# THE KINETICS OF THE DEHYDROCHLORINATION OF SUBSTITUTED HYDROCARBONS

# PART IV. THE MECHANISM OF THE THERMAL DECOMPOSITION OF TERT.-BUTYL CHLORIDE

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tert.-Butyl chloride decomposes by a unimolecular mechanism over the temperature range  $290-341^\circ$  C to give stoichiometrically *iso*butene and hydrogen chloride. The pertinent first-order rate equation is

 $k = 10^{12.4} \pm 0.2 \text{ e}^{-(41,400 \pm 600)}/\mathbf{R}T \text{ sec}^{-1}.$ 

Reproducible results are only obtained when the reactor walls are coated with a carbonaceous film. With clean walled reactors a faster heterogeneous reaction supersedes the homogeneous decomposition. A general discussion distinguishes two homogeneous mechanisms for thermal dehydrochlorination and relates them to molecular structure.

In Parts II and III of this series 1 the mechanisms of thermal dehydrochlorination of ethyl chloride, 1:1-dichlorethane and 1:2-dichlorethane were established by kinetic measurements. In continuation of this work we have now studied the thermal decomposition of tert.-butyl This reaction had already been examined from a similar point chloride. of view by Brearley, Kistiakowsky and Stauffer<sup>2</sup> who showed that it was homogeneous and exhibited first-order kinetics. Although it was concluded that the mechanism of the reaction was probably unimolecular, this was not in fact established, for no tests for a radical chain mechanism were applied.

The effect of quartz or glass in promoting the heterogeneous decom-position of organic compounds is well known. In many cases this heterogeneous reaction is replaced by a slower and homogeneous first-order process as the reactor walls become coated with a carbonaceous film.<sup>3</sup> We have noted similar effects with the chlorinated hydrocarbons so far employed in this series. Since it is usually only assumed, without proof, that the initial faster reactions are of a heterogeneous nature it seemed desirable to establish this point conclusively for one compound in our series. This we have now done for tert.-butyl chloride.

#### Experimental

Materials.—Technical, *tert*.-butyl chloride was purified by the method used previously for other chlorinated hydrocarbons.<sup>1</sup> The following constants were recorded and are compared with the mean of the best literature values (in parentheses).

B.p. 50.6° C corr. (50.7° corr.); from : 51.0°; <sup>4</sup> 50.7°; <sup>5</sup> 50.7°; <sup>6</sup> 50.6°.7

<sup>1</sup> Barton and Howlett, J. Chem. Soc., 1949, 155, 165. <sup>2</sup> Brearley, Kistiakowsky and Stauffer, J. Amer. Chem. Soc., 1936, **58**, 43. <sup>3</sup> E.g. see Ramsperger and Leermakers, *ibid.*, 1931, **53**, 2067; Schultz and Kistiakowsky, *ibid.*, 1934, **56**, 395; Choppin, et al., *ibid.*, 1939, **61**, 3176. <sup>4</sup> Timmermans, Bull. Soc. chim. Belg., 1921, **30**, 66. <sup>5</sup> Norris and Rigby, J. Amer. Chem. Soc., 1932, **54**, 2088. <sup>6</sup> Timmermans, and Delcourt, J. Chim. Phys., 1934, **31**, 85. <sup>7</sup> Baker and Smyth, J. Amer. Chem. Soc., 1939, **61**, 2798.

M.p. (sulphur dioxide vapour pressure thermometer),  $-27.85^{\circ}$  C  $(-26.4^{\circ})$ ; from :  $-28.5^{\circ}$ ;  $^{4}$   $-27.1^{\circ}$ ;  $^{8}$  -25.4;  $^{9}$   $-24.6^{\circ}$ .  $d_{4^{\circ}}^{23^{\circ}}$  o.8375 (o.8401 interpolated); from  $d_{4^{\circ}}^{20^{\circ}}$  o.8457;  $^{10}$   $d_{4^{\circ}}^{25^{\circ}}$  o.8370;  $^{5}$ 

0.8347; <sup>11</sup> 0.8376.<sup>12</sup>

I·3835 (I·3837 interpolated); from:  $n_{\rm D}^{25^{\circ}}$  I·3828;  $n_{\rm D}^{20^{\circ}}$  I·3839; <sup>18</sup>  $n_{\rm D}^{23}$ 1·3847; 7 1·3853.14

Apparatus.—The apparatus and technique employed have already been described in detail by Barton and Howlett.<sup>1</sup> Modifications were not found necessary in the present work.

## Results

Brearley, Kistiakowsky and Stauffer<sup>2</sup> experienced difficulty in attaining reproducible results in their study of the tert.-butyl chloride decomposition and ascribed this to interference by a heterogeneous reaction at the reactor walls. We have confirmed this difficulty. Our initial experiments were carried out in a Pyrex glass reactor which had been coated by the thermal decomposition of 1:1:1:2-tetrachlorethane vapour, but which had subsequently been exposed to air at room temperature. In this reactor about zo runs were required before reproducibility of results was attained. Accidental breakage of the spoon gauge and admission of air at the reaction temperature destroyed the effectiveness of the coating. Recoating of the walls was assisted by co-decomposition of tert.-butyl chloride with small quantities (ca. 10 %) of propylene, but even with this aid about 40 runs were required before the reproducibility of rate constants could be regained. Stoichiometry.—That the reaction studied was the quantitative decom-

position of *tert*.-butyl chloride to *iso*butene and hydrogen chloride was established in two ways. Firstly the final pressure in the reactor after many hours was close to twice the initial pressure (Table I). This also showed that the equilibrium

Temp. °K	Initial Pressure \$\$p_0\$ (mm.)	Time of Reaction (hr.)	Final Pressure p <sub>f</sub> (mm.)	Ps/Po
577:5	105.7	13	212.5	2.01
586.8	120.2	14	243.7	2.03
585·7	167.5	22	330.0	1.92
5 <sup>8</sup> 7·4	119.3	13	237.6	1.99
587.6	97.4	15	199 <b>·1</b>	2.04
604.5	127.3	17	257.7	2.02
598-2	133.0	18	261.0	<b>1</b> •96
596.1	114.4	17	228·I	1.99
598·o	122.6	17	244.9	2.00
597.0	96.6	16	191.0	1.99
597.2	92.1	60	176.7	1.95
579.6	116.5	17	235.2	2.02
571.8	105.6	15	216.1	2.05
563.7	116.4	15	230.0	1.98
561.4	108.3	16	216.3	2.00

TABLE I

in the tert.-butyl chloride-isobutene-HCl system was substantially 100 % on the side of the dissociation products over the temperature range employed. This can, indeed, be calculated from the equilibrium constants recorded by Kistiakowsky and Stauffer <sup>13</sup> for this system. Secondly, the amount of hydrogen chloride formed by the decomposition was given closely by the pressure increase.

- <sup>8</sup> Timmermans, Bull. Soc. chim. Belg., 1935, 44, 17. <sup>9</sup> Turkevich and Smyth, J. Amer. Chem. Soc., 1940, **62**, 2468.
- <sup>10</sup> Vogel, J. Chem. Soc., 1943, 636.
- <sup>11</sup> Quayle, Owen and Beavers, J. Amer. Chem. Soc., 1939, 61, 3107.
   <sup>12</sup> Smyth and Dornte, *ibid.*, 1931, 53, 545.
   <sup>13</sup> Kistiakowsky and Stauffer, *ibid.*, 1937, 59, 165.

- <sup>14</sup> Mayo and Dolnick, *ibid.*, 1944, **66**, 985.

This is shown by the data illustrated in Fig. 1, where the line is drawn at the theoretical slope of  $45^{\circ}$ . Measurements of the pressure increase with time constitute, therefore, a satisfactory method of following the kinetics of the reaction.



FIG. 2.

**Kinetics.**—In agreement with Brearley, Kistiakowsky and Stauffer,<sup>2</sup> the decomposition followed first-order kinetics. When reproducibility of results had been attained the reaction was first-order to at least 80 % decomposition, as illustrated by the typical runs plotted in Fig. 2, but for runs before this the

727

first-order rate tended to fall off at rather lower percentage decompositions. Even at the lowest temperatures studied there was no indication of any induction period, such as was found to be a characteristic feature of the i:2-dichlorethane decomposition.

As with the chlorinated ethanes examined previously <sup>1</sup> the velocity constants of the *tert*-butyl chloride decomposition showed no significant variation with initial pressure over the pressure range 40-240 mm. This is illustrated by the data in Table II, obtained at  $614^{\circ}$  K. The correlation coefficient <sup>16</sup>

$$\frac{\Sigma(x-\bar{x})(y-\bar{y})}{\sqrt{\Sigma(x-\bar{x})^2}\times\Sigma(y-\bar{y})^2}$$

for the results in this Table was found to be -0.22. The probability of such a value being obtained by chance from 22 expt. is greater than 0.10 and it may, therefore, be concluded that there is no significant correlation.

\$\$\$p_0 (mm.)	$k \times 10^3 (\text{sec.} -1)$	<i>p</i> ₀ (mm.)	$k \times 10^3$ (sec1
50•2	4.72	123.7	4.70
52.9	4.24	126.7	4.95
69.6	5.01	130.8	4.85
70^9	4.75	135.7	4.65
82.2	4.61	143.8	4.47
96.5	4.78	143.9	4.54
100.0	4.30	149.1	4.68
103.0	4.70	154.9	4.46
104.4	4.56	178.1	4.62
112.9	4.40	194.1	4.46
119.5	4.67	202.7	4.30

TABLE II

For each set of runs over the temperature range  $563-614^{\circ}$  K the reproducibility of first-order rate constants was satisfactory. This is shown in the summarized data set out in Table III. At no temperature did the standard deviation of the mean exceed 1.6 % of the mean value.

TABLE III

Temp. (°K)	No. of Runs	Mean Velocity Constant (sec1)	°/ <sub>o</sub> Standard Devia- tion of the Mean*
563.0	5	$0.22 \times 10^{-3}$	I•2
571.0	7	0.37	1.4
579.5	8	0.01	1.1
587.0	22	o•94	1.0
596.5	9	1.70	1.3
604.0	IO	2.64	1.3
607.5	8	3.28	1.0
614.0	24	4.56	1.5

\* Given by  $\operatorname{Ioo} \sqrt{\frac{\overline{\Sigma}(x-\overline{x})^3}{n(n-1)}} / \overline{x}$  where the symbols have the obvious significance.

The logarithm of the mean rate constant plotted against the reciprocal of the absolute temperature gave a good straight line (Fig. 3). This line has been drawn by the least squares method giving the proper statistical weight to each point. The corresponding rate equation was found to be

 $k = 10^{12.4 \pm 0.2} e^{-(41,400 \pm 600)/RT} sec.^{-1}$ 

The error limits in this equation were fixed as follows. It was assumed that all the error resided in the  $\log_{10} k$  values and none in the temperature measurements. The root mean square of the deviations of the logarithms of the mean

<sup>15</sup> See Fisher, Statistical Methods for Research Workers (Oliver and Boyd, 1934).

velocity constants from the least squares line (viz. 0.009) was then applied positively and negatively to the two ends of the least squares line at the extreme temperatures of the experimental range to give the error limits shown. Although this procedure may err in ascribing too high a degree of precision to our



10<sup>3</sup>/T °K.

FIG. 3.

measurements, we intend to adopt it as a convenient method for comparing the agreement of our results from paper to paper and have, therefore, described it in detail on this occasion.

Effect of **Propylene**.—In previous parts of this series <sup>1</sup> and elsewhere <sup>18</sup> we have shown that propylene constitutes a powerful inhibitor for the decompositions of chlorinated hydrocarbons which proceed by a chain mechanism. The effect of adding propylene to decomposing *tert*.-butyl chloride was therefore studied. As with ethyl chloride and I : I-dichlorethane, propylene had no influence on the rate of decomposition. This is illustrated in Fig. 4 where the *tert*.-butyl chloride initial pressures varied from 76 to 206 mm.

TABLE IV \*

Pressure of $Cl_2 \times 100$ Initial Pressure of $(CH_3)_3$ . CCl	Observed First Order Velocity Constant k (sec1)	k from Rate Equation (sec.~1)
0.82 0.21 8.0 0.70 1.66	$0.195 \times 10^{-3}$ 0.205 Non-linear 0.22 0.23	$\left.\right\} 0.502 \times 10^{-3}$

\* All experiments at 562.2° K.

Effects of Chlorine and Oxygen.—Small amounts of chlorine and oxygen are powerful inducing agents for the decomposition of I:2-dichlorethane.<sup>91</sup> As the data summarized in Tables IV and V, which refer to chlorine and oxygen

729

respectively, show, these two elements have no significant effect on the course of the *tert*.-butyl chloride decomposition. For both addenda the kinetics were satisfactorily first order for less than 2% additions.



FIG. 4.

The Heterogeneous Decomposition of *tert*.-Butyl Chloride on Glass.— Three series of experiments were carried out in the following reactors; series A, empty Pyrex glass reactor with a surface area to volume ratio of  $2 \cdot 72$  cm.<sup>-1</sup>; series B, Pyrex glass reactor packed with Pyrex tubing with a surface area to volume ratio of  $9 \cdot 98$  cm.<sup>-1</sup>, and series C, Pyrex glass reactor packed with soft

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Temp. °K	$\frac{\text{Pressure of } O_2 \times 100}{\text{Initial Pressure of}} \\ (CH_3)_3 . CC1$	Observed First Order Velocity Constant k (sec1)	k from Rate Equation (sec1)
562·5 562·9 562·9 563·1 563·1	0.13 0.28 0.35 1.15 1.91	$ \begin{array}{r} 0.20 \times 10^{-3} \\ 0.23 \\ 0.23 \\ 0.225 \\ 0.225 \end{array} $	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$

soda glass wool and having a very large surface area to volume ratio. The reactors were constructed from tubing that had been well washed with distilled water and before use each was evacuated at  $200^{\circ}$  under 0.1 mm. pressure for 16 hr.

The first runs in both series A and B showed zero-order kinetics. The runs immediately following proceeded at much faster rates but the apparent order of the reaction increased, in series B to predominantly first order, and in series A to an order varying between first and second. For comparison the results of series A, with the exception of the first zero-order run, have been expressed as first-order rate constants, calculated from the initial stages (first 25 %) of each experiment, where the deviation from first-order kinetics was not large.

The first eight runs all performed within the same day, for the two sets of experiments, are compared in Table VI. The series B in the packed reactor proceeded at 2-3 times the rate of the series A in the empty reactor. In both series the rate was considerably higher with the clean walled reactors than for the homogeneous reaction (calculated first-order velocity constant  $k = 1.44 \times 10^{-6}$  sec.<sup>-1</sup> at 496° K from the rate equation given above) in the coated reactor.

Series A			S	eries B			
Temp. °K	Initial Pressure of (CH <sub>3</sub> ) <sub>3</sub> . CCl (mm.)		First-order Velocity Constant (sec1)	Temp. °K	Initial Pressure of (CH <sub>3</sub> ) <sub>3</sub> . CCI (mm.)	t1/t1	First-order Velocity Constant (sec1)
497·1 496·2 497·1 496·7 496·9 496·3 497·4 498·1	27.9 70.0 68.7 146.5 116.6 78.8 48.4 33.5	2.0 2.54 2.93  3.09 3.26 3.24	$ \begin{array}{c} 0.88 \times 10^{-3} \\ 1.08 \\ 1.03 \\ 1.19 \\ 1.40 \\ 1.45 \\ 1.45 \\ 1.45 \end{array} $	495.8 495.8 495.8 495.8 495.8 495.8 495.8 495.4 495.9 495.9	31.0 76.1 75.9 160.3 119.6 81.4 55.8 32.6	2.0 2.38 2.52 2.50 2.43 2.38 2.54 2.48	$2.77 \times 10^{-3}$ 2.92 2.99 2.97 2.87 2.72 2.79

TABLE VI

Whereas similar experiments with ethyl bromide showed <sup>16</sup> a rapid ageing of the glass surface this effect is very slow with chlorinated hydrocarbons as we have noted previously for I:2-dichlorethane.<sup>1</sup> In series A the next 14 runs, made within 24 hr., although showing bad reproducibility from run to run, gave little indication of any overall downward trend in velocity constants.



FIG. 5.

These results are summarized for various temperatures in Fig. 5, from which it may be deduced that the process studied had the low activation energy of roughly 15,000  $\pm$  6,000 cal.

Experiments to determine the effect of oxygen on the surface were made with the reactor used for series A. Immediately after the reaction products of a normal run had been pumped out of the reactor, a known pressure of oxygen

<sup>16</sup> Daniels and Veltman. J. Chem. Physics, 1939, 7, 756.

was admitted, allowed to remain in the reactor for 15 min., then pumped out and the test run started at once. The results, summarized in Table VII, show

Pressure of Oxygen used for	First Order Vel	ocity Constant
All experiments at 510° K	Control Run (sec1)	Test Run (sec1)
8.0 5.9 0.6 0.7 (admitted with the <i>tert.</i> -butyl chloride)	3·21 × 10 <sup>-3</sup> 2·94 3·60 3·31	5·76 × 10 <sup>-3</sup> 6·08 4·71 3·35

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that this pre-treatment with oxygen caused a marked increase in the velocity of heterogeneous decomposition. However, similar pressures of oxygen admitted with the *tert*.-butyl chloride at the beginning of a run did not increase the rate significantly (Table VII).

The initial runs at 490° K in series C were extremely fast, the *tert*.-butyl chloride decomposing as rapidly as it was admitted to the reactor. This was shown by allowing the pressure in the system to become steady (about 1 min.) condensing out the reaction products and titrating for hydrogen chloride. The pressure of the latter, calculated from the analysis, corresponded to half the final pressure in the system (Table VIII). Two runs were made at about 410° K, the lowest temperature attainable using mercury as thermostatic liquid. Even at this temperature the rate was so high that the initial pressure  $p_0$  had to be calculated from the time-pressure curve. This was done by adapting Guggenheim's method,<sup>17</sup> or in the following way. If  $p_0$  is the true initial pressure,  $p_1$  the first observed pressure at time  $t_0$ ,  $p_n$  the pressure at time  $t_{n-1}$  and  $\Delta t_{(n-1)} = t_{(n-1)} - t_0$ , then it is easily shown that, for a first-order reaction,

$$p_n \cdot e^{\Delta t_{(n-1)}} = e^{\Delta t_{(n-1)}} \cdot 2p_0 - (2p_0 - p_1)/e^k.$$

Thus by plotting  $p_n \cdot e^{\Delta t_{(n-1)}}$  against  $e^{\Delta t_{(n-1)}}$  the slope of the straight line gives  $2p_0$ . An average rate constant of  $11\cdot7 \times 10^{-3}$  sec.<sup>-1</sup> was observed under these conditions.

Final Pressure p <sub>f</sub>	<i>p</i> <sub>1</sub> /2	HCl by Analysis
(mm.)	(mm.)	(mm.)
132·6	66•3	69·5
215·2	107•6	104·0

TABLE VIII

### Discussion

The decomposition of *tert*.-butyl chloride corresponds by all experimental criteria with the similar reactions of ethyl chloride and of I: I-dichlorethane.<sup>1</sup> Thus it is not inhibited by propylene, shows no induction period and from the experiments of Brearley, Kistiakowsky and Stauffer<sup>2</sup> is homogeneous. Furthermore its rate equation has a normal non-exponential term of  $10^{12.4}$  sec.<sup>-1</sup> and the reaction is not induced by chlorine or oxygen. By the arguments given previously<sup>1</sup> it must, therefore, be a unimolecular decomposition.

<sup>17</sup> Guggenheim, Phil. Mag., 1926 [7], 2, 538.

Our rate equation for the reaction,

 $k = 10^{12.4} \pm 0.2 \text{ e} - (41,400 \pm 600)/RT \text{ sec.}^{-1}$ 

is in fair agreement with that found previously,

 $k = 10^{13.9 \pm 0.7} e^{-(45,000 \pm 1,900)/RT} sec.^{-1}$ 

by Kistiakowsky.<sup>2, 13</sup> We consider that our result is the more reliable for the following reasons. Firstly, the error limits given by Kistiakowsky, indicated by the dotted lines in Fig. 3, are larger than those given here, though, of course, the method of calculation may be different. Secondly, Kistiakowsky's rate equation is based on 25 observations of which 15 were obtained over a 7° temperature range, whereas the results in this paper cover 93 observations spread over the whole temperature range studied.

We have shown above that the initial fast decomposition of *tert*.-butyl chloride in clean walled reactors is heterogeneous in origin and that the rates of reaction only approach complete reproducibility after many runs when the reactor walls have been uniformly coated. At the same temperatures as Kistiakowsky<sup>2</sup>.<sup>13</sup> employed we have been able to obtain velocity constants identical with his, but on repeating the runs many times the constants have always fallen eventually to the values we give above.

General Mechanisms of Dehydrochlorination (with K. E. Howlett). —We have now reached a stage in our investigations where it is convenient to summarize our views on the three general mechanisms of dehydrochlorination which we have established. The three mechanisms are (i) heterogeneous decomposition on glass surfaces as exemplified by our study on *tert*.-butyl chloride reported here and which is obviously of general application, (ii) homogeneous first-order unimolecular decomposition as exemplified by ethyl chloride,<sup>1</sup> I : I-dichlorethane,<sup>1</sup> *tert*.-butyl chloride and *iso*propyl chloride <sup>18</sup> and (iii) homogeneous first-order decomposition by radical chains as exemplified by I : 2-dichlorethane to predict which of the two homogeneous mechanisms (ii) and (iii) will be applicable to a particular chloro-compound from an inspection of its molecular structure. The correlation proceeds as detailed below.

A chloro-compound will decompose by a radical chain mechanism only so long as neither the compound itself nor the reaction products are inhibitors for the chains. In general the unimolecular mechanism will be of more universal application than the radical chain mechanism. The latter may be characterized by four steps comparable to those already shown to apply for the I:2-dichlorethane decomposition.

(a) Initiating step or steps which are kinetically of the first-order and which lead to the production of chlorine atoms.

(b) First propagation step involving an attack of a chlorine atom on the substrate with abstraction of hydrogen and the formation of a "large" chlorine-containing radical.

"large" chlorine-containing radical.
(c) Decomposition of the "large" radical to give the olefine or chloroolefine and a further chlorine atom which can participate again in step (b).

(d) Terminating step comprising the attack of a chlorine atom on the "large" radical to give non-radical products.

Steps (b) and (c) explain the stoichiometry of the reactions, step (d) the observed first-order kinetics. Inhibitors may suppress the reaction by interference in steps (b) and (c).

Now when ethyl chloride is attacked by chlorine atoms it affords not the 2-chlorethyl radical (I) but the 1-chlorethyl radical (II). This is

demonstrated by the formation of I: I-dichlorethane by radical chlorination of ethyl chloride in the gas phase.<sup>19</sup> \* Similarly radical chlorination of I: I-dichlorethane gives predominantly I: I: I-trichlorethane as the trichloro-fraction.<sup>19</sup> This shows that the I: I-dichlorethyl radical (III) must be formed as intermediate rather than the 2: 2-dichlorethyl radical (IV). An analogous attack of chlorine atoms on I: 2-dichlorethane must, for structural reasons, furnish the I: 2-dichlorethyl radical (V).

> . CH2. CH2CI . CHCI. CH2 . CCl<sub>2</sub>CH<sub>3</sub> (II) (III) (I) . CH<sub>2</sub>. CHCl<sub>2</sub> . CHCl. CH.Cl (IV) (V)

Whereas the latter radical may furnish a chlorine atom and a stable olefine by fission of a single valency bond, radicals (II) and (III) can only give these reaction products provided the migration of a hydrogen atom accompanies the process. It is possible to understand, therefore, why ethyl chloride and I : I-dichlorethane may act as inhibitors for their own radical chain decompositions. Similarly it is easily understood why the molecular structures of the two tetrachlorethanes permit them to decompose by the radical chain mechanism.

TABLE IX

Chloro compound -		Predicted Homogeneous First-order Mechanism			
		Unimolecular	Radical Chain		
Ethyl chloride I : I-Dichlorethane I : 2-Dichlorethane I : I : I-Trichlorethane I : I : 2-Trichlorethane I : I : 2 : 2-Tetrachlorethane		× (already observed) × (already observed)	× (already observed) × × × (already observed) × (already observed) ×		
1-Chloropropane 2-Chloropropane 1 : 2-Dichloropropane . 1 : 2 : 3-Trichloropropane .		× × (already observed) ×	×		
<i>n</i> -Butyl chloride <i>tert</i> Butyl chloride	:	$\stackrel{ imes}{ imes}$ (already observed)			
2: 2'-Dichlorethyl ether . $\beta$ -Chloroethylbenzene . $\alpha$ -Chlorethylbenzene.	• • •	×	Possibly Possibl <b>y</b>		

tert.-Butyl chloride is an example of a molecule which should not, itself, be an inhibitor for the radical mechanism but its decomposition product, isobutene, should possess this power. isoPropyl chloride would be expected to exhibit both types of inhibition.

Table IX summarizes prediction and observation, so far as experiment has progressed in this field. We intend to examine the decomposition

\* It is an unexplained observation that attack by chlorine atoms on an alkyl chloride in solution 20 leads to substitution at a position remote from the chlorine atom originally present. In the gas phase exactly the opposite occurs.<sup>19</sup> <sup>19</sup> Vaughan and Rust, J. Org. Chem., 1940, **5**, 449. <sup>20</sup> Kharasch and Brown, J. Amer. Chem. Soc., 1939, **61**, 2142; compare Taft and Stratton, Ind. Eng. Chem., 1948, **40**, 1485.

characteristics of the various chloro compounds which we have not so far studied in order to test the validity of our suggestions.

It is attractive to speculate that only substances which can decompose by the radical chain mechanism can have their decomposition induced by oxygen or chlorine.<sup>21</sup> In the majority of the cases so far studied, such would appear to be the case.

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<sup>21</sup> Barton, Nature, 1946, 157, 626; J. Chem. Soc., 1949, 148.