The Pyrolysis of Chloroalkenes. Part II.* Trichloroethylene.

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Trichloroethylene decomposes in the temperature range 385—445° and in vessels whose walls are covered with a carbonaceous layer by simultaneous homogeneous radical-chain and bimolecular mechanisms. The final reaction products are hydrogen chloride and hexachlorobenzene in theoretical yield. The chain reaction is inhibited relatively weakly by one of the reaction products and strongly by propylene and *n*-hexane. The pressure range investigated is 17—42 mm. and the reaction is discussed in connection with Slater's theory of unimolecular reactions.

SLATER (*Phil. Trans.*, 1953, *A*, **246**, 57) has concluded that only molecules with six or more atoms should show unimolecular rates of decomposition approaching k_∞ at pressures as

* Part I, preceding paper.

low as 2 atm. It was felt that trichloroethylene would provide a possible test of this conclusion because all the many dehydrohalogenations so far examined kinetically by the conventional static method (Biltz and Kuppers, *Ber.*, 1904, **37**, 2398; Lessig, *J. Phys. Chem.*, 1932, **36**, 2325; and the series of papers by Daniels, Vernon, Fugassi, and Veltman, *J. Amer. Chem. Soc.*, 1933, **55**, 922; 1938, **60**, 771; *J. Chem. Phys.*, 1939, **7**, 756; by Kistiakowsky, Brearley, and Stauffer, *J. Amer. Chem. Soc.*, 1936, **58**, 43; 1937, **59**, 165; by Maccoll, Green, Harden, and Thomas, *J. Chem. Phys.*, 1949, **17**, 1350; 1951, **19**, 977; 1953, **21**, 178; by Barton, Head, Howlett, Onyon, Williams, and Goodall, *J.*, 1949, 148, 155, 165; 1951, 2033, 2039; 1952, 453, 3695, 4487; 1953, 113, 945; and preceding paper; *Trans. Faraday Soc.*, 1949, **45**, 725, 735; 1950, **46**, 114; 1952, **48**, 25; *J. Amer. Chem. Soc.*, 1950, **72**, 988) have involved polyatomic molecules containing more than six atoms and none of them has shown a molecularity greater than unity. Trichloroethylene is a product of the pyrolysis of both tetrachloroethanes (Barton and Howlett, *J.*, 1951, 2033; Barton, *J.*, 1949, 148), and from some perfunctory experiments, its rate of reaction seemed to be negligible in comparison with the rates of decomposition of the saturated compounds. Another purpose of the present work was to re-examine this conclusion.

Experimental

Apparatus and Materials.—Both the static and the dynamic apparatus used were described in Part I (*loc. cit.*). Commercial trichloroethylene was shaken twice with concentrated sulphuric acid and once each with water, aqueous sodium hydrogen carbonate, and water. The liquid was dried, fractionated twice, and immediately admitted to the apparatus; it had b. p. 87·0° (corr.), n_D^{20} 1·4780, d_4^{20} 1·4616.
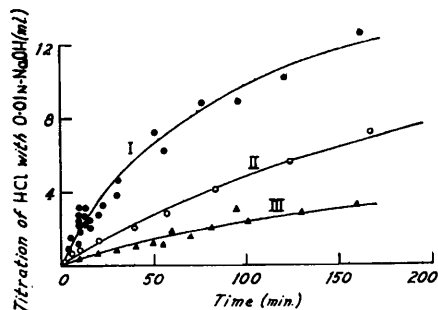
Results.—The pyrolysis of trichloroethylene was studied kinetically at 385—445°. The investigation was hampered by the deposition of a solid product in the stopcocks of the

Fig. 1.
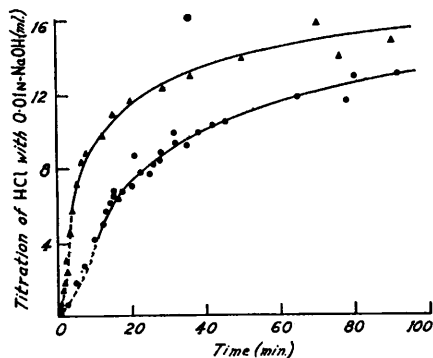
● 410°, $p_0 = 42·5$ mm.
▲ 444·5°, $p_0 = 42·5$ mm.
Reactor volume = 190 ml.

Fig. 2.

I. 444·5°, 42·5 mm. C_2HCl_3 + 5 mm. C_3H_6.
II. 410°, 42·5 mm. C_2HCl_3 + 5 mm. C_3H_6.
III. 444·5°, 18·3 mm. C_2HCl_3 + 5 mm. C_3H_6.

apparatus even when these were heated to 100° (cf. Barton and Howlett, *loc. cit.*). Hence, after each few runs the static apparatus had perforce to be filled with hydrogen, and the solid removed. As with allyl chloride (Part I), the pressure changes accompanying decomposition were complex, the pressure actually falling during the later stages of reaction, and the kinetics of the reaction were therefore followed by hydrogen chloride determinations. In a series of overnight experiments these determinations agreed closely with those expected from the elimination of 1 mol. of hydrogen chloride from trichloroethylene. The average experimental values were 0·99 at 444·5°, 1·10 at 425°, and 0·99 at 385°. The measured kinetics were therefore those of the dehydrochlorination of trichloroethylene.

It was soon apparent that the kinetics were complex. The reaction showed an induction period at all temperatures (see Fig. 1). It is unlikely that this arose from a trace impurity acting as an inhibitor because consistent results were obtained with several samples of trichloroethylene over very varying stages of reservoir exhaustion. Even after allowance for the

induction period a graph drawn from the experimental results relating log $d[C_3HCl_3]/dt$ to log $[C_3HCl_3]$ at constant temperature is markedly curved, showing that the reaction was not of constant order throughout its course. At the end of the induction period the order was 2—3, and it rose to a value impossibly high for a single process. The reaction was therefore either proceeding to an equilibrium or it was inhibited by the reaction products. Consistent with either of these hypotheses, it was shown that the reaction was retarded by excess of the reaction products. The possibility of an equilibrium (unlikely from consideration of the long-term hydrogen chloride analyses) may be rejected by considering the effect of propylene upon the kinetics. Propylene acted as a powerful inhibitor, maximum inhibition being reached with about 2 mm. pressure of propylene. It was shown that this maximally inhibited rate was invariant with propylene concentration up to at least 10 mm., and *n*-hexane was found to reduce the rate constant to the same limit. For the inhibited experiments, therefore, an initial propylene pressure of 5 mm. was used. The maximally inhibited non-chain reaction was found to be devoid of induction period and to be of second order. This is illustrated in Fig. 2, which shows experimental results obtained at 410° and 444·5°, and where the full lines are calculated on the assumption that the reaction is of second order. The constancy of the order of this residual reaction (see also Table 1) proves that the dehydrochlorination cannot go to an equilibrium.

TABLE 1.

Temp.	385°	410°	444·5° a	444·5° b	444·5° c	444·5° p
10^2k	1·38	5·67	17·0	20·6	20·7	20·8

a, $p_0 = 18·3$ mm. c, $p_0 = 42·5$ mm.
b, $p_0 = 28·3$ mm. p, packed vessel, $p_0 = 42·5$ mm.

The reaction was also studied in a packed reaction vessel of approx. 11-fold increase in surface/volume ratio over that of the " empty " vessel. The maximally inhibited reaction was independent of surface/volume ratio. The mean observed rate constants are given in Table 1. They may be summarised as $k = 10^{12·08}e^{-42,000/RT}$ sec.$^{-1}$ mole^{-1} l.

The reaction occurring in the presence of 5 mm. of propylene is non-chain in character; it will therefore have no mechanistic interconnection with the suppressible, radical-chain part of

FIG. 3.

⊙ 444·5°, 42·5 mm. pyrolysed for 40 min. and 33 mm. added in unpacked reactor.
▲ 444·5°, $p_0 = 42·5$ mm., packed reactor, volume 138 ml.
● 444·5°, $p_0 = 16$ mm., unpacked reactor, volume 190 ml.
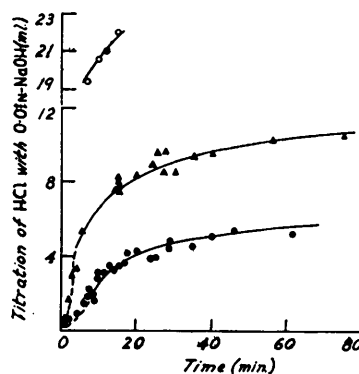
the pyrolysis. Subtraction of the maximally inhibited rate from the uninhibited rate at any particular concentration thus gives the instantaneous rate of the chain decomposition. Trial and error methods showed that this part of the reaction was fitted by an empirical equation, Rate = $k'[C_3HCl_3]^2/[HCl]$, from the end of the induction period as far as reaction has been followed (*ca.* 75% decomposition), implying that the chain reaction was of second order and was inhibited by one of the products. Fig. 3 shows the fit of this equation to some of the results.

Owing to the complicated form of the hydrogen chloride titration *versus* time curves, the runs used for elucidating the kinetics have been started from standard initial concentrations of reactant. The experimental values of k' are given in Table 2. From these results $k' =$

TABLE 2.

Temp.	385°	410°	425°	444·5°	444·5° p
$10^5k'$ (sec.$^{-1}$)	5·0	16·6	33·3	53·3	53·3

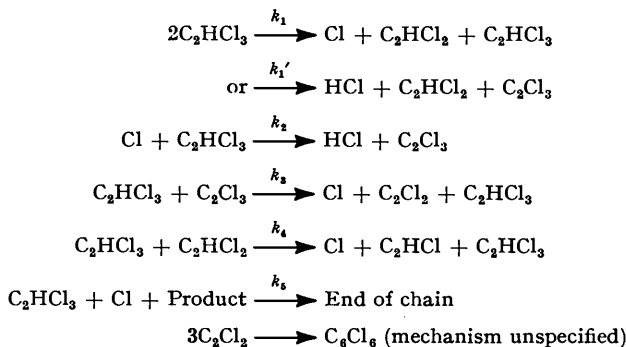$10^{7 \cdot 52} e^{-35,400/RT}$ (the velocity constant at 444·5° is given 3 times the weight of the others because it is averaged from 3 series of runs differing in initial pressure or surface/volume ratio of the reaction vessel). Table 2 also shows that packing the reaction vessel had no effect upon the chain part of the reaction, so that the whole decomposition was homogeneous.

Some attempts were made to confirm the partial radical nature of trichloroethylene pyrolysis by accelerating the reaction at 425° by the admission of 2 mm. of 1 : 1 : 1-trichloroethane to the reaction vessel 10 sec. before adding 40 mm. of trichloroethylene. Trichloroethane decomposes rapidly at this temperature by a reaction involving chlorine and trichloroethyl radicals (Barton and Onyon, *J. Amer. Chem. Soc.*, 1950, **72**, 988). The titration figures obtained, however, after 10 min. were close to those expected from a sum of the separate decompositions, so that no large amount of induced decomposition of the trichloroethylene was occurring.

The solid product of trichloroethylene pyrolysis, also obtained in small yield from the decomposition of both tetrachloroethanes, was suggested on m. p. evidence by Barton and Howlett (*loc. cit.*) to be hexachlorobenzene. It has now been collected in larger quantity by the use of the flow technique and recrystallised from ethyl acetate as feathery needles (Found : Cl, 74·2%; *M*, 283. Calc. for C_6Cl_6 : Cl, 74·7%; *M*, 285), m. p. 222—223° (lit., m. p., 223—224°). Furthermore, in a dynamic experiment run at 490° with a hot contact time of 2 min., 0·025 mole of crude hexachlorobenzene was obtained concurrently with the production of 0·071 mole of hydrogen chloride.

DISCUSSION

The chain part of the thermal decomposition of trichloroethylene presents certain novel features, *e.g.*, the dependence of the rate upon the square of the reactant concentration is unusual, and this also applies to the definite inhibition by one of the reaction products, and to the pressure dependence of the induction periods (see Fig. 1 and p. 2603). The following alternative reaction schemes, which employ bimolecular steps in the decompositions of small molecules and radicals,* are consistent with the pyrolytic features described above.

$$2C_2HCl_3 \xrightarrow{k_1} Cl + C_2HCl_2 + C_2HCl_3$$

$$\text{or} \xrightarrow{k_1{'}} HCl + C_2HCl_2 + C_2Cl_3$$

$$Cl + C_2HCl_3 \xrightarrow{k_2} HCl + C_2Cl_3$$

$$C_2HCl_3 + C_2Cl_3 \xrightarrow{k_3} Cl + C_2Cl_2 + C_2HCl_3$$

$$C_2HCl_3 + C_2HCl_2 \xrightarrow{k_4} Cl + C_2HCl + C_2HCl_3$$

$$C_2HCl_3 + Cl + \text{Product} \xrightarrow{k_5} \text{End of chain}$$

$$3C_2Cl_2 \longrightarrow C_6Cl_6 \text{ (mechanism unspecified)}$$

The trichloroethylene merely participates in step 5 for initial stabilisation of the reaction product. Either scheme leads directly to an expression of the type Rate = d[HCl]/dt = $([C_2HCl_3]^2 k_1 k_2)/(k_5[\text{Product}])$ (cf. Robb, *Nature*, 1953, **172**, 1055) in agreement with the experimental equation. The expression d[HCl]/dt = $k[C_2HCl_3]^2 + k'[C_2HCl_3]^2/[\text{Product}]$ has been tested against all the experimental results. The full lines in Figs. 1 and 3 are theoretical, being obtained by graphical integration of this last equation, because it is impracticable to use the cumbrous integrated form of the rate equation

$$kt = \frac{A[\text{Product}]_t}{[C_2HCl_3]_t} + \frac{B \ln [C_2HCl_3]_0 (\lambda + [\text{Product}]_t)}{\lambda [C_2HCl_3]_t}$$

where

$$A = \frac{1}{[C_2HCl_3]_0 + \lambda}, \quad B = -\frac{\lambda}{([C_2HCl_3]_0 + \lambda)^2}, \quad \lambda = k'/k$$

and the subscripts 0 and t have the obvious meaning. The rate equation fits the experimental results over the whole of the pressure range investigated and is still valid in

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* We thank the referees for a suggestion which avoids anomalies in our formulation.

the presence of considerable quantities of reaction products (see Fig. 3). As shown by the dynamic experiments, the dichloroacetylene initially produced, rapidly and completely polymerises to hexachlorobenzene (cf. Berthelot and Jungfleisch, *Annalen*, 1870, Suppl. 7, 255; Nicodemus, *J. pr. Chem.*, 1911, **83**, 312; Ott and Dittus, *Ber.*, 1943, **76**, 80). This explains the final fall in pressure towards p_0 found in the static experiments. The degree of inhibition in runs performed in the presence of reaction products from previous experiments was quantitatively consistent with the idea that the concentration of inhibitor was equal to the sum of the old and the new products. As there was no loss of inhibitory efficiency with time, this suggested that the inhibitor was hexachlorobenzene. The overall rate of trichloroethylene decomposition is certainly negligible in comparison with those of the tetrachloroethanes, and further, although the latter are pyrolysed by radical-chain mechanisms, it seems most unlikely from the co-decompositions with $1:1:1$-trichloroethane that the tetrachloroethanes would sensitise the decomposition of trichloroethylene. As with allyl chloride, therefore, trichloroethylene reacts much more slowly than the saturated compound(s) from which it may be derived pyrolytically, a conclusion in agreement with the preliminary findings of Barton and Howlett (*loc. cit.*).

The reaction is also interesting from the point of view of Slater's theory (*loc. cit.*). The pyrolysis of trichloroethylene is the first reported dehydrohalogenation reaction whose homogeneous non-chain mode of reaction is of second-order at a pressure of *ca.* 50 mm. This is in complete agreement with Slater's deduction. As the experimental difficulties attending observation of the pyrolysis of trichloroethylene precluded working at higher pressures, it is intended to carry out such a study with other hexatomic molecules of this type. There is also some evidence that the chain-initiating step is bimolecular rather than unimolecular. As emphasised previously (Barton and Howlett, *J.*, 1951, 2033), the observation of induction periods allows one to decide on some of the more intimate aspects of a reaction mechanism. In all cases of first-order radical-chain dehydrochlorination reactions so far reported the induction periods are independent of the initial pressure to a first approximation. We have applied Howlett's approximate treatment (*Trans. Faraday Soc.*, 1952, **48**, 25; cf. also Benson, *J. Chem. Phys.*, 1952, **20**, 1605) relating the induction period with rate of build-up towards the stationary state, to our theoretical scheme, and to the alternative scheme in which steps 1, 3, and 4 are unimolecular. Thus from our mechanism $[C_2Cl_3] = k_2[Cl]/k_3 = 2k_1k_2[C_2HCl_3]/k_3k_5[\text{Product}]$ in the steady state, and $d[C_2Cl_3]/dt \approx 2k_1[C_2HCl_3]^2$ during the induction period. Therefore induction period $\approx k_2/k_3k_5[C_2HCl_3]'[\text{Product}]'$ where $[C_2HCl_3]'$ and $[\text{Product}]'$ are the concentrations at the end of the induction period when the chain reaction has just reached the steady state. The mechanism following a unimolecular initial step leads by similar reasoning to an induction period of $k_2[C_2HCl_3]'/k_3k_5[\text{Product}]'$.

At $444\cdot5°$ the induction period found by extrapolating back the full lines of Fig. 3 to zero [Product] are $0\cdot9$ min. and $6\cdot2$ min. at $42\cdot5$ mm. and 16 mm., respectively. Clearly, this rapid inverse dependence of the induction period on the initial pressure is in agreement with the behaviour expected from a bimolecular chain-initiating reaction, and therefore the chain part of the thermal decomposition of trichloroethylene also supports Slater's deduction.

The induction periods associated with chloroethylene pyrolyses generally and other quantitative aspects of their reaction mechanisms will be discussed in a later paper.