCl$ may be neglected, a conclusion in agreement with the dynamic experiments reported in Part I (preceding paper).

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

TABLE I.

Temp.	Time of reaction, mins.	Initial $C_2H_4Cl_2$, mols. × 10^{-6}.	HCl calc. from pressure change, mols. × 10^{-6}.	C_2H_2 found, mols. × 10^{-6}.
437°	55	318	163	9
444 *	23	134	55	5
444 *	29	139	69	6
444 *	28	168	82	6
461	60	300	272	11
461	60	322	292	11
461	60	328	297	16
485	12	350	256	7
485	12	347	254	12

* Runs in packed vessel.

TABLE II.

Temp.	Initial press., p_i, mm.	Time, hrs.	Final press., p_t, mm.	p_t/p_i.
357° *	89·5	69	179·5	2·00
359 *	48·5	38	98	2·02
368 *	60	18	118	1·97
371 *	54·5	17	108	1·98
371 *	74	18	144	1·95
375 *	37	16	73·5	1·99
377 *	83	18	162·5	1·96
400 *	68	21	134	1·97
400 *	73·5	20	146	1·98
422	32	16	67	2·09
424	60	17	126	2·10
424°	65·5	17	136	2·08
437	49·5	16	105	2·12
437	51	13½	108	2·12
437	51	17	108	2·12
437	89·5	17	189·5	2·12
437	115	17	232·5	2·02
437	121	17	245	2·02
446	24	17	53·5	2·23
461	38	17	86	2·26
470	47	17	101	2·15

* Experiments using only partially coated walls.

FIG. 3.

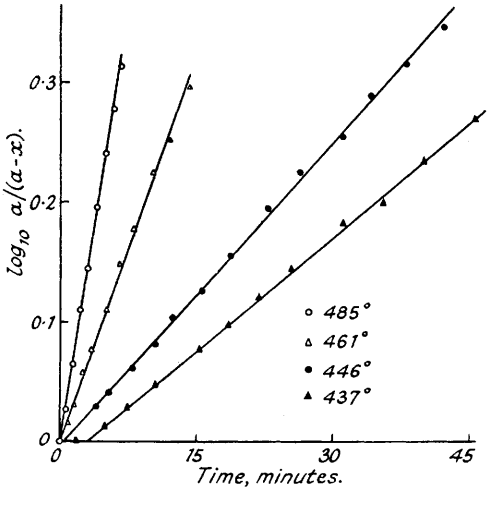
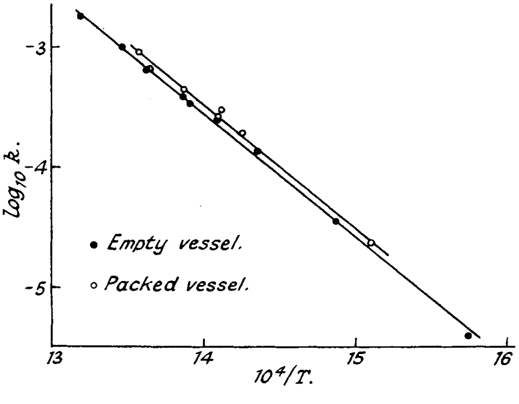


FIG. 4.



With these facts established, the decomposition was studied over the temperature range 362—485°, initial pressures of 1 : 2-dichloroethane of 20—200 mm. being used. At all pressures and temperatures the reaction was found to be of first order up to at least half-decomposition. All velocity constants in this and the following papers of the series were determined by plotting $\log_{10} a/(a - x)$ against t, where the symbols have the usual significance. Some typical examples of the results thus obtained for 1 : 2-dichloroethane are illustrated in Fig. 3. Over the initial pressure range investigated there was no falling off in velocity constant (see Table III), though there was better adherence to first-order kinetics beyond the half-decomposition point at the lower pressures.

The latter observation suggested a slight inhibitory effect from the products of the reaction. This was confirmed by the experiments shown in Table IV, where a certain initial pressure of 1 : 2-dichloroethane was taken to half decomposition, and then more 1 : 2-dichlorethane admitted and the velocity constant again determined.

TABLE III.

Initial press., mm.	$k \times 10^5$, sec.$^{-1}$.	Initial press., mm.	$k \times 10^5$, sec.$^{-1}$.	Initial press., mm.	$k \times 10^5$, sec.$^{-1}$.	Initial press., mm.	$k \times 10^5$, sec.$^{-1}$.
Temp. 437°.				Temp. 470°.		Temp. 485°.	
20	30·6	70	2[illegible]·6	20	102	20	182
35	30·6	75	23·0	25	118	20	197
50	23·6	90	29·2	40	100	40	187
50	26·6	95	28·1	60	125	45	182
60	25·2	110	20·4	120	101	50	182
60	25·5	160	23·8			60	192
						120	168
						120	173

TABLE IV.

Temp.	p_1.*	p_2.*	First vel. const., $k_1 \times 10^5$, sec.$^{-1}$.	Second vel. const., $k_2 \times 10^5$, sec.$^{-1}$.	k_2/k_1.	Temp.	p_1.*	p_2.*	First vel. const., $k_1 \times 10^5$, sec.$^{-1}$.	Second vel. const., $k_2 \times 10^5$. sec.$^{-1}$.	k_2/k_1.
424°	25	80	14·7	14·6	0·99	448°	45	40	44·8	41·3	0·92
424	50	90	14·9	14·2	0·95	448	40	70	43·5	44·3	1·02
424	50	85	12·6	12·9	1·02	448	45	50	43·6	43·0	0·99
448	45	40	41·5	37·4	0·90	450	25	50	45·0	43·0	0·95
448	40	40	37·4	34·8	0·93						

* Pressures of 1 : 2-dichloroethane admitted (in mm.).

The reproducibility attained with 1 : 2-dichloroethane was only fair, as will be seen from the specimen results in Tables III and IV. In order to obtain reliable average velocity constants numerous runs were made at each temperature over a wide temperature range. The accuracy of the final averages of the measurements will be seen from Table V. The Arrhenius plot of $\log_{10} k$ against $1/T$ (see Fig. 4) gave a good straight line from the slope of which a value of 47 kcals. was obtained by the method of least squares for the activation energy of the reaction. The relevant rate equation can be expressed by $k = 6{\cdot}4 \times 10^{10}e^{-47{,}000/RT}$.

TABLE V.

Temp.	No. of runs.	Mean vel., const., sec.$^{-1}$ ($\times 10^5$).	Mean error ($\times 10^5$) of mean vel. const.*	Temp.	No. of runs.	Mean vel., const., sec.$^{-1}$ ($\times 10^5$).	Mean error ($\times 10^5$) of mean vel. const.*
362°	1	0·40	—	448°	24	39·0	±0·8
400	3	3·62	±0·02	461	18	64·8	±0·8
424	10	13·9	±0·1	470	10	101	±2·3
437	26	25·2	±0·14	485	12	184	±2·3
446	9	34·1	±0·6				

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

In all runs with 1 : 2-dichloroethane at sufficiently low temperatures there was a marked induction period which showed moderate reproducibility. It is illustrated by the first-order plots given in Fig. 5, where the straight line does not cut the time axis at the zero point. Since these induction periods varied in a regular manner with temperature, they can be treated as representing a rate. In Fig. 6 $\log_{10} 1/I$, where I is the induction period, is plotted against $1/T$ and gives a rough straight line. From this plot the activation energy of the process can be evaluated as 78 ± 10 kcals.

FIG. 5.

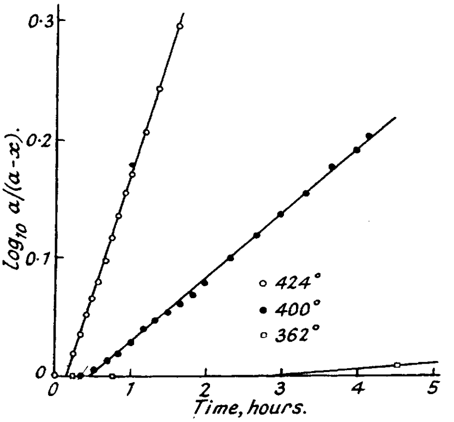
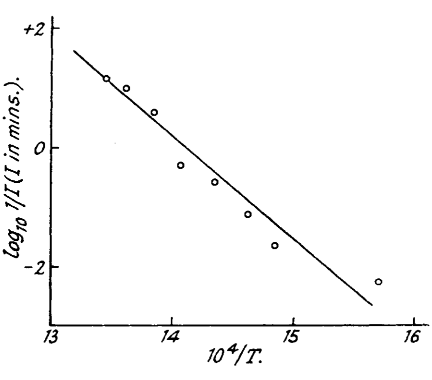


FIG. 6.



The inhibiting effect of small amounts of propylene or nitric oxide has become recognised as a characteristic test for radical-chain reactions. At all temperatures investigated (437—480°) propylene diminished the rate of decomposition of 1 : 2-dichloroethane to a limiting rate, independent of further increase in propylene pressure. This limiting figure was reached with a surprisingly low propylene concentration as may be seen from Figs. 7, 8, and 9 (at temperatures of 437°, 457°, and 480° respectively) showing the inhibition curves observed.

FIG. 7.

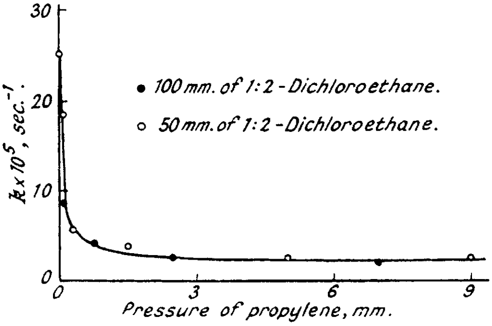


FIG. 8.

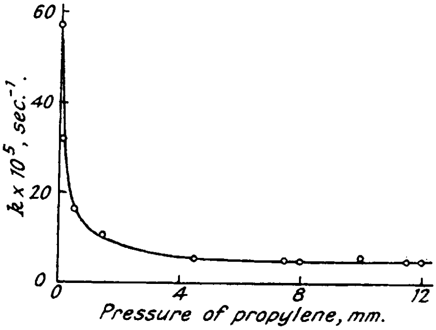


FIG. 9.

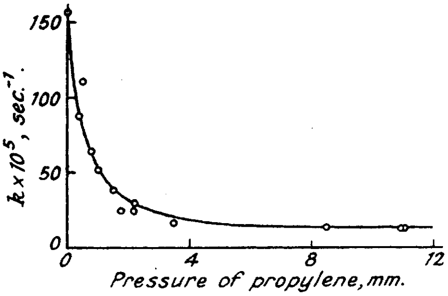


FIG. 10.

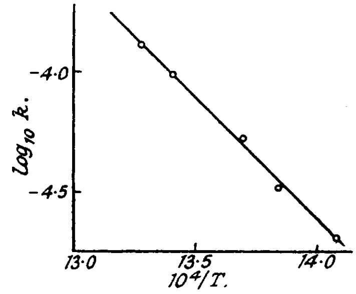
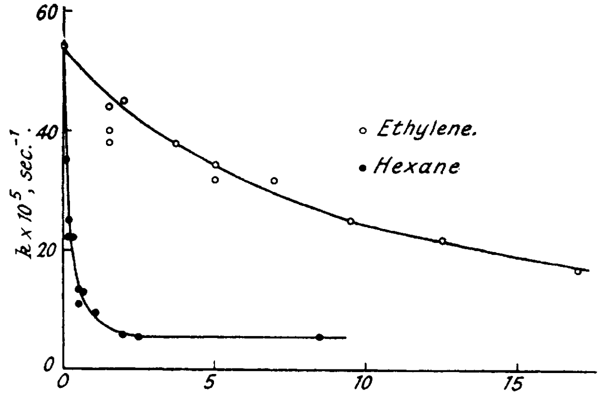


FIG. 11.



The inhibited decompositions were still first-order reactions, and the effect of a given quantity of propylene was found to be independent of the 1 : 2-dichloroethane pressure; *i.e.*, the decomposition rate of 1 : 2-dichloroethane is dependent on the absolute quantity of propylene present, not on the 1 : 2-dichloroethane/propylene ratio. This is similar to the effect of nitric oxide on the diethyl ether decomposition (Smith and Hinshelwood, *Proc. Roy. Soc.*, 1942, *A*, **180**, 237). The inhibitor gave no indication of being consumed during reaction; *e.g.*, with 0·1 mm. of propylene and 50 mm. of 1 : 2-dichloroethane the reaction followed first-order kinetics to beyond half-decomposition.

Considering the maximally inhibited reaction, a plot of $\log_{10} k$ against $1/T$, as shown in Fig. 10, gives a straight line from which an activation energy of 46 kcals. may be calculated. The appropriate rate equation is $k = 6{\cdot}3 \times 10^9 e^{-46,000/RT}$.

The effects of *n*-hexane and of ethylene in inhibiting the 1 : 2-dichloroethane decomposition have also been studied, the results being illustrated in Fig. 11. Both sets of hydrocarbon-inhibited experiments showed first-order kinetics. The behaviour of *n*-hexane was clearly similar to that of propylene and gave the same maximally inhibited rate, but the inhibiting action of ethylene was relatively slight and the experiments were not nearly so reproducible. With both inhibitors the rate was independent of the 1 : 2-dichloroethane pressure, and dependent only on the inhibitor pressure—behaviour identical with that shown by propylene.

In order to establish the homogeneity of the 1 : 2-dichloroethane decomposition, a reaction vessel identical with that used above was packed with glass tubing to give a three-fold increase in surface and a five-fold increase in the surface : volume ratio. It was coated in the same way as the empty reaction vessel in order to secure reproducible results. The rate of decomposition in this vessel was slightly greater than in the empty one, but otherwise identical in all respects. A plot of $\log_{10} k$ against $1/T$ (Fig. 4) gave exactly the same activation energy as the reaction in the empty vessel and followed the rate equation $k = 7{\cdot}5 \times 10^{10}e^{-47{,}000/\boldsymbol{R}T}$. There was, therefore, an 18% increase in reaction velocity. The errors in the measurements are indicated below :

Temp.	No. of runs.	Mean vel. const., sec.$^{-1}$ ($\times 10^5$).	Mean error of the mean vel. const. ($\times 10^5$).*	Temp.	No. of runs.	Mean vel. const., sec.$^{-1}$ ($\times 10^5$).	Mean error of the mean vel. const. ($\times 10^5$).*
389°	1	2·4	—	448°	7	44	±2·0
429	3	19·6	±0·3	460	11	65	±2·5
436	5	28·5	±1·7	464	6	91	±3
437	3	26·8	±0·4				

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

The addition of propylene to 1 : 2-dichloroethane in the packed vessel gave a maximally inhibited rate which was approximately twice that found in the empty vessel. Thus at 443·5° in the packed vessel the maximally inhibited rate was $5{\cdot}0 \times 10^{-5}$. The interpolated figure at this temperature for the empty vessel is $2{\cdot}9 \times 10^{-5}$. Packing thus increases the inhibited reaction by 75% whereas the normal reaction is only increased by 18%, from 30×10^{-5} to 35×10^{-5}.

A few experiments were made to ascertain the effect of nitrogen on the decomposition. Commercial " oxygen-free " nitrogen caused a great increase in rate owing to the presence of residual traces of oxygen, but, after these had been removed by contact with molten sodium for many hours, the nitrogen was found to exert a slight inhibiting effect, as shown below for experiments at 446°. The reactions showed good first-order kinetics at all nitrogen concentrations.

Press. of $CH_2Cl{\cdot}CH_2Cl$, mm.	—	50	25	100	50	60	40
Press. of N_2, mm.	0	20	20	100	60	80	160
$k \times 10^5$, sec.$^{-1}$	39·0	35·6	33·0	38·1	35·8	34·1	30·0

DISCUSSION.

The first point that must be established with regard to the experiments now recorded is that we have, indeed, been studying the non-induced decomposition of 1 : 2-dichloroethane and not a reaction caused by adventitious traces of oxygen (see preceding paper). The following are our reasons for rejecting such a hypothesis. First, although the reproducibility of individual runs was not completely satisfactory, the reproducibility of the average of a number of experiments was in good agreement for differently treated samples of 1 : 2-dichloroethane in different apparatus (of the same design) over a period of many months. Secondly, since oxygen is consumed in the induced decomposition, it would be anticipated that traces of oxygen would lead to reactions showing fast initial rates falling off rapidly to the true rate, whereas such behaviour has not been noted. Thirdly, it would be generally expected that the activation energy of the oxygen-induced reaction would be considerably less than that observed for comparable compounds not decomposing by a chain mechanism (see following paper). Fourthly, the most powerful argument of all, the oxygen-induced reaction is very strongly retarded by packing the vessel (see preceding paper), whereas in the experiments reported here such packing leads to a slight increase in rate.

The inhibiting properties of small amounts of propylene and *n*-hexane show that the decomposition must proceed by a radical-chain mechanism. This view is strongly supported by the temperature-dependent induction periods observed at the lower part of the temperature range employed. These induction periods of high activation energy (78 ± 10 kcals.) may be reconciled with that of the primary process in the chain. As primary steps the following deserve consideration :

$$\text{(A)}\quad CH_2Cl{\cdot}CH_2Cl \xrightarrow{k_1} C_2H_4 + Cl_2 \qquad E_A = 72 \text{ kcals.}$$

followed by

$$Cl_2 + C_2H_4Cl_2 \xrightarrow{k_1'} HCl + Cl + CHCl{\cdot}CH_2Cl$$

$$\text{(B)}\quad CH_2Cl{\cdot}CH_2Cl \xrightarrow{k_1} 2CH_2Cl{\cdot} \qquad E_A = 85 \text{ kcals.}$$

$$\text{(C)}\quad CH_2Cl{\cdot}CH_2Cl \xrightarrow{k_1} CH_2Cl{\cdot}CH_2{\cdot} + Cl \qquad E_A = 80 \text{ kcals.}$$

$$\text{(D)}\quad CH_2Cl{\cdot}CH_2Cl \xrightarrow{k_1} CH_2Cl{\cdot}CHCl{\cdot} + H \qquad E_A = 97 \text{ kcals.}$$

The required activation energies given for these processes have been computed as follows :

(A) Sherman, Quimby, and Sutherland (*J. Chem. Physics*, 1936, **4**, 732) calculated by the semi-empirical method that the activation energy for the addition of chlorine to ethylene was about 25 kcals. We have recalculated this constant using modern bond energies (see Appendix) and find it to be 28·7 kcals. Adding this to the exothermicity of the reaction, 43·7 kcals. (determined by direct measurement by Conn, Kistiakowsky, and Smith, *J. Amer. Chem. Soc.*, 1938, **60**, 2764), we obtain 72·4 kcals. for the required activation energy of the reverse step.

(B), (C), (D). These were calculated from the appropriate bond-energy values (see Appendix) on the very reasonable and customary assumptions that the reverse reactions do not require activation energy. Since these three primary steps demand considerably more activation energy than step (A), the latter is probably the correct one.* It leads to the radical-chain scheme below.

$$\begin{array}{lll}
\text{(i)}\ CH_2Cl{\cdot}CH_2Cl \xrightarrow{k_1} C_2H_4 + Cl_2 & & E_A = 72\ \text{kcals.} \\
\text{(i}'\text{)}\ Cl_2 + C_2H_4Cl_2 \xrightarrow{k_1'} HCl + Cl + CH_2Cl{\cdot}CHCl{\cdot} & & \\
\text{(ii)}\ Cl + C_2H_4Cl_2 \xrightarrow{k_2} HCl + CH_2Cl{\cdot}CHCl{\cdot} & & E_A = 5\ \text{kcals.} \\
\text{(iii)}\ CH_2Cl{\cdot}CHCl{\cdot} \xrightarrow{k_3} CH_2{:}CHCl + Cl & & E_A = 21{\cdot}5\ \text{kcals.} \\
\text{(iv)}\ Cl + CH_2Cl{\cdot}CHCl{\cdot} \xrightarrow{k_4} HCl + C_2H_2Cl_2 & & E_A = 3\ \text{kcals.}
\end{array}$$

The activation energy for step (ii) is undoubtedly small and, from strictly analogous reaction steps (Steacie, " Atomic and Free Radical Reactions ", A.C.S. Monograph 102, 1946, Chap. IX), it is taken as 5 kcals. The activation energy for step (iii) is computed as follows :

We have $C_2H_4 + H_2 \longrightarrow C_2H_6 + 32{\cdot}8$ kcals. (Conant and Kistiakowsky, *Chem. Rev.*, 1937, **20**, 181)

$$\begin{aligned}
&\longrightarrow + 2(C{-}H) - (H{-}H) - (C{=}C) \\
&\longrightarrow + 194{\cdot}8 - 103{\cdot}4 - (C{=}C)
\end{aligned}$$

whence $(C{=}C) = 58{\cdot}6$ kcals.

Also $C_2H_4 + Cl_2 \longrightarrow CH_2Cl{\cdot}CH_2Cl + 43{\cdot}7$ kcals. (see above)

$$\begin{aligned}
&\longrightarrow + 2(C{-}Cl) - (Cl{-}Cl) - (C{=}C) \\
&\longrightarrow + 2(C{-}Cl) - 57{\cdot}8 - 58{\cdot}6
\end{aligned}$$

whence $(C{-}Cl) = 80{\cdot}0$ kcals.

We have, therefore,

$$CH_2Cl{\cdot}CH_2Cl \longrightarrow C_2H_4Cl + Cl - 80{\cdot}0\ \text{kcals.}$$

and

$$CH_2Cl{\cdot}CH_2Cl \longrightarrow C_2H_4 + 2Cl - 43{\cdot}7 - 57{\cdot}8\ \text{kcals.}$$

whence, by subtraction,

$$C_2H_4Cl \longrightarrow C_2H_4 + Cl - 21{\cdot}5\ \text{kcals.}$$

The corresponding endothermicity for decomposition of the 1 : 2-dichloroethyl radical would not be very different from this figure, possibly a few kcals. less owing to the extra resonance energy in vinyl chloride. The activation energy for step (iv) must be less than that for step (ii) and is, therefore, assigned the value shown.

By setting up stationary states for Cl_2, $\cdot CHCl{\cdot}CH_2Cl$, and Cl in accordance with the above scheme and solving, we find

$$[\cdot CHCl{\cdot}CH_2Cl] = [CH_2Cl{\cdot}CH_2Cl]\ \sqrt{k_1k_2/k_3k_4}$$

and

$$[Cl] = \sqrt{k_1k_3/k_2k_4}$$

Hence the measured rate of reaction

$$\begin{aligned}
&= dp/dt = k_3[\cdot CHCl{\cdot}CH_2Cl] \\
&= [CH_2Cl{\cdot}CH_2Cl]\ \sqrt{k_1k_2k_3/k_4}
\end{aligned}$$

This predicts first-order kinetics, in agreement with experiment, and shows that the overall energy of activation should be $\frac{1}{2}(E_1 + E_2 + E_3 - E_4) = \frac{1}{2}(72 + 5 + 22 - 3) = 48$ kcals., in close agreement with the experimental value of 47 kcals.

---

* It should be pointed out that mechanism (A) is only valid provided that the activation energy for step (i′) is not so high that the concentration of molecular chlorine, in the stationary state, becomes significant. If it should subsequently be shown that mechanism (B) requires about 15 kcals. less activation energy than that for the rupture of the C–C bond in ethane, then (B) would be preferred. Mechanism (C) seems excluded because any decrease in activation energy would be compensated by an increase in step (iii) in the chain sequence.

It is possible to set up radical-chain mechanisms without difficulty from the other alternative primary processes. All these lead to rate equations of the type

$$\text{rate} = [\mathrm{CH_2Cl{\cdot}CH_2Cl}]\sqrt{k_1k_2k_3/k_4}$$

similar to the scheme above. The calculated overall activation energies are 54·5, 52, and 59·5 kcals. for (B), (C), and (D), respectively; (D) is excluded on this basis, but (B) and (C) remain a possibility.

Mechanism (A) being accepted for the 1 : 2-dichloroethane decomposition, it is possible to compute the chain length; thus for 477° (750° K.) :

$$\text{Chain length} = \frac{k_2\,[\mathrm{CH_2Cl{\cdot}CH_2Cl}]}{k_4\,[\mathrm{{\cdot}CHCl{\cdot}CH_2Cl}]} = \sqrt{\frac{k_2k_3}{k_1k_4}}$$

$$\text{Hence}\quad \frac{\text{chain length}}{k} = \sqrt{\frac{k_2k_3}{k_4k_1}}\bigg/\sqrt{\frac{k_1k_2k_3}{k_4}} = 1/k_1$$

$$\text{Therefore chain length} = k \times 10^{-13}e^{72{,}000/RT} = 9{\cdot}8 \times 10^4 \text{ at } 477^\circ$$

In the latter calculation it is only assumed that the non-exponential term of the rate equation for the initial rupture of the molecule has the normal value of 10^{13}. Too much precision should not, however, be claimed for this calculation for an error of a factor of 10 in this non-exponential term and of 5 kcals. in E_1 would alter the value of $9{\cdot}8 \times 10^4$ by a factor of 270. The experiments with propylene as inhibitor support the view that the chain length must be at least 500, since even at the lowest concentrations (0·1 mm.) of inhibitor there was no indication of the consumption of the propylene during the course of the experiment.

The inhibition experiments with propylene lend themselves to quantitative analysis. Since the rate is dependent only on the propylene concentration, the inhibitor must be destroying a chain-carrying species which is *not* involved in reaction with 1 : 2-dichloroethane. This can only be the case if the radical destroyed is the 1 : 2-dichloroethyl radical, *i.e.*,

$$\text{(v)}\quad \mathrm{{\cdot}CHCl{\cdot}CH_2Cl + CH_3{\cdot}CH{:}CH_2 \xrightarrow{k_5} CHCl{:}CH_2 + HCl + {\cdot}CH_2{\cdot}CH{:}CH_2}$$

The formulation of this step is supported by its approximate thermoneutrality and especially by the fact that the inhibiting behaviour of propylene in the reaction is so very different from that in reactions where the inhibiting step is thought to be radical addition to the olefinic linkage. The fate of the resonance-stabilised allyl radical is not important provided it disappears by dimerisation, as is likely, or by reaction with a further 1 : 2-dichloroethyl radical.

Granted the correctness of this chain-terminating step, then analysis by the stationary-state method leads to

$$\begin{aligned} \mathrm{d}p/\mathrm{d}t &= k_3[\mathrm{{\cdot}CHCl{\cdot}CH_2Cl}] \\ &= k_3[\mathrm{CH_2Cl{\cdot}CH_2Cl}]\left\{\frac{-\dfrac{k_2}{k_4}\cdot k_5[\mathrm{P}] + \sqrt{\left(\dfrac{k_2}{k_4}\cdot k_5[\mathrm{P}]\right)^2 + 8k_1\cdot\dfrac{k_2}{k_4}(k_5[\mathrm{P}] + 2k_3)}}{2(k_5[\mathrm{P}] + 2k_3)}\right\} \end{aligned}$$

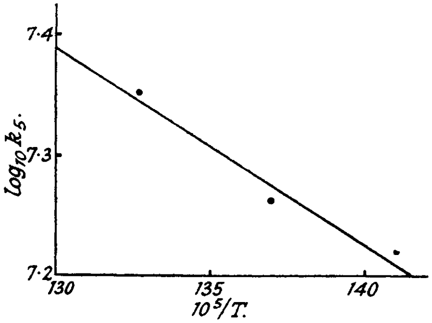
where [P] represents the concentration of propylene in suitable units. In agreement with experiment the rate is first-order with respect to 1 : 2-dichloroethane and the rate constant is a function only of the propylene concentration as variable.

From the treatment of chain length given above it will be clear that k_3, k_2/k_4, and k_1 can be calculated at a given temperature from the data for the non-inhibited reaction. If these constants are inserted in the inhibited-rate equation and suitable values of k_5 selected, then a very close fit to the experimental data is obtained. The full lines in Figs. 7, 8, and 9 have been drawn by taking the values of k_5 given below. A plot of $\log_{10} k_5$ against $1/T$ gives a good straight line (Fig. 12) from which one can deduce the rate equation $k_5 = 3{\cdot}4 \times 10^9e^{-7{,}500/RT}$, where k_5 is in (g.-mol./l.)$^{-1}$ sec.$^{-1}$. The non-exponential term is in agreement with that normal for bimolecular reactions, and the activation energy has the anticipated value.

The experiments using ethylene as inhibitor give further support to our view that the radical-destroying action of propylene is as formulated above and *not* addition to the ethylenic linkage. From the curve for the ethylene-inhibited reaction shown in Fig. 11 it is easily calculated, on the assumption that the non-exponential term in the bimolecular rate equation is the same for both propylene and ethylene, that the activation energy of the radical-destroying step is the reasonable one of about 15 kcals.

The experiments with *n*-hexane, which gave the same maximally inhibited rate as that observed with propylene, provide further evidence that this rate is due to the (partly heterogeneous) decomposition of 1 : 2-dichloroethane by a non-chain and doubtless non-radical mechanism.

FIG. 12.



Temp.	$k' \times 10^4$,* secs.$^{-1}$.	$k_1 \times 10^{10}$,† secs.$^{-1}$.	$k_3 \times 10^{-6}$,‡ sec.$^{-1}$.	$\left(\frac{k_2}{k_4}\right) \times 10^5$. §	$k_5 \times 10^{-7}$, sec.$^{-1}$.
437°	2·10	6·85	3·43	1·88	1·65
457	5·22	27·7	5·16	1·91	1·83
480	14·1	126	8·03	1·96	2·23

* This k' is the rate constant for the unhibited reaction *less* the rate constant for the maximally inhibited reaction at the same temperature. It is, in fact, the rate constant for that part of the decomposition which proceeds by a chain mechanism.

† Calculated from the equation $k_1 = 10^{13}e^{-72,000/RT}$.

‡ Calculated from the equation $k_3 = 10^{13}e^{-21,000/RT}$.

§ Calculated from the relationship $(k_2/k_4) = k'^2/k_1k_3$. Theoretically (k_2/k_4) should vary as $e^{-2,000/RT}$ and should have a value of approximately $2{\cdot}5 \times 10^{-1}$ over this temperature range. The discrepancy here is due to the fact that the product of the non-exponential terms of the chain steps does not have the theoretical value of $(10^{13})^2$ but is actually $(6{\cdot}4 \times 10^{10})^2$. The method of calculation used here places all this discrepancy on the ratio of the non-exponential terms of the two bimolecular steps This is possibly justified because of the reasonable interpretation of the inhibited reaction which is thereby obtained.

APPENDIX.

It is well known that the cause of the present uncertainty regarding bond energies in organic molecules is lack of knowledge of the latent heat of sublimation of carbon. Long and Norrish (*Proc. Roy. Soc.*, 1946, *A*, **187**, 337) have recently reviewed the subject and have advanced arguments in favour of the " high values " for the C–H bond energy in methane. Their conclusions are in agreement with bond energies determined by kinetic methods by Kistiakowsky and his collaborators (Andersen, Kistiakowsky, and Van Artsdalen, *J. Chem. Physics*, 1942, **10**, 305; Van Artsdalen, *ibid.*, p. 653; Andersen and Kistiakowsky, *ibid.*, 1943, **11**, 6; Andersen and Van Artsdalen, *ibid.*, 1944, **12**, 479; Kistiakowsky and Van Artsdalen, *ibid.*, p. 469) and by Polanyi and his associates (Butler and Polanyi, *Nature*, 1940, **146**, 129; *Trans. Faraday Soc.*, 1943, **39**, 19; Baughan and Polanyi, *Nature*, 1940, **146**, 685; *Trans. Faraday Soc.*, 1941, **37**, 648; Baughan, *Nature*, 1941, **147**, 542; Baughan, Evans, and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377). They are also in agreement with the bond energies determined by electron impact by Stevenson (*J. Chem. Physics*, 1942, **10**, 291; *J. Amer. Chem. Soc.*, 1943, **65**, 209; Stevenson and Hipple, *ibid.*, 1942, **64**, 1588, 2766; Hipple and Stevenson, *Physical Rev.*, 1943, **63**, 121). In this paper the averages of the bond energies given by the last three groups of authors have been employed for the C–H, C–C, and C=C bonds. Other bond energies were taken from Pauling (" The Nature of the Chemical Bond ", Cornell Univ. Press, 1942, p. 53). Fundamental vibrational frequencies used in the activation-energy calculations were taken from Herzberg (" Molecular Spectra ", Vol. I, Prentice-Hall Inc., 1939; Vol. II, D. Van Nostrand Co., 1945). The method of calculation was as outlined by Daniels (" Chemical Kinetics ", Cornell Univ. Press, 1938, pp. 220 *et seq.*).

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