196. *Studies on Unimolecular Chlorohydrocarbon Decompositions. Part IV.**

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2 : 2-Dichloropropane decomposes at 370° ± 40° by a homogeneous unimolecular process to give hydrogen chloride and monochloropropene. 1 : 1-Dichloropropane yields similar products at 410° ± 30° by simultaneous unimolecular and radical-chain reactions. The latter mode is suppressed by *iso*butene. The non-exponential terms of the unimolecular rate constants for these pyrolyses are shown to be in agreement with an earlier suggestion, and previous discussions concerning prediction of the mode of decomposition for chloroalkanes are extended.

In Part III * a suggested explanation was given for the marked correlation between the Arrhenius parameters of the velocity constants for homogeneous unimolecular decomposition of chloroalkanes, noted by Barton, Head, and Williams (*J.*, 1951, 2039). It was pointed out that the decomposition rate constant of 1 : 1-dichloroethane is anomalous in this respect and it was tentatively suggested that other simple dichlorides of type $>CH{\cdot}CCl_2{\cdot}$ might show the same behaviour. In pursuance of this idea the pyrolyses of 1 : 1- and 2 : 2-dichloropropane have been studied.

Experimental

Apparatus and Materials.—The apparatus used has been described in Part II (*J.*, 1952, 3695). All results refer to a constant-volume reaction vessel whose walls are covered by a carbonaceous film.

1 : 1- and 2 : 2-Dichloropropane were prepared by treating the appropriate carbonyl compounds with phosphorus pentachloride (cf. Henne, Renoll, and Leicester, *J. Amer. Chem. Soc.*, 1939, **61**, 938; Turkevich and Smyth, *ibid.*, 1940, **62**, 2468). The 2 : 2-isomer thus prepared was found, on pyrolysis, to give kinetics characterised by fast starts. This effect was noted in other reactions by Barton, Head, and Williams (*loc. cit.*) and was there eliminated by removing the impurity responsible by sulphuric acid. Both compounds for the present study were therefore shaken quickly with concentrated sulphuric acid, washed with water, and refractionated. (Prolonged contact with the acid causes some decomposition.) This purified material was saisfactory from the kinetic point of view. 2 : 2-Dichloropropane had b. p. 69·2° (corr.), n_D^{18} 1·4158; 1 : 1-dichloropropane had b. p. 88·1° (corr.), n_D^{18} 1·4288.

Results.—Both pyrolyses were first shown to result in dehydrochlorination, the extent of hydrogen chloride production being measurable by the pressure increase in the system. Table 1 compares the amounts of hydrogen chloride formed, both calculated from pressure changes, and found by condensation of the reaction products followed by titration with 0·01N-alkali. It was demonstrated that the measured rate of reaction referred to the elimination of only one molecule of hydrogen chloride from the substrate by determining the ratios of final to initial pressures when the reaction was allowed to proceed for *ca.* 20 times that required for the elimination of 0·5 molecule of hydrogen chloride per molecule of dichloropropane. Table 2 shows that the p_f/p_i ratio is 2 for both reactions, indicating that the measured reaction is in each case $C_3H_6Cl_2 \longrightarrow C_3H_5Cl + HCl$. Overnight runs gave, in general, pressure increases in excess of 100% (cf. Barton and Head's results, *Trans. Faraday Soc.*, 1950, **46**, 114, for decomposition of 1 : 2-dichloropropane).

Table 1.

1 : 1-Dichloropropane at 425°							
HCl (calc.), equiv. × 10⁻⁴	1·34	0·53	0·39	0·86	0·18	1·23	0·69
HCl (found), equiv. × 10⁻⁴	1·37	0·58	0·40	0·82	0·19	1·19	0·64
2 : 2-Dichloropropane at 398°							
HCl (calc.), equiv. × 10⁻⁴	0·30	0·16	0·42	0·74	1·33	1·53	1·00
HCl (found), equiv. × 10⁻⁴	0·32	0·16	0·45	0·80	1·29	1·56	1·05

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* Part III, *J.*, 1952, 4487.

The pyrolysis of 2 : 2-dichloropropane was found to be of the first order and to be uninfluenced by the presence of propene. This is illustrated in Table 3, and is good evidence for the absence of any chain reaction. With 1 : 1-dichloropropane alone, indifferent first-order constants were observed, together with an obvious rise in rate constant on decreasing the initial pressure below *ca.* 30 mm. When the reaction was carried out in the presence of at least 10 mm. of *iso*butene, the results became consistently of the first order over the whole of the pressure range studied. These observations are also included in Table 3 and show that the decomposition of the 1 : 1-isomer alone consists of simultaneous unimolecular and radical-chain reactions. The radical part of the reaction can be suppressed by the strong inhibitor *iso*butene or by larger amounts of the weak inhibitors present when the compound is pyrolysed alone.

TABLE 2.

1 : 1-Dichloropropane at 449°		2 : 2-Dichloropropane at 397°			
p_i, mm.	p_f/p_i	p_i, mm.	p_f/p_i	p_i, mm.	p_f/p_i
8·12	1·98	9·51	1·97	17·0	1·90
13·75	2·02	14·5	2·02	18·0	1·96
26·4	1·97	16·1	1·95	19·5	1·96

TABLE 3.

	1 : 1-Dichloropropane at 425°					
Alone p_i, mm.	17·8	20·8	29·7	61·0		
Alone 10^5k, sec.$^{-1}$	79	66	52·2	48·9		
Plus 10 mm. *iso*-C_4H_8 p_i, mm.	6·36	16·6	38·1			
Plus 10 mm. *iso*-C_4H_8 10^5k, sec.$^{-1}$	49·6	53·0	48·8			
	2 : 2-Dichloropropane					
At 352° p_i, mm.	11·5	16·1	20·3	25·5	41·7	
At 352° 10^5k, sec.$^{-1}$	40·0	41·0	38·9	38·3	38·6	
At 413·5° p_i, mm.	8·5	10·0 *	13·4	14·0 *	17·2	21·7 *
At 413·5° 10^5k, sec.$^{-1}$	1020	870	1090	1050	960	1130

* In the presence of *ca.* 10 mm. of propene.

In the case of 2 : 2-dichloropropane the homogeneity of the reaction has been demonstrated by the negligible increase in specific reaction rate observed on increasing the surface/volume ratio of the reaction vessel *ca.* 10 times. By analogy with the numerous dehydrochlorinations now established as homogeneous, a similar conclusion may undoubtedly be drawn for the decomposition of 1 : 1-dichloropropane. (The carbonaceous reactor surfaces, over which all these pyrolyses are carried out, are ineffectual catalysts for this type of reaction.)

TABLE 4.

1 : 1-Dichloropropane			2 : 2-Dichloropropane					
Temp.	No. of runs	10^5k, sec.$^{-1}$	Temp.	No. of runs	10^5k, sec.$^{-1}$	Temp.	No. of runs	10^5k, sec.$^{-1}$
384°	5	5·41	330·5°	4	10·8	378°	6	144
410·5	10	25·3	352	5	39·4	393	8	345
425	6	50·9	369·5	6	98	398	2	475
443	8	139·2	370 ^{p}	3	116	413·5	11	1000

p = packed reaction vessel.

The decomposition of 1 : 1-dichloropropane (in the presence of not less than 10 mm. of *iso*butene) has been studied from 384° to 443° and over the initial pressure range 6—60 mm. The decomposition of 2 : 2-dichloropropane has been examined from 330·5° to 413·5° and over the pressure range 7—40 mm. The mean rate constants are quoted in Table 4. From these figures the Arrhenius equations for unimolecular decomposition of 1 : 1- and 2 : 2-dichloropropane were computed by the method of least squares to be $k = 10^{12\cdot76}\ e^{-51,200/\mathbf{R}T}$ and $k = 10^{11\cdot90}\ e^{-43,900/\mathbf{R}T}$, respectively.

DISCUSSION

It is clear that these two rate equations support the suggestion made in Part III (*loc. cit.*), that relatively low non-exponential terms might be expected in such reactions. When the Arrhenius parameters *A* and *E* for the pyrolyses of 1 : 1- and 2 : 2-dichloropropane are compared with Fig. 9 given by Barton, Head, and Williams (*loc. cit.*) correlating these quantities for monochloroalkanes and 1 : 2-dichloropropane, the non-exponential terms relevant to 1 : 1-dichloroethane and the two compounds studied here are all about a factor of 10 lower than the frequency factors reviewed by Barton *et al.*

As stated in Part II (*loc. cit.*), evidence obtained from co-decomposition studies supports Barton, Head, and Williams's arguments concerning the negligible chain lengths expected in radical decompositions from the predominance of the attack of chlorine atoms on β-hydrogen atoms in, *e.g.*, ethyl chloride (cf. Ash and Brown, " Records of Chemical Progress," 1948, p. 81). In the case of 2 : 2-dichloropropane, chlorine-atom attack could only be upon β-hydrogen atoms, as in the comparable case of 1 : 1 : 1-trichloroethane (Barton and Onyon, *J. Amer. Chem. Soc.*, 1950, **72**, 988), and even in 1 : 1-dichloropropane only one α-hydrogen atom is present. In none of these cases, however, does the chain mode of decomposition reach overwhelming proportions. Little complication from chain processes has therefore been observed to arise from the attack of chlorine atoms in β-methyl or alkyl-substituted methyl groups. Only chloro- or chloroethoxy-substituted methyl groups have so far been found to be markedly susceptible in this way.

From a survey of the published work on dehydrochlorinations an interesting list may now be compiled of those olefinic compounds which act as strong and as weak inhibitors of the radical-chain type of dehydrochlorination. Thus ethylene, vinyl chloride, vinylidene dichloride, trichloroethylene, 1-chloropropene, and divinyl ether are weak inhibitors since relatively large quantities must be present to produce effective retardation. On the other hand, propene, *iso*butene, and probably menthene (and also *n*-hexane and acetaldehyde) are strong inhibitors. Since the competing reaction responsible for inhibition is probably metathetical (Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25), it appears likely that the inhibitor's power depends upon the presence of C–H bonds of relatively low bond-dissociation energy.

These considerations concerning the type of reaction products which favour or inhibit the occurrence of radical-chain decompositions, extend the conclusions reached by Barton, Onyon, and Howlett (*ibid.*, 1949, **45**, 733) upon the restrictions to radical decomposition imposed by the substrate, and enable us to be more certain in predicting whether a chloroalkane will decompose in a unimolecular manner or not.

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