20. *The Mechanisms of the Thermal Decompositions of 1 : 4-Dichlorobutane and 1 : 1 : 2-Trichloroethane.*

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1 : 4-Dichlorobutane decomposes at 673—727° K by a first-order reaction to form hydrogen chloride and butadiene (the dimerisation of which is relatively slow). The rate constant is represented by $k = 10^{14 \cdot 36}e^{-56,500/RT}$ sec.$^{-1}$. Reasonably reproducible induction periods were observed, the rate constants increasing and the induction periods decreasing with increase of pressure, both becoming sensibly constant above 60 mm. (initial). Propylene inhibits the reaction, extending the induction periods and diminishing the rate constants.

With 1 : 1 : 2-trichloroethane the reaction at 715° K is of the first order, exhibits induction periods, and is strongly inhibited by small amounts of propylene. It is concluded that these decompositions proceed by radical-chain reactions.

In a series of papers (Barton, Head, Howlett, Onyon, and Williams, *J.*, 1949, 148, 155, 165; *Trans. Faraday Soc.*, 1949, **45**, 725, 735; 1950, **46**, 114; *J. Amer. Chem. Soc.*, 1950, **72**, 988; *J.*, 1951, 2033, 2039; 1952, 453) the thermal dehydrochlorination of a number of saturated aliphatic chlorinated hydrocarbons has been described. The resultant olefins or chlorinated olefins are relatively stable under the experimental conditions. Three mechanisms have been recognised for these pyrolyses: (i) heterogeneous decomposition on the clean glass surface, (ii) homogeneous unimolecular decomposition, and (iii) homogeneous radical chain decomposition. Of these (i), which is much faster than (ii) or (iii), appears to be of universal application but can be largely suppressed by deposition of a carbonaceous film on the surface owing to polymerisation and cracking of the products.

Homogeneous decomposition will proceed by a radical chain decomposition provided that neither the products of the reaction nor the reactant itself is capable of acting as an efficient inhibitor for the radical chains. Inhibition by the products is experienced if they possess allylic hydrogen atoms (*e.g.*, propene, butene) and by the reactant if the direction of radical chlorination is such that β-chloro-radicals (which readily lose a chlorine atom to continue the chain) are not formed or are formed in insufficient proportions (see, especially Barton, Head, and Williams, *J.*, 1951, 2039).

In order further to confirm these statements, the thermal decompositions of 1 : 1 : 2-trichloroethane and 1 : 4-dichlorobutane have now been investigated.

EXPERIMENTAL

Materials.—Commercial 1 : 4-dichlorobutane, purified as described for *n*-propyl chloride (Barton, Head, and Williams, *loc. cit.*) and fractionally distilled under reduced pressure, had b. p. 153·9° (corr.)/760 mm. (153·5°, Rust and Vaughan, *J. Org. Chem.*, 1941, **6**, 479; 155·0°, Mumford and Phillips, *J.*, 1950, 75), f. p. (SO_2 vapour-pressure thermometer) −37·3°, d_4^{12} 1·1498 (mean 1·1496, interpolated from d_4^{1} 1·1612, d_4^{25} 1·1340, d_4^{40} 1·1175, Heston, Hennelly, and Smyth, *J. Amer. Ch*e*m. Soc.*, 1950, 72, 2071; d_4^{20} 1·1408, d_4^{25} 1·1353, Mumford and Phillips, *loc. cit.*), n_D^{21} 1·4559 (n_D^{25} 1·4530, Heston *et al.*, *loc. cit.*; n_D^{20} 1·4549, Mumford and Phillips, *loc. cit.*).

Commercial 1 : 1 : 2-trichloroethane, purified by the method used for 1 : 1 : 1-trichloroethane by Barton and Onyon (*J. Amer. Chem. Soc.*, 1950, 72, 988), had b. p. 113·5° (corr.)/760 mm. (114·1°, Mumford and Phillips, *loc. cit.*; 113·67°, Dreisbach and Martin, *Ind. Eng. Chem.*, 1949, **41**, 2875; 113·5°, Timmermans, *Bull. Soc. chim. Belg.*, 1913, **27**, 334; 113·65°, Lecat, "Tables Azeotropiques," Brussels, 1949), f. p. (SO_2 vapour-pressure thermometer) −36·6° (−36·57°, Dreisbach and Martin, *loc. cit.*; −36·65°, Timmermans, *loc. cit.*; −37·4°, Henne and Hubbard, *J. Amer. Chem. Soc.*, 1936, **58**, 404), d_4^{12} 1·4445 (1·4480, extrapolated from d_4^{20} 1·4395, d_4^{25} 1·4319, Dreisbach and Martin, *loc. cit.*; d_4^{20} 1·4424, d_4^{25} 1·4355, Mumford and Phillips, *loc. cit.*; d_4^{20} 1·4411, Henne and Hubbard, *loc. cit.*).

Apparatus.—The apparatus and technique were those described by Barton and Howlett (*J.*, 1949, 155). Owing to the relatively low vapour pressures involved all external tubing was electrically heated to *ca.* 160°. Results are for reactors in which the heterogeneous decomposition had been suppressed by a carbonaceous coating and the kinetics were elucidated by following the pressure increase at constant volume.

RESULTS

Stoicheiometry.—The reaction with 1 : 4-dichlorobutane was assumed to be $Cl{\cdot}[CH_2]_4{\cdot}Cl = CH_2{:}CH{\cdot}CH{:}CH_2 + 2HCl$ by analogy with that of 2 : 2′-dichlorodiethyl ether (Barton, Head, and Williams, *loc. cit.*). This view was supported by some long-term runs in which it was found that 40-mm. initial pressure of reactant trebled its pressure in 18 hours at 695—727° K. In view of the known polymerisation of butadiene at these temperatures this was fortuitous but it was found that 40-mm. initial pressure of butadiene under the same conditions first decreased and then increased to a steady value within 2% of the original pressure. These facts taken together indicate that two molecules of hydrogen chloride are eliminated. Calculations based on Rowley and Steiner's results (*Discuss. Faraday Soc.*, 1951, **10**, 198) showed that the dimerisation of butadiene could be neglected over the first portion of the decomposition, for initial pressures of reactant less than 50 mm.

1 : 1 : 2-Trichloroethane was assumed to decompose analogously to 1 : 1 : 1-trichloroethane (Barton and Onyon, *loc. cit.*) and, indeed, overnight pressure ratios at 714° K were found to be identical (2·5).

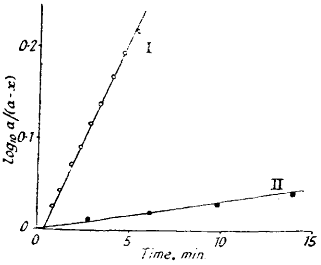
Kinetics.—1 : 4-Dichlorobutane was found to decompose by a first-order process. Temperature-dependent induction periods were noted, similar to those with 2 : 2′-dichlorodiethyl ether. The induction periods decreased and the rate constants increased with increasing initial pressure but both became sensibly constant above about 60 mm. initial pressure. The rate constants, for initial pressures of 40 mm., were given by $k = 10^{14\cdot36}e^{-56,500/\boldsymbol{R}T}$ sec.$^{-1}$ and the variation of the induction periods (except at the highest temperature where errors in measurement are relatively larger) could be represented by the expression $I = 10^{-16\cdot5}e^{54,700/\boldsymbol{R}T}$min. In accordance with previous custom no error limits are given for these constants for the chain reaction. The data are summarised in Table 1 which includes values for the rate constants and induction periods calculated from the above equations.

TABLE 1. *Unpacked reactor; initial pressure,* 40 *mm.*

Temp. (K)	No. of runs	Mean 10^3k (sec.$^{-1}$)	Standard error of mean k * (%)	$10^3k_{\text{calc.}}$ (sec.$^{-1}$)	Mean induction period (I), sec.	Standard error of mean I * (%)	$I_{\text{calc.}}$ (sec.)
673·0°	6	0·104	0·6	0·102	1036	2	1092
683·5	5	0·200	0·8	0·200	728	2	586
687·5	3	0·256	0·8	0·257	518	4	466
695·0	14	0·404	1·1	0·389	308	2	301
704·0	6	0·645	0·6	0·660	191	4	181
710·5	4	0·99	1·1	0·96	133	4	125
715·0	7	1·30	1·0	1·23	102	3	100
727·0	12	2·38	1·0	2·40	31	4	—

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

Addition of propylene, which is diagnostic for radical chains in these decompositions, prolonged the induction periods and considerably reduced the final rate. Both effects increased rapidly with the proportion of propylene (to about 4%) after which only a slow increase was noted. The data are summarised in Table 2.



I, *Without propylene.*
II, *With propylene at* 715° K.

In contrast to the above results 1 : 1 : 2-trichloroethane gave poor reproducibility and was not suited to detailed kinetic analysis. This was almost certainly due to the inhibiting effect of products noted by Barton and Onyon (*loc. cit.*) in the pyrolysis of 1 : 1 : 1-trichloroethane.

TABLE 2. *Unpacked reactor at* 712° K.

p_0, mm. of $C_4H_8Cl_2$	p, mm. C_3H_8	100 p/p_0	Mean 10^3k (sec.$^{-1}$)	Induction period (sec.)
Mean	—	—	1·02	118
41·3	0·1	0·25	0·76	135
40·6	0·2	0·5	0·69	155
40·6	0·4	1·0	0·51	186
40·8	1·6	4·0	0·42	260
40·8	4·2	10·5	0·35	270
40·6	16·3	40·8	0·30	320

Over 100 kinetic runs were carried out, a typical example (initial pressure 60 mm.; temp. 714° K) being depicted in the Figure. In each case the kinetics were of the first order and induction periods were observed. Addition of 2·5% of propylene reduced the rate constant 18-fold as shown by the lower line in the Figure where the elimination of the induction period can also be seen.

DISCUSSION

Both the above decompositions exhibit as their main features temperature-dependent induction periods and positive inhibition by small quantities of propylene. These features are the same as for 1 : 2-dichloroethane, 1 : 1 : 1-trichloroethane, both tetrachloroethanes, and 2 : 2′-dichlorodiethyl ether (Barton *et al.*, *loc. cit.*) and clearly indicate the essential radical-chain nature of the decompositions.

The results accord with theory for 1 : 1 : 2-trichloroethane, as radical chlorination must yield a β-chloro-radical, $CHCl_2 \cdot \dot{C}HCl$ or $\dot{C}Cl_2 \cdot CH_2Cl$, capable of readily eliminating a chlorine atom to continue the chain, simultaneously forming chlorinated ethylenes. From previous studies (Barton and Onyon, *loc. cit.*) it is known that chlorinated ethylenes are only feebly inhibitory.

In the case of 1 : 4-dichlorobutane the radical-chain reaction detected implies that radical chlorination must take place largely at the 2-position, a directive effect in accord with the principles proposed by Ash and Brown ("Records of Chemical Progress," 1948, p. 81). Since however some attack will occur at the 1-position, leading to "dead" radicals incapable of readily losing a chlorine atom, the radical chains cannot be expected to be long. This is supported qualitatively by the results of addition of propylene which produced proportionately a far lower retardation of rate than in the case of 1 : 1 : 2-trichlorethane, indicating that non-chain processes must also be of considerable importance Lack of inhibition by the product, butadiene, is comparable to the case of ethylene, already shown to be a poor inhibitor (Barton and Howlett, *loc. cit.*).

I am indebted to Dr. D. H. R. Barton for helpful discussions during this work which was carried out during the tenure of a Courtaulds' Postgraduate Scholarship.

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[*Received, August 28th,* 1952.]