

451. *The Kinetics of the Dehydrochlorination of Substituted Hydrocarbons. Part VII.* The Mechanism of the Thermal Decompositions of 1:1:2:2- and 1:1:1:2-Tetrachloroethane.*

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1:1:2:2-Tetrachloroethane decomposes in the temperature range 263—382° by a homogeneous first-order reaction to give trichloroethylene and hydrogen chloride. The rate constant equation is $k = 10^{9.62} e^{-36,500/RT}$ sec.⁻¹. There is no variation in rate constant over the initial pressure range 19—83 mm. The reaction shows well-defined temperature-dependent induction periods which obey the equation $I = 10^{-15.0} e^{44,000/RT}$ min. and are independent of the initial pressure and of the surface area: volume ratio. They can be prolonged indefinitely by the addition of propylene, the prolongation being proportional to the amount of propylene added.

1:1:1:2-Tetrachloroethane decomposes similarly in the temperature range 310—378° and kinetic investigations give results as above.

The decompositions of both tetrachloroethanes must be exclusively of the radical-chain type, the propagation steps involving chlorine atoms and tetrachloroethyl radicals. The chain lengths, estimated from the inhibition experiments, are about 500 at 369° for 1:1:2:2-tetrachloroethane and about 370 at 367° for the 1:1:1:2-isomer.

In previous communications the mechanisms of the thermal decompositions of ethyl chloride, 1:1- and 1:2-dichloroethane, *tert.*-butyl chloride, *isopropyl* chloride, 1:2-dichloropropane, and 1:1:1-trichloroethane have been elucidated (Barton and Howlett, *J.*, 1949, 155, 165; Barton and Onyon, *Trans. Faraday Soc.*, 1949, 45, 725; *J. Amer. Chem. Soc.*, 1950, 72, 988; Barton and Head, *Trans. Faraday Soc.*, 1950, 46, 114). In continuation of the programme of work outlined by Barton and Onyon (*loc. cit.*), attention has been directed to the two tetrachloroethanes. According to the theoretical relation correlating mode of thermal decomposition with molecular structure (*idem, ibid.*), these two compounds should decompose by chain mechanisms. This inference has now been proved correct.

No previous physicochemical investigation of these decompositions has been reported.

EXPERIMENTAL.

Materials.—The 1:1:2:2- and 1:1:1:2-tetrachloroethanes were purified as described by Barton and Howlett (*loc. cit.*) for 1:2-dichloroethane, except that fractional distillation was carried out under reduced pressure. The following physical constants were recorded (the means of the best literature values are in parentheses): 1:1:2:2-Tetrachloroethane, b. p. 103° (corr.)/186 mm. (100°/186 mm., interpolated from Herz and Rathmann, *Chem. Zeit.*, 1912, 36, 1417), f. p. (sulphur dioxide vapour-pressure thermometer) —44.0° (mean, —43.2°; from —43.8°, Timmermans, *Chem. Zentr.*, 1914, I, 618; —42.5°; *idem, Bull. Soc. chim. Belg.*, 1927, 36, 504). 1:1:1:2-Tetrachloroethane, b. p. 129.5° (corr.) (129.3° from 129—129.7°, Phillips, Davies, and Mumford, *J.*, 1929, 548; 129.2°, Henne and Hubbard, *J. Amer. Chem. Soc.*, 1936, 58, 404), f. p. (ammonia vapour-pressure thermometer, calc. from data of Stock, Henning, and Kuss, *Ber.*, 1921, 54, 1126) —69.0° (—68.1°, Henne and Hubbard, *loc. cit.*).

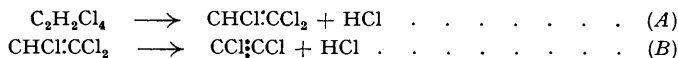
Apparatus.—The apparatus and experimental technique were as used in previous work (Barton and Howlett, *loc. cit.*). In view of the low vapour pressures of the two tetrachloroethanes the dead space in the capillaries and spoon gauge was heated to about 200° by an external electrical winding. All the results recorded below were obtained in reaction vessels, the walls of which had been coated with a carbonaceous film (*cf. idem, loc. cit.*). The overnight pyrolysis of either of the tetrachloroethanes under the conditions mentioned below rapidly leads to the deposition of such films and there was no difficulty in repressing the heterogeneous mode of decomposition.

RESULTS.

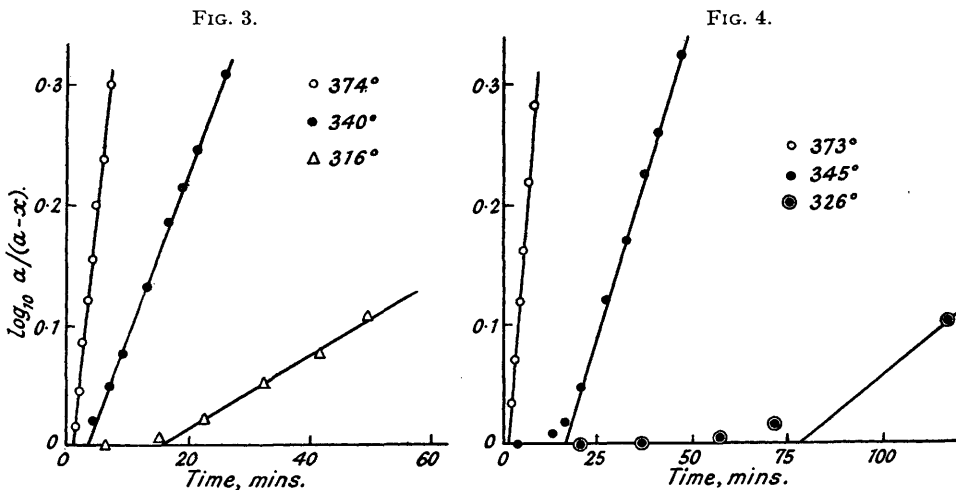
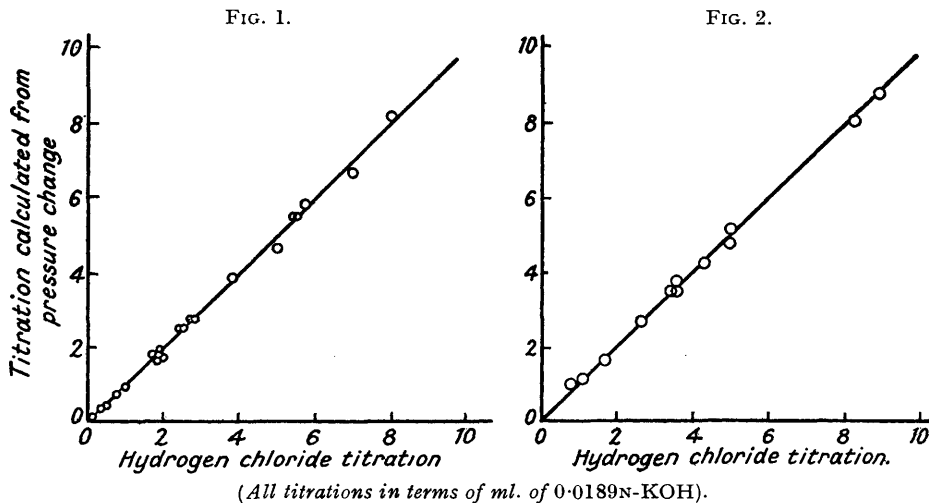
Stoichiometry.—As in the earlier work of this series, the course of reaction was determined by the increase in pressure at constant volume. Figs 1 and 2, where the straight lines are drawn at the theoretical slope of 45°, refer respectively to 1:1:2:2- and 1:1:1:2-tetrachloroethane and show that the hydrogen chloride produced is equivalent to the pressure increase. The data summarised refer to

* Part VI, *J. Amer. Chem. Soc.*, 1950, 72, 988.

various temperatures and initial pressures and were obtained from decompositions up to 75% completion. This agrees with the stoichiometry (A) previously established (cf. Barton, *J.*, 1949, 148) for these reactions, but does not exclude the further possibility of reaction (B). That (B) was probably insignificant during the times required for 75% decomposition of the tetrachloroethanes was shown by a separate study with trichloroethylene. At 361°, where the half-lives of both the tetrachloroethanes were about



10 minutes, the rate of increase of pressure of trichloroethylene alone showed that its decomposition proceeded to about 10% in 3 hours. A representative hydrogen chloride titration proved that the



pressure increase was a real measure of the latter decomposition and that it was not invalidated by dichloroacetylene polymerisation. The results on trichloroethylene are shown in Table I.

TABLE I.

$p_0(\text{C}_2\text{HCl}_2)$, mm.	25	36	60
Time, min.	200	120	164
Δp , mm.	2.5	3	5.5 ^a

^a Titre of 0.0187N-KOH: Calc., 0.55 ml. Found, 0.55 ml.

Overnight runs with the tetrachloroethanes at the higher temperatures studied showed pressure increases of 120–130%. This is undoubtedly caused by the partial occurrence of reaction (B).

After about 50 experiments with each of the tetrachloroethanes a few mg. of deposit had appeared in the exit tap between the reactor and the pumping line. This was collected, dissolved in light petroleum (b. p. 40–60°), and chromatographed over alumina to remove silicone grease. The (95:5) light petroleum–benzene eluate furnished hexachlorobenzene which recrystallised from ethyl acetate–light petroleum as needles, m. p. 223–225° alone or mixed with an authentic specimen (m. p. 223–225°). It must be formed by the polymerisation of dichloroacetylene (Ott and Dittus, *Ber.*, 1943, **76**, 80; cf. Berthelot and Jungfleisch, *Compt. rend.*, 1869, **69**, 542; Nicodemus, *J. pr. Chem.*, 1911, [ii], **83**, 312). The isolation of hexachlorobenzene is further positive evidence for the occurrence of reaction (B).

FIG. 5.

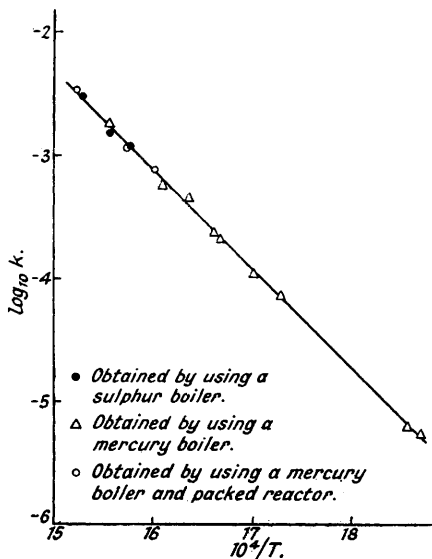


FIG. 6.

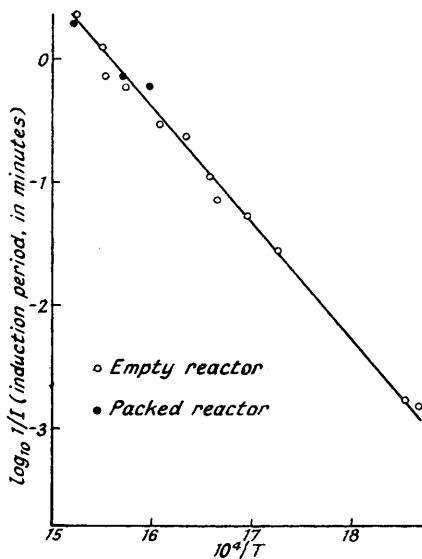


FIG. 7.

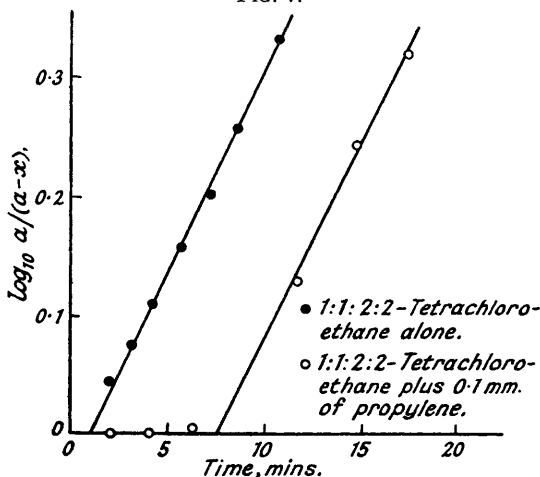
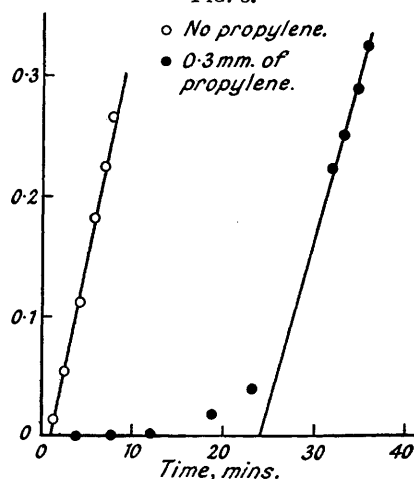


FIG. 8.



Kinetics.—With these preliminary facts established, the decompositions were studied over the temperature ranges 263–382° (for 1:1:2:2-) and 310–378° (for 1:1:1:2-tetrachloroethane). Because of the low vapour pressures of the tetrachloroethanes the results reported are not so reliable as those for 1:2-dichloroethane (Barton and Howlett, *loc. cit.*). A fairly comprehensive study has been made of the 1:1:1:2:2-tetrachloroethane decomposition but only a cursory investigation is reported for the 1:1:1:2-isomer. Nevertheless, as will be seen later, there can be no doubt as to the mechanisms involved.

At all temperatures the reactions followed first-order kinetics up to at least 60% decomposition. Some typical runs are illustrated in Fig. 3 for the symmetrical, and in Fig. 4 for the unsymmetrical, compound. As with 1:2-dichloroethane (*idem, loc. cit.*) and 1:1:1-trichloroethane (Barton and Onyon, *loc. cit.*), the reactions showed well-defined temperature-dependent induction periods of moderate

reproducibility. These are also illustrated in Figs. 3 and 4. As shown by the data in Table II, there was no variation in first-order velocity constant over the pressure ranges 19—83 mm. and 31—85 mm. for the 1 : 1 : 2 : 2- and the 1 : 1 : 1 : 2-compound, respectively.

TABLE II.

Temp.	p_0 (C ₂ H ₂ Cl ₄), mm.	10 ⁵ k , sec. ⁻¹ .	Induction period (I), min.	Temp.	p_0 (C ₂ H ₂ Cl ₄), mm.	10 ⁵ k , sec. ⁻¹ .	Induction period (I), min.
(a) 1 : 1 : 2 : 2-Tetrachloroethane.							
316°	27	12.0	9	362°	22	114	0.8
316	64	11.9	15	362	29	128	0.8
316	70	12.0	17	362	36	118	1.5
339	19	46	3.0	362	40	121	1.1
339	27	45	3.5	362 ^a	47	131	0.9
339	38	47	5.7	362	51	121	1.2
339	44	50	3.7	362 ^a	83	116	1.5
339	56	42	5.0				
(b) 1 : 1 : 1 : 2-Tetrachloroethane.							
345	32	45	16	373	31	155	1.1
345	58	45	11	373	43	167	1.9
345	72	45	5	373	55	154	1.5
345	85	42	17	373	62	171	1.3
				373	75	152	1.4

Table III gives the observed first-order rate constants for 1 : 1 : 2 : 2-tetrachloroethane. A graph of $\log_{10}k$ against $1/T$ gave a satisfactory straight line, as illustrated in Fig. 5. The rate constant equation for 1 : 1 : 2 : 2-tetrachloroethane, calculated by the least-squares method, the same statistical weight being given to every observation, was found to be $k = 10^{9.62} e^{-36,500/RT}$ sec.⁻¹. As usual with the chain-type decompositions in our series of investigations, we prefer not to attach error limits to this expression.

TABLE III.

Temp.	No. of runs.	Mean 10 ⁵ k , sec. ⁻¹ .	% Mean error of mean k . ^a	Mean I , min.	% Mean error of mean I . ^a	Temp.	No. of runs.	Mean 10 ⁵ k , sec. ⁻¹ .	% Mean error of mean k . ^a	Mean I , min.	% Mean error of mean I . ^a
<i>Empty reactor.</i>											
263°	1	0.56	—	724	—	339°	14	47	4.2	4.0	36
266	1	0.65	—	600	—	349	2	57	5.2	3.5	20
306	2	7.3	2.7	34	6	362 ^b	28	120	3.3	1.99	17
316	5	11.6	3.5	16	14	370 ^b	10	156	3.2	1.29	13
328	1	22	—	14	—	371	11	187	2.7	0.79	14
330	4	24	1.7	9	16	380 ^b	9	307	2.0	0.43	32
<i>Packed reactor.</i>											
352	7	77	3.2	1.70	11	382	6	343	2.3	0.62	15
362.5	6	119	5.9	1.35	8						

^a Calculated from the formula $\sigma = \sqrt{\frac{\sum(x - \bar{x})^2}{n(n-1)}} \times \frac{100}{\bar{x}}$, where the symbols have their usual significance. ^b Results obtained by using sulphur as thermostatic vapour. In all other experiments mercury was employed.

A number of experiments were made in a packed reactor where the surface area : volume ratio had been increased by a factor of about 4 over that in the empty reactor. The data, summarised in Table III and illustrated in Fig. 5, show that the rate of decomposition was unaffected by packing. The reaction must, therefore, be homogeneous (see also below).

The induction periods for 1 : 1 : 2 : 2-tetrachloroethane were substantially independent of initial pressure; if anything there was a tendency for them to be longer at higher pressures (see Table IIa). A graph of \log_{10} of the mean induction periods (Table III) against $1/T$ gave a straight line (Fig. 6), the equation of which may be expressed as $I = 10^{-15.0} e^{44,000/RT}$ min., where I is the observed induction period. Table III and Fig. 6 also show that packing did not alter the length of the induction periods.

For the 1 : 1 : 1 : 2-tetrachloroethane decomposition the mean rate constant (from 7 runs) at 353.5° was $60 \pm 3 \times 10^{-5}$ sec.⁻¹. In the packed reactor (approximately 4-fold increase in surface area : volume ratio) at 354° the result (6 runs) was $72 \pm 1 \times 10^{-5}$ sec.⁻¹. This reaction is therefore also homogeneous. The induction periods seemed to be independent of initial pressure and of packing.

One of the most interesting features of the 1 : 1 : 2 : 2-tetrachloroethane pyrolysis was the effect of adding propylene. Previously, we have shown that this hydrocarbon is a powerful inhibitor for the chain-type decompositions of 1 : 2-dichloroethane and of 1 : 1 : 1-trichloroethane, the rate constant being thereby reduced to a limiting figure independent of further propylene addition. With 1 : 1 : 2 : 2-tetrachloroethane, propylene caused a lengthening of the induction period already present. Throughout most of the prolonged induction period the reaction velocity appeared to be zero, and at the end, the

rate of decomposition rose again quite rapidly to the normal value. Fig. 7 illustrates some typical results from experiments carried out at 370°. It was confirmed by hydrogen chloride titrations that little, if any, decomposition occurred during these propylene-induced induction periods. The increase in the length of the induction period (for a standard initial pressure of 1 : 1 : 2 : 2-tetrachloroethane) was approximately proportional to the amount of propylene added. The data in Table IV, obtained at 369°, illustrate this point.

TABLE IV.

$p_0(\text{C}_2\text{H}_2\text{Cl}_4)$, mm.	$p(\text{C}_3\text{H}_6)$, mm.	I , min.	$p(\text{C}_3\text{H}_6)$ corr. to	$\Delta I/\text{corr.}$ $p(\text{C}_3\text{H}_6)$.	$p_0(\text{C}_2\text{H}_2\text{Cl}_4)$, mm.	$p(\text{C}_3\text{H}_6)$, mm.	I , min.	$p(\text{C}_3\text{H}_6)$ corr. to	$\Delta I/\text{corr.}$ $p(\text{C}_3\text{H}_6)$.
			$p_0(\text{C}_2\text{H}_2\text{Cl}_4)$ = 50 mm.					$p_0(\text{C}_2\text{H}_2\text{Cl}_4)$ = 50 mm.	
1 : 1 : 2 : 2-Tetrachloroethane.					1 : 1 : 1 : 2-Tetrachloroethane.				
—	0	1.2	0	—	—	0	1.5	—	—
42	0.03	5	0.036	106	41	0.12	12	0.15	70
41	0.05	7	0.061	95	58	0.3	25	0.26	90
58	0.10	9	0.086	91	89	0.3	22	0.17	121
45	0.20	25	0.22	107	53	0.5	50	0.47	103
33	0.60	75	0.91	81	50	1.0	90	1.0	89

The effect of propylene on the 1 : 1 : 1 : 2-tetrachloroethane decomposition (at 367°) was similar, the addition prolonging the already present induction period (Fig. 8). The increase in the length of the induction period (for a standard initial pressure) was again approximately proportional to the amount of propylene added. Table IV, showing results at 367°, illustrates this. Titrations of hydrogen chloride confirmed that there was no significant decomposition during the artificially prolonged induction periods.

When the rate of a homogeneous chemical reaction is retarded by relatively small additions of a molecular species not normally participating in the reaction and, after a time, the rate of reaction increases again to the normal value, at least two interpretations can be put forward. The first, and seemingly more probable view (see Staveley and Hinshelwood, *Proc. Roy. Soc.*, 1937, *A*, **159**, 192) holds that the inhibitor is completely consumed during the initial period. Echols and Pease (*J. Amer. Chem. Soc.*, 1937, **59**, 766; 1938, **60**, 1701; 1939, **61**, 1024), however, during a study of the inhibition of butane pyrolysis by nitric oxide, obtained evidence that the inhibitor was not wholly removed during this time. They suggested that the transient retardation was due to the setting up of an equilibrium between nitric oxide, the various radicals in the system, and the "nitric oxide complexes" formed therefrom. When sufficient of these complexes had been produced it was thought that there was a "feed back" of radicals, so that reaction proceeded again at the normal rate. Propylene was found to behave similarly although the evidence was somewhat less conclusive.

To distinguish between these possibilities in our case, 0.5 mm. of propylene was added to 50 mm. of 1 : 1 : 2 : 2-tetrachloroethane at 367°. When the induction period was over and the rate had just reached normal (about 1 hour), the contents of the reactor were condensed out in a liquid-nitrogen trap. Only about 15% of the 1 : 1 : 2 : 2-tetrachloroethane had by that time decomposed, so that if an equilibrium had been set up, an appreciable quantity of propylene should have remained. The liquid-nitrogen trap was allowed to warm up and the first 8 mm. of gaseous products were returned to the reactor. Since any "propylene complexes" are presumably less volatile than propylene itself, the returned gas should have been enriched in this olefin. However, admixture with a further 50 mm. of 1 : 1 : 2 : 2-tetrachloroethane gave only the normal induction period and rate. Such experiments indicate that the propylene is completely consumed during the induction period.

DISCUSSION.

The existence of temperature-dependent induction periods, and especially the remarkable inhibition produced by very small amounts of propylene, is a proof that the thermal decompositions of 1 : 1 : 2 : 2- and 1 : 1 : 1 : 2-tetrachloroethane proceed by a homogeneous radical-chain mechanism. The fact that, in each case, the addition of propylene causes a directly proportional increase in the length of the induction period (and that no decomposition occurs during this time) means that the reactions must proceed entirely by this chain mechanism. As far as we are aware, this is the first occasion on which such a phenomenon has been noted in the pyrolysis of organic compounds (compare Goldfinger, *Faraday Soc. Discussion*, 1947, **2**, 149).

Our interpretation of the more intimate aspects of the 1 : 1 : 2 : 2-tetrachloroethane pyrolysis follows closely upon our similar treatment of the 1 : 2-dichloroethane decomposition. The reaction mechanism may be represented by the following four steps.

- Initiation.* (i) Kinetically first-order decomposition of the 1 : 1 : 2 : 2-tetrachloroethane to furnish, either directly or indirectly, chlorine atoms.
- Propagation.* (ii) $\text{Cl} + \text{CHCl}_2\cdot\text{CHCl}_2 \longrightarrow \text{HCl} + \cdot\text{CCl}_2\cdot\text{CHCl}_2$.
 (iii) $\cdot\text{CCl}_2\cdot\text{CHCl}_2 \longrightarrow \text{CCl}_2\cdot\text{CHCl} + \text{Cl}$.
- Termination.* (iv) $\text{Cl} + \cdot\text{CCl}_2\cdot\text{CHCl}_2 \longrightarrow \text{HCl} + \text{CCl}_2\cdot\text{CCl}_2$.

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Steps (ii) and (iii) explain the stoichiometry of the reaction, steps (i) and (iv) the first-order kinetics.

By assuming in the propylene inhibition experiments that one molecule of propylene prevents the occurrence of one kinetic chain, it is possible to compute the chain length of the 1 : 1 : 2 : 2-tetrachloroethane decomposition. Thus we have :

Chain length = Rate of overall reaction/Rate of initiating reaction. At 369° the initial overall rate of decomposition of 50 mm. of the reactant is 5.2 mm. min.⁻¹. At this temperature the rate of consumption of propylene (= rate of initiating step) was (see p. 2037) 1/96 mm. min.⁻¹. Hence the chain length is 5.2 × 96 (= about 500).

The more detailed mechanism of the 1 : 1 : 1 : 2-tetrachloroethane decomposition may be represented similarly. A calculation of the chain length at 367°, similar to that made for the symmetrical isomer, indicates a value of 3.9 × 95 (= about 370).

So far in this series of papers we have not discussed the origin of the naturally occurring induction periods found with chlorinated hydrocarbons which decompose by the radical-chain mechanism. Two reasonable explanations may be advanced : (a) that the induction period represents the time required to destroy inhibitors, and (b) that it represents the time required to build up the steady-state concentration of the chain-carrying species. It should be possible to distinguish between these alternatives by admitting reactant to the reactor, pumping it out again into a cold trap at the end of the induction period, and then readmitting it. If (a) is correct then on readmission of the reactant there should be no further induction period, while if (b) is correct the induction period should be unchanged no matter how many times this experiment is repeated. The vapour pressures of the tetrachloroethanes are inconveniently low for this test to be applied, but experiments on 1 : 1 : 1-trichloroethane (Onyon, Ph.D. Thesis, London, 1950) show that (b) is correct for this compound, and similar results have been obtained with 1 : 2-dichloroethane (Barton and Head, unpublished). It is very probable that the same explanation holds for the two tetrachloroethanes, especially as we believe that we have been working with pure specimens of these compounds.

The fact that the induction periods are unaltered on packing the reactor is of importance for a finer aspect of the mechanism of the decomposition of the two tetrachloroethanes and also of 1 : 2-dichloroethane. A radical-chain reaction of this type, if initiated *and terminated* on the reactor walls, might well appear homogeneous when the reactor is packed. However, if the induction periods arise in the way we believe, and they are unchanged, as we have observed, on packing the reactor, then the chains cannot be initiated at the walls. Thus these decompositions are truly homogeneous radical-chain reactions. The chain-carrying species responsible for the induction periods would seem to be the "large" chlorinated alkyl radical, *e.g.*, $\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$ in the case of 1 : 2-dichloroethane.

A more quantitative treatment of the induction periods found with 1 : 2-dichloroethane and other aspects of mechanism will be discussed by one of us (K. E. H.) in a later paper.

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