35. The Kinetics of the Dehydrochlorination of Substituted Hydrocarbons. Part I. Induced Dehydrochlorination.

By D. H. R. Barton.

The rates of dehydrochlorination of substituted ethanes in the presence of small amounts of oxygen or chlorine have been studied by a flow method using clean-walled glass tubes. Although the decomposition rates of 1 : 2-dichloroethane, 1 : 1 : 2-trichloroethane, and 1 : 1 : 2 : 2-tetrachloroethane are enormously increased by such additions, there is relatively no effect with the rest of the chlorinated ethanes. The mechanisms of these processes are of the radical-chain type.

During a comprehensive investigation of possible improvements in methods of manufacture of vinyl chloride (Barton, Ph.D. Thesis, London, 1942) it was felt desirable to examine the effect of various volatile substances on the rate of the thermal decomposition of 1 : 2-dichloroethane. Biltz and Küppers (*Ber.*, 1904, **37**, 2398) had previously studied this reaction, without intentional addition of " catalyst," and, although they had obtained peculiar and irreproducible results, had been able to establish that the main products of the reaction were vinyl chloride and hydrogen chloride. It has now been found that highly purified 1 : 2-dichloroethane has its decomposition rate greatly increased by small amounts of oxygen or chlorine. The presence of the former element must be held responsible for the erratic results of the German authors.

1 : 2-Dichloroethane purified only by fractional distillation always contains ethylene chlorohydrin, for this substance is normally present in the technical material and forms an azeotrope with pure 1 : 2-dichloroethane (Kaplan, Grishin, and Skvortsova, *J. Gen. Chem. Russia*, 1937, **7**, 538). This ethylene chlorohydrin is, like other alcohols, an inhibitor of the oxygen-induced decomposition. Its presence explains the reproducibility which we obtained in initial experiments without intentional addition of " catalyst " as compared with the difficulties encountered by Biltz and Küppers (*loc. cit.*).

Experimental.

Dehydrochlorination without Addition.

Apparatus.—All reactions were studied by streaming the vapour of the chloro-compound under investigation at a constant rate through hard-glass combustion tubes of 1·1 cm. internal diameter unless specified to the contrary. The tubes were 90 cm. in length of which 75 cm. were heated in an electric furnace inclined at a slight angle to the horizontal. The temperature of the reaction vessel was roughly uniform over a length of 60 cm. and all calculations of rate constants are based on this length. Temperatures were measured with a calibrated base-metal thermocouple placed 20 cm. from the exit end of the furnace. Preliminary experiments showed that there was little difference between temperatures measured inside or outside the vessel, and the latter alternative was chosen for all the experiments recorded in this paper. A clean reactor was employed for each of the series of experiments described below. Complete details of the apparatus and methods have been given by the author (*loc. cit.*).

Materials and Reaction Products.—(i) *Ethyl chloride.* Material purchased as " pure for anæsthesia " was employed, with a flow rate of 8·8 g./hr. Sole reaction products up to 550° were ethylene and hydrogen chloride.

(ii) 1 : 1-*Dichloroethane* (*ethylidene dichloride*). This was prepared by treating paraldehyde with phosphorus pentachloride, and purified by shaking out with concentrated sulphuric acid or aqueous acid permanganate followed by fractional distillation; b. p. 58·0—58·7°. Flow rate, 45 g./hr. Sole reaction products up to 500° were vinyl chloride and hydrogen chloride.

(iii) 1 : 2-*Dichloroethane* (*ethylene dichloride*). Purified by fractional distillation, this had b. p. 83·5—83·7°. Flow rate, 27 g./hr. Up to 500° insignificant amounts of acetylene were formed and the sole reaction products were vinyl chloride and hydrogen chloride.

(iv) 1 : 1 : 2-*Trichloroethane.* This was prepared by addition of chlorine to vinyl chloride, antimony trichloride being used as catalyst, and purified by shaking out ten times with its own volume of water, followed by fractional distillation; b. p. 113·0—113·5°. Flow rate, 31 g./hr. The sole reaction products up to 500° were *cis*- and *trans*-1 : 2-dichloroethylene, 1 : 1-dichloroethylene (vinylidene dichloride), and hydrogen chloride. The molar ratio of 1 : 1-dichloroethylene to *cis*- and *trans*-1 : 2-dichloroethylene was about 4 : 1 : 1.

(v) 1 : 1 : 1 : 2-*Tetrachloroethane.*—Prepared by addition of hydrogen chloride to trichloroethylene in the presence of aluminium trichloride (Prins, *Rec. Trav. chim.*, 1926, **45**, 80), and purified by shaking out with concentrated sulphuric acid followed by fractional distillation, this had b. p. 129·0°. Flow rate, 39 g./hr. Sole reaction products up to 450° were trichloroethylene and hydrogen chloride.

(vi) 1 : 1 : 2 : 2-*Tetrachloroethane* (*acetylene tetrachloride*). Purified as for (v) above; b. p. 146—147°. Flow rate, 30 g./hr. The sole reaction products up to 400° were trichloroethylene and hydrogen chloride.

(vii) *Pentachloroethane.*—Purified by shaking out with concentrated sulphuric acid followed by fractional distillation in a vacuum. Flow rate, 26 g./hr. The sole products up to 450° were perchloroethylene and hydrogen chloride.

(viii) 1 : 2-*Dichloropropane* (*propylene dichloride*). Purified by shaking out with concentrated sulphuric acid or with dilute sodium hydroxide solution followed by fractional distillation; b. p. 96·5—96·6°. Flow rate, 32 g./hr. Up to 450° the sole reaction products were monochlorinated propenes (chiefly 1-chloro-) and hydrogen chloride in equivalent amounts, together with some allyl chloride.

(ix) 2 : 3-*Dichlorobutane.* Purified as for (iv) above; b. p. 116·0—116·7°. Flow rate, 42 g./hr.

(x) 1-*Chloroethylbenzene.* A pure specimen was supplied by the Distillers Co. Ltd. Flow rate, 18 g./hr. The sole reaction products up to 400° were styrene and hydrogen chloride.

(xi) 2-*Chloroethylbenzene.* Prepared from 2-phenylethyl alcohol by treatment with thionyl chloride. Purified by shaking out 10 times with its own volume of water followed by fractional distillation in a vacuum. Flow rate, 24 g./hr. Reaction products up to 500° as for (x).

Results.—In order to calculate first-order velocity constants in dynamic experiments it is necessary to know the contact times. Since, in all the dehydrochlorinations studied, one mol. of reactant gives rise to 2 mols. of products, t, the average contact time, may be defined by

$$t = \frac{lA \times 3{\cdot}6 \times 273}{m \times 22{\cdot}4} \times \frac{1}{T(1 + \frac{1}{2}a)}$$

where l = length of the reaction vessel in cm. (60 cm.), A = cross-sectional area of vessel (in c.c.), m = input of chloride in g.-mol./hr., T = temperature of vessel (in °K.), and a = " degree of dissociation " of the chloride at the exit end of the furnace.

First-order velocity constants can then be calculated by the equation $k = (1/t)\log_e a/(a - x)$, where the symbols have the usual significance. All k values in this paper are in terms of sec.$^{-1}$ and have been calculated, unless specified to the contrary, on the assumption that the hydrogen chloride produced in the reaction is a mol. for mol. measure of the extent of the reaction. As will be seen from the results given above, this is experimentally justified.

A series of experiments with 1 : 2-dichloroethane using, in this case only, a 1·5 cm. internal diameter Pyrex glass tube, at 570° gave a satisfactory first-order constant as will be seen from the following results :

Flow rate, g. of $C_2H_4Cl_2$ per hr.	61	55	40	29	26
Conversion of $C_2H_4Cl_2$ into C_2H_3Cl, % *	24	26	32	39	45
t, secs.	10·0	10·9	16·2	19·6	21·2
k, sec.$^{-1}$	0·030	0·030	0·027	0·029	0·032

* Calculated by direct observation of the volume of liquid vinyl chloride produced.

The activation energy for the 1 : 2-dichloroethane decomposition was obtained in the usual manner by plotting $\log_{10} k$, calculated as above, against the reciprocal of the absolute temperature (Fig. 1). In view of the fact that a very large temperature range was covered (250°) the straight-line plot obtained must be regarded as satisfactory. Data obtained for some of the other compounds studied are conveniently summarised in a similar way in Figs. 2, 3, and 4.

In the pyrolysis of organic compounds in clean-walled vessels it is often impossible to secure reproducibility. Results to be published in later Parts of this series show that this difficulty is also observed in the compounds investigated here when the decompositions are studied by static means. In the present dynamic experiments, where all results were obtained in a given vessel within a few days and where the measurements were not very precise, such effects were not noted.

Fig. 1.

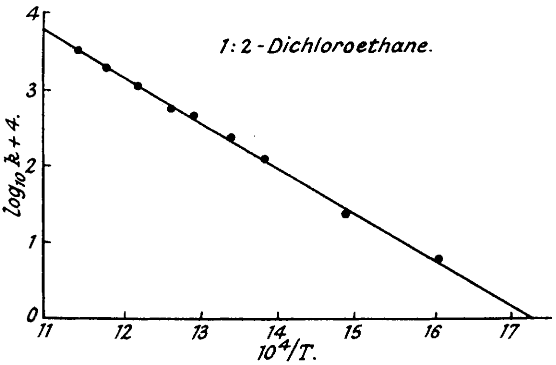


Fig. 2.

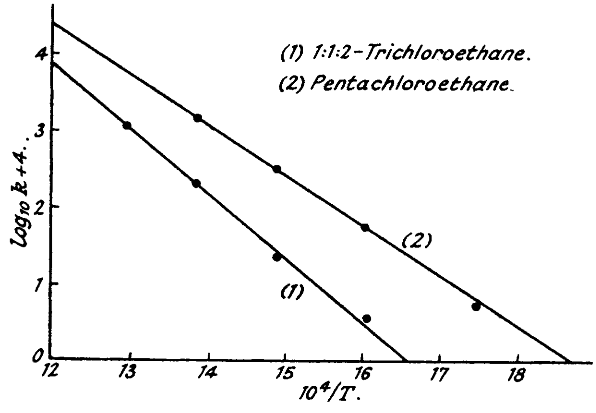


Fig. 3.

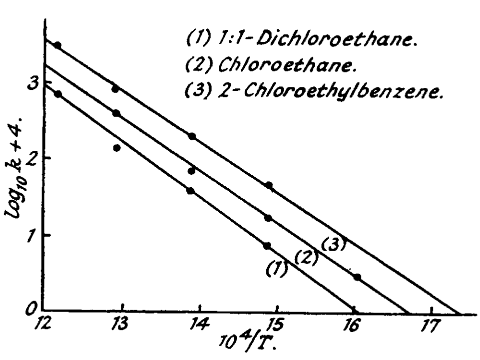
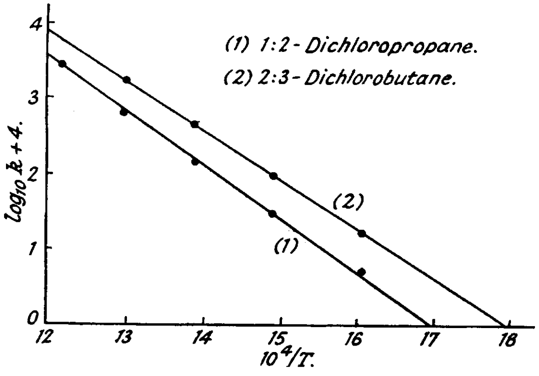


Fig. 4.



The results are conveniently summarised in terms of the appropriate first-order rate equation $k = Be^{-E_A/RT}$ as shown in Table I.

Induced Dehydrochlorination.

The apparatus employed was as indicated above but with suitable modification to admit " catalyst " and/or inhibitor vapours. When necessary a slow carrier stream of nitrogen was used for this purpose.

TABLE I.

Compound.	*B*.	E_A (cals.).	Compound.	*B*.	E_A (cals.).
Ethyl chloride	$3{\cdot}80 \times 10^7$	32,000	Pentachloroethane ...	$8{\cdot}13 \times 10^7$	29,200
1 : 1-Dichloroethane ...	$5{\cdot}89 \times 10^7$	33,900	1 : 2-Dichloropropane	$1{\cdot}62 \times 10^8$	34,200
1 : 2-Dichloroethane ...	$1{\cdot}59 \times 10^6$	27,100	2 : 3-Dichlorobutane	$5{\cdot}13 \times 10^7$	30,400
1 : 1 : 2-Trichloroethane	$5{\cdot}50 \times 10^9$	38,000	2-Chloroethylbenzene	$1{\cdot}00 \times 10^8$	32,300

In every case the percentage conversion was determined by titration of the hydrogen chloride produced. The accuracy of this simple technique follows from the experiments above and it was further checked in appropriate places.

Preliminary experiments on the effect of adding various substances, in a concentration of 0·5% by weight, to 1 : 2-dichloroethane before passage through the furnace indicated that halogenating and oxidising agents might prove of interest for inducing the decomposition. Experiments with oxygen itself were initially irreproducible until it was realised that the past history of the 1 : 2-dichloroethane was of great importance. This compound had always been purified from the technical material by fractional distillation, and there was only slight indication of an oxygen-induced reaction when it was passed through the reaction vessel. However, 1 : 2-dichloroethane recovered from such experiments and purified by further fractional distillation showed quite different reactivity, a marked decomposition being induced by the addition of oxygen. This suggested that an " inhibitor " was removed during the first passage of the 1 : 2-dichloroethane–oxygen mixture, which suggestion was, indeed, confirmed by experiments summarised in Table II. These experiments refer to a reactor temperature of 350° and a flow rate of 39 g. of 1 : 2-dichloroethane per hour mixed with 0·5% by weight of oxygen. Without the addition of oxygen no reaction could be detected.

TABLE II.

Method of purification of technical $CH_2Cl{\cdot}CH_2Cl$.*	Conversion into $CH_2{:}CHCl$, %.				
	Fract. I, b. p. <83·5°.	Fract. II, b. p. 83·5—83·6°.	Fract. III, b. p. 83·6—83·7°.	Fract. IV, b. p. >83·7.	Before fractionation.
A	13	50	58	18	15
B	14	48	58	18	15
C	14	51	58	22	18
D	29	—	60	18	16
E	13	54	56	18	1
F	—	53		—	10 †

* *Methods of purification :* (A) Refluxed with excess of alkaline $KMnO_4$, steam-distilled, dried ($CaCl_2$), and fractionated. (B) Refluxed with excess of aqueous CrO_3; steam-distilled, dried ($CaCl_2$), and fractionated. (C) Shaken for 12 hours with its own vol. of 2N-NaOH, washed, dried ($CaCl_2$), and fractionated. (D) Shaken with one-half its own vol. of conc. H_2SO_4, washed, dried ($CaCl_2$), and fractionated. (E) Shaken ten times with its own vol. of water, dried ($CaCl_2$), and fractionated. (F) Purified by fractional distillation (b. p. 83·5—83·7°); treated as in (A), above.

† Before treatment with alkaline $KMnO_4$.

Oxygen-induced Decomposition of 1 : 2-*Dichloroethane.*—In the experiments described below a flow-rate of 39 g. of 1 : 2-dichloroethane per hour, a reaction temperature of 350°, and an oxygen concentration of 0·5% by weight were employed unless specified to the contrary. In general, 1 : 2-dichloroethane purified as in Table II was used.

(a) *Inhibitors of the reaction.* The results recorded in Table II suggested that the inhibitor in the main 1 : 2-dichloroethane fractions was probably an alcohol. It was identified as ethylene chlorohydrin from the chloride-ion concentration produced on shaking the fractionated 1 : 2-dichloroethane with dilute sodium hydroxide solution, and from the determination by Deckert's reagent of the ethylene oxide thus produced (Deckert, *Z. anal. Chem.*, 1930, **82**, 297; 1937, **109**, 166; see also Lubatti, *J. Soc. Chem. Ind.*, 1932, **51**, 361; 1935, **54**, 424; Kerckov, *Z. anal. Chem.*, 1937, **108**, 249). The chloride-ion concentration was equivalent to 0·27% by weight of ethylene chlorohydrin, a figure which was in agreement with that (0·27%) obtained by determination of the ethylene oxide. The inhibitors in the first runnings were probably aliphatic hydrocarbons, including a major proportion of olefinic hydrocarbons, and in the still residues probably saturated hydrocarbons.

Chlorinated hydrocarbons may also have been present as is shown by the experiments with various inhibitors recorded in Table III. The qualitative nomenclature in this table is as follows: strong inhibitors (*s*) completely suppressed the reaction at 0·1—0·01% concentration by weight, medium inhibitors (*m*) reduced the rate to about one-fifth of its usual value over the same concentration range, and weak inhibitors (*w*) behaved in a similar manner to ethylene chlorohydrin (see above); lack of inhibiting action is indicated by 0.

(b) *Effect of packing the reaction vessel.* Packing the vessel with glass scrap to only four times the surface area caused almost complete suppression of the reaction. This is illustrated by the following data :

Reaction vessel (1·1 cm. internal diam.).	1 : 2-Dichloroethane.	Conversion, %.	
		Without packing.	With packing.
Combustion tubing	As in table on p. 149 before complete purification	10	0
Pyrex	Partly freed from inhibitors	42	2

TABLE III.

Inhibitors.	Inhibiting action.
(Water.)	0
Hydrocarbons.	
Ethylene	*m*
Benzene	*w*
Toluene	*s*
n-Hexane	*s*
*cyclo*Hexane	*s*
*cyclo*Hexene	*s*
Ketones.	
Methyl ethyl	*m*
*cyclo*Hexanone	*m*
Ethers.	
Diethyl	*m*
Dioxan	*m*
Acids and derivatives.	
Acetic acid	0
Acetyl chloride	0
Acetonitrile	0
Benzoyl chloride	0
Alcohols.	
Methyl	*s*
Ethyl	*s*
n-Propyl	*s*
*iso*Propyl	*s*
Aldehydes.	
Acetaldehyde	*m*
Crotonaldehyde	*m*
Nitrogenous bases.	
Ammonia	0
Diethylamine	*s*
Aniline	0
Pyridine	0
Chlorinated aliphatic hydrocarbons.	
1 : 1-Dichloroethane	*w*
2 : 3-Dichlorobutane	*m*
n-Amyl chloride	*m*

(c) *The effect of varying oxygen concentration.* Smaller concentrations of oxygen than 0·5% by weight gave smaller values for percentage conversions. Higher concentrations of oxygen also led to a falling off in reaction rate. The results are summarised in Fig. 5.

FIG. 5.

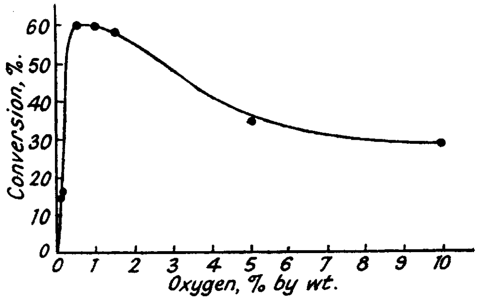
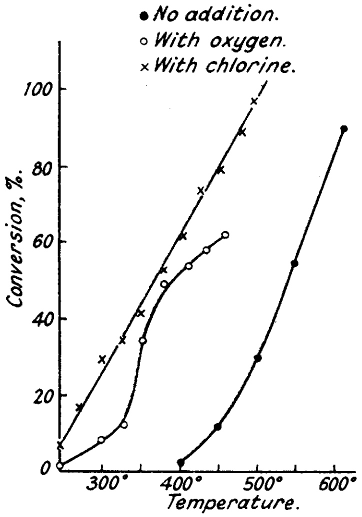


FIG. 6.



(d) *Variation of percentage conversion with temperature.* The results are summarised in Fig. 6. The 1 : 2-dichloroethane was not quite so pure as that employed in previous experiments and gave only 37% conversion at 350°.

(e) *Variation of percentage conversion with vessel diameter.* Since it has been shown under (b) above that the walls of the vessel have a pronounced chain-breaking effect, it would be expected that, for a constant linear streaming velocity of 1 : 2-dichloroethane, higher percentage conversions should be obtained with wide than with narrow vessels. This view is confirmed by the data below, which relate to vessels of Pyrex glass.

Reaction vessel.				
Internal diam., cm.	Cross-sectional area, sq. cm.	Flow rate, g./hr.	Flow rate/cross-sectional area, g. hr.$^{-1}$ cm.$^{-2}$.	Conversion, %.
0·90	0·64	25	40	28
1·10	0·95	39	41	46
1·40	1·54	64	42	50

Chlorine-induced Decomposition of 1 : 2-*Dichloroethane.*—In all the experiments described below a flow rate of 39 g. of 1 : 2-dichloroethane per hour, a temperature of 350°, and a chlorine concentration of 0·5% by weight were employed unless specified to the contrary. All results are corrected for the hydrogen chloride produced from the added chlorine itself. 1 : 2-Dichloroethane purified as in Table II was used unless stated otherwise.

(a) *The effect of varying chlorine concentration.* The experiments are summarised in Fig. 7. In comparison with the oxygen-induced decomposition chlorine is effective at much lower concentrations.

(b) *Variation of reaction rate with contact time.* The results are summarised in Table IV. On calculation of first-order velocity constants a fairly satisfactory result was obtained for dynamic experiments of this type.

TABLE IV.

Flow rate, g. $C_2H_4Cl_2$/hr.	17	22	25	26	30	42	54	81
Conversion, %	67	64	62	61	60	53	43	26
Contact time, secs.	22·5	17·2	15·4	14·8	12·8	9·3	7·4	5·6
k, sec.$^{-1}$	0·049	0·059	0·063	0·064	0·072	0·081	0·076	0·054

(c) *Variation of percentage conversion with temperature.* Results in these experiments are summarised in Fig. 8 in the form of a $\log_{10} k$–$1/T$ plot, where k is the first-order velocity constant in sec.$^{-1}$. From the slope the apparent activation energy is 12,200 cals. A comparative plot is also given in Fig. 6 of percentage conversion against temperature.

FIG. 7.

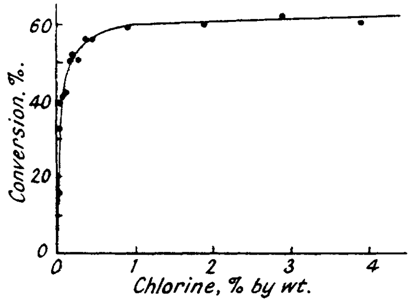
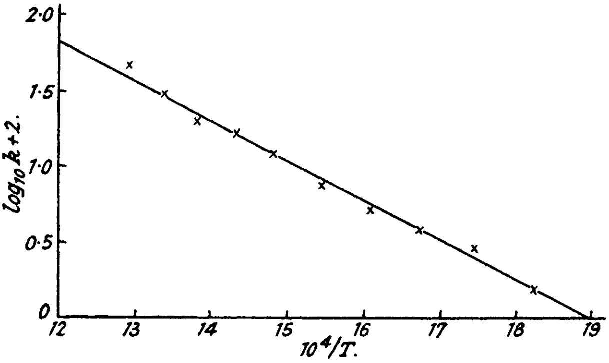


FIG. 8.



(d) *Effect of packing the reaction vessel.* As with the oxygen-induced reaction, packing of the vessel, in this case to give only twice the surface area, caused a remarkable inhibition of the reaction. This is shown by the data below (a flow rate of 32 g./hr. of only partly purified 1 : 2-dichloroethane was used) :

	Conversions, %.			Conversions, %.	
Vessel temp.	Unpacked vessel.	Packed vessel.	Vessel temp.	Unpacked vessel.	Packed vessel.
310°	21	1	350°	36	12

(e) *Variation of percentage conversion with diameter of vessel.* It would be anticipated, in view of the experiments with packed vessels, that similar results would be obtained on varying the diameter of the vessel, with constant linear streaming velocity, as with the oxygen-induced reactions. The data in Table V show that this was, indeed, the case, soft-glass reactors being used.

TABLE V.

Reaction vessel.				
Internal diam., cm.	Cross-sectional area, sq. cm.	Flow rate, g./hr.	Flow rate/cross-sectional area, g. hr.$^{-1}$ cm.$^{-2}$.	Conversion, %.
2·00	3·14	129	41	63
1·60	2·01	82	41	58
1·40	1·54	64	41	55
1·10	0·95	39	41	52
0·90	0·64	26	41	49

(f) *Comparison of chlorine with other halogens.* The results obtained with 1 : 2-dichloroethane which had not been completely freed from inhibitors (flow rate, 32 g./hr.) are summarised below (M = mol. wt. of halogen). The almost complete inertness of iodine will be noted.

Halogen.	Concn., % by wt.	Conversion, %.	Conversion (%) × M/1000.
Chlorine	0·5	44	3·1
Bromine	0·5	33	5·3
Iodine	0·5	1	0·2

The Effect of Oxygen and Chlorine in inducing the Decomposition of Other Chlorinated Hydrocarbons.—The inducing action of oxygen and chlorine is by no means universal in the chlorinated ethane series, and the remarkable enhancement of reaction rates seen with 1 : 2-dichloroethane has been observed only with 1 : 1 : 2-trichloro- and 1 : 1 : 2 : 2-tetrachloro-ethane amongst other chlorinated ethanes. Fig. 6 summarises the position with regard to 1 : 2-dichlorethane, and Fig. 9 shows the corresponding conversion–temperature relationship for 1 : 1 : 2-trichloroethane. Pentachloroethane is a typical example (Fig. 10) of a substance whose decomposition rate is scarcely influenced by the addition of oxygen.

The possibility arises that the differences in reactivity observed with the chlorinated ethanes may be due to inhibitors (compare the experiments with 1 : 2-dichloroethane recorded above), but all reasonable precautions were taken to eliminate such contaminants. A special test case was made with 1 : 1-dichloroethane, which was purified repeatedly with concentrated sulphuric acid, sodium hydroxide solution, and alkaline permanganate without altering in any way its decomposition rate in the presence of oxygen.

A comparison of the behaviour of the 1- and 2-chloroethylbenzene was of some theoretical interest. Whilst the decomposition rate of the former isomer was not altered by the addition of oxygen, that of the other was increased over the higher temperature range, as shown in Fig. 11.

FIG. 9.

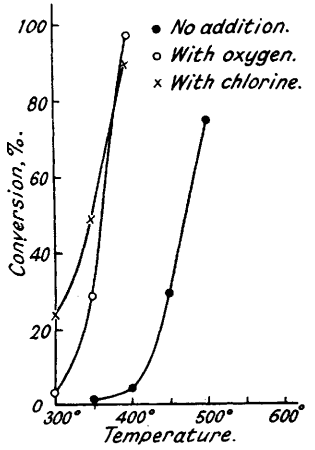


FIG. 10.

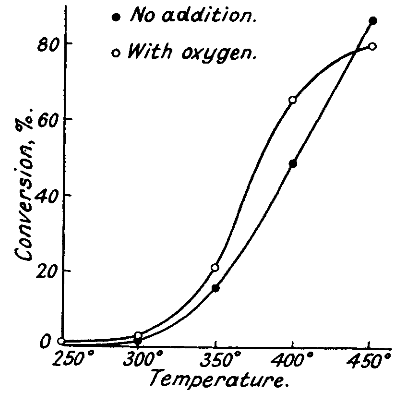
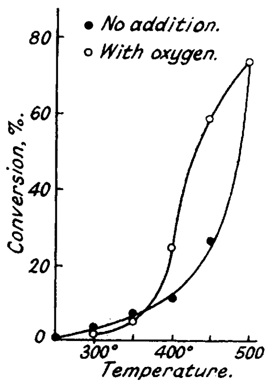


FIG. 11.



DISCUSSION.

The oxygen-induced decomposition of 1 : 2-dichloroethane must be of the radical-chain type. This is shown by the great increase in rate caused by only small additions of oxygen and by the extreme susceptibility of the induced reaction to inhibitors. The reaction chains must be broken at the walls, as is demonstrated by the inhibition observed on packing the reactor and by the increase in reaction rate noted as the diameter of the reactor is increased whilst preserving a constant contact time (compare Semenoff, " Chemical Kinetics and Chain Reactions ", Oxford Univ. Press, 1935, pp. 462 *et seq.*). The same conclusion must be reached with regard to the chlorine-induced reaction, where extremely small amounts of chlorine cause a marked increase in reaction rate and where a similar inhibition is produced by packing the reaction vessel or by reducing its diameter.

It has not, as yet, been ascertained whether the other induced decompositions show the same experimental criteria of radical-chain reactions, but it seems highly probable that this will prove to be the case. With regard to chlorinated hydrocarbons other than derivatives of ethane, the position is doubtless complicated by the possibility of part of the substrate molecule itself acting as an inhibitor for the chain type of reaction. Extensive inhibition studies have not been made with chlorine-induced reactions, but for the oxygen-induced decomposition of 1 : 2-dichloroethane all aliphatic and alicyclic hydrocarbons are strong inhibitors. It is understandable, therefore, that the pyrolysis of, say, *n*-amyl chloride is not influenced by the addition of oxygen (Barton, *loc. cit.*).

It should be pointed out that the relationship between the iodine-catalysed decomposition of organic substances discovered by Hinshelwood and his collaborators (see Hinshelwood, " Kinetics of Chemical Change ", Oxford Univ. Press, 1940, p. 243) and the halogen-induced reactions reported here is only superficial. The efficiency of iodine over chlorine and bromine in inducing the decomposition of, *e.g.*, acetaldehyde is due to its ease of dissociation into the atomic form, but with, *e.g.*, 1 : 2-dichloroethane, iodine is almost without effect and chlorine and bromine are much superior. Nevertheless, the halogen-induced reactions of chlorinated hydrocarbons may still proceed by a mechanism involving chlorine atoms.

The detailed mechanism of these chain reactions will be discussed in a further communication.

This work was carried out during 1940 and 1941 in the Department of Organic Chemistry, Imperial College, under the supervision of Professor Sir Ian Heilbron, D.S.O., F.R.S., to whom I wish to express my grateful thanks. I am also indebted to Drs. M. Mugdan and H. M. Stanley, of the Distillers' Company, for much helpful advice and criticism and to the Directors of that Company for financial assistance and permission to publish this paper. The industrial application of the results recorded is covered by B.PP. 573,532 and 573,559.

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