# THE KINETICS OF THE DEHYDROCHLORINATION OF SUBSTITUTED HYDROCARBONS

## PART V.—THE MECHANISM OF THE THERMAL DECOMPOSITIONS OF 2-CHLOROPROPANE AND 1: 2-DICHLOROPROPANE

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2-Chloropropane decomposes in the temperature range  $367-406^{\circ}$  C by a nearly homogeneous first-order reaction to give propylene and hydrogen chloride. The relevant rate equation is

 $k = 10^{13\cdot4 \pm 0\cdot2} e^{-50,500 \pm 700/\mathbf{R}T} sec.^{-1}.$ 

There is no variation in rate constant with initial pressure. Additions of propylene and, in small amounts, of oxygen and chlorine do not affect the rate.

I: 2-Dichloropropane decomposes in the temperature range  $416-452^{\circ}$  C by a nearly homogeneous first-order reaction, for which the relevant approximate rate equation is  $k = 10^{13\cdot8} e^{-54,900/\text{RT}} \text{ sec.}^{-1}$ . For both substances the mechanism of the decomposition is unimolecular, in agreement with the theory previously advanced.

Previous studies in this series 1, 2 have dealt with the thermal decompositions of ethyl chloride, 1:1- and 1:2-dichlorethanes and *tert*.-butyl

<sup>&</sup>lt;sup>1</sup> Barton and Howlett, J. Chem. Soc., 1949, 155, 165.

<sup>&</sup>lt;sup>2</sup> Barton and Onyon, Trans. Faraday Soc., 1949, 45, 725.

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Whilst there are still a number of minor features with regard chloride. to the 1:2-dichlorethane pyrolysis which require further examination, there can be no doubt in every case as to the correctness of the established mechanism of reaction. Three general mechanisms of dehydrochlorination have been detected, one of which is heterogeneous and most marked in clean-walled reaction vessels. The two homogeneous mechanisms are respectively unimolecular and radical chain in character. In Part IV of this series <sup>2</sup> we drew up a general theoretical scheme purporting to predict the mechanism of decomposition of a saturated chlorinated hydrocarbon merely by inspection of its molecular formula. This general scheme refers to the propagation steps in the hypothetical chain sequence and predicts whether the chain will, in fact, be propagated or not. Of course the existence of the necessary structural requirements for the propagation of the chain mechanism of decomposition does not of itself guarantee that a compound will decompose in such a manner, because for each substance there might be competition between the two different homogeneous mechanisms. The rigid application of the generalization enables us to predict which compounds cannot decompose by a chain mechanism, as contrasted with those which may. In actual fact it has been a common feature of our experience so far that saturated chlorinated hydrocarbons do decompose by the chain mechanism whenever the structural requirements are satisfied and inhibitors are absent.

Continuing our work in directions already indicated <sup>2</sup> we have now turned our attention to 2-chloropropane and 1:2-dichloropropane. Both of these compounds should <sup>2</sup> decompose by the unimolecular mechanism, which prediction we have now proved to be correct.

## Experimental

Materials .- Technical 2-chloro- and 1: 2-dichloropropane were purified by the method used previously for other chlorinated hydrocarbons,<sup>1</sup> except that it did not prove possible to submit the dichloro-compound to fractional crystal-lization since it afforded a glass on cooling.<sup>3</sup> The following constants were recorded and are compared with the mean of the best literature values (in parentheses).

B.p. 35.0° C corr. (34.8° corr.); from 34.8°.4

 $d_{4^\circ}^{22^\circ} \circ \cdot 8585 \text{ (o} \cdot 8591 \text{ interpolated) ; from } d_{4^\circ}^{0^\circ} \circ \cdot 8869, {}^4d_{4^\circ}^{15^\circ} \circ \cdot 8680, {}^4d_{4^\circ}^{16^\circ} \circ \cdot 8657, {}^5$  $d_{4^{\circ}}^{20^{\circ}}$  0.8629,5  $d_{4^{\circ}}^{30^{\circ}}$  0.8491.4

 $n_{\rm D}^{22^{\circ}}$  1·3770 (1·3772 extrapolated); from  $n_{\rm D}^{15^{\circ}}$  1·38110.4

(b) I:2-DICHLOROPROPANE

B.p. 96·1-96·2° C corr. (96·6° corr.); from 96·8°,6 96·4°,7

 $d_{4^{\circ}}^{29^{\circ}}$  I·1464 (1·1461 interpolated); from  $d_{4^{\circ}}^{14^{\circ}}$  1·1656,6  $d_{4^{\circ}}^{20^{\circ}}$  1·1578;8 d42.1° 1.1294.8

 $n_{\rm D}^{22^{\circ}}$  1.4389 (1.4391); from  $n_{\rm D}^{20^{\circ}}$  1.4393,8  $n_{\rm D}^{20^{\circ}}$  1.4388.8

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

<sup>3</sup> Cf. Timmermans, Bull. Soc. chim. Belg., 1927, 36, 504.

- <sup>4</sup> Timmermans and Martin, J. Chim. Phys., 1928, 25, 422.

- <sup>5</sup> Vogel, J. Chem. Soc., 1943, 636. <sup>6</sup> Linnemann, Annalen, 1872, 161, 62. <sup>7</sup> Nelson and Young, J. Amer. Chem. Soc., 1933, 55, 2429. <sup>8</sup> Voxel J. Chem. Soc. 1948, 644
- <sup>8</sup> Vogel, J. Chem. Soc., 1948, 644.
- <sup>9</sup> Goudet and Schenker, Helv. chim. Acta., 1927, 10, 132.

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<sup>(</sup>a) 2-CHLOROPROPANE

#### Results

In Part IV of this series <sup>2</sup> we explained the difficulty of obtaining reproducible results in the pyrolysis of chlorinated hydrocarbons due to the variable catalytic activity of the surface of the reactor. Satisfactory reproducibility was only obtained after this heterogeneous reaction had been suppressed by the deposition of a uniform carbonaceous coating. Similar effects were noticed also in the thermal decompositions reported here, and the results outlined below were only obtained after the walls had been "aged" in the usual manner.<sup>1, 2</sup> Stoichiometry.—Previous parts <sup>1, 2</sup>, <sup>10</sup> in this series have established that

**Stoichiometry.**—Previous parts <sup>1, 2, 10</sup> in this series have established that the pyrolysis of saturated chlorinated hydrocarbons leads to the production of an olefin or chlorinated olefin and hydrogen chloride, in equimolecular amounts. The further pyrolysis of the olefin or chlorinated olefin under the same reaction conditions is slow enough to be neglected. That the reaction studied, in the case of 2-chloropropane, was the production of propylene and hydrogen chloride was confirmed by a series of long term (15-hr.) experiments in which the pressure finally attained was close to double the initial pressure (Table I). This also showed that the equilibrium position in the 2-chloropropane–propylene–HCl system was substantially 100 % on the side of the dissociation products over the temperature range employed.

Previously we had found <sup>10</sup> that up to 723° K the pyrolysis of 1:2-dichloropropane afforded a mixture of monochloropropenes and hydrogen chloride. In a series of long term (15-hr.) experiments the ratio of final to initial pressure was definitely greater than 2 (Table I) due, no doubt, as in the case of 1:2dichlorethane,<sup>1</sup> to the splitting out of a second molecule of hydrogen chloride.

Temp. (°K)	Initial Pressure $p_0$ (mm.)	Final Pressure $p_f$ (mm.)	\$
2-Chloropropane			
640	123.8	241.7	1.92
663	56.3	110.0	1.95
663	80.3	159.9	1.99
663	55.6	107.9	1.94
663	61.1	122.6	2.01
664	70.1	136.5	1.92
664	38.6	75.3	1.95
664	86•1	170.8	1.98
665	66.6	132.2	1.99
665	108.5	210.6	1.94
665	38.7	77.5	2.00
665	77.7	153.3	1.92
675	65.5	129.0	1.92
t : 2-Dichloropropa	ine		
678	105.2	257.3	2.44
678	106.1	248.4	2.34
678	82.9	194.8	2.35
678	120.0	287.6	2.39
678	116.0	273.5	2.36
705	122.5	308.9	2.52
714	89.5	228.6	2.56
714	80.1	210.6	2.63

TABLE I

**Kinetics.**—Both thermal decompositions followed first-order kinetics, as illustrated by the data in Fig. 1 for 2-chloropropane and in Fig. 2 for 1:2dichloropropane. In neither case was there any indication of the temperaturedependent induction periods which are a characteristic feature of the chaintype thermal dehydrochlorinations. Further, as is demonstrated in Table II, with neither substance was there any significant variation of velocity constant

<sup>10</sup> Barton, J. Chem. Soc., 1949, 148.

with initial pressure in the pressure ranges studied. This is a common feature of the reactions that we have examined so far in this series.

Having established these facts, the rate of decomposition of 2-chloropropane was determined at various temperatures in the range  $367^{\circ}$ - $406^{\circ}$  using initial



FIG. I.



FIG. 2.

pressures of about 100 mm. The results obtained are summarized in Table III and it will be seen from the standard deviation of the mean (always < 1.3 %) that the reproducibility was satisfactory. The plot of  $\log_{10} k + 4$  against the reciprocal of the absolute temperature gave a satisfactory straight line

(Fig. 3), drawn by the least squares method, giving the same statistical weight to every run. The relevant rate equation is

$$k = 10^{13\cdot4} \pm 0.2 e^{-50,500} \pm 700/\mathbf{RT} sec.^{-1}$$

where the error limits are computed by the method described previously.<sup>2</sup>

2-Chloropropane.*		1 : 2-Dich loropropane †	
Þ <sub>0</sub> (mm.)	k (sec. <sup>-1</sup> )		k (sec1)
59.6	$9.15 \times 10^{-4}$	81.4	$9.34 \times 10^{-4}$
62.5	8.77	88.2	9.35
78.4	9.08	89.5	9.18
82.4	9.08	97.0	9.13
88.3	9.02	100.2	9.50
96.4	8.97	102.1	9.44
103.9	9.21	107.1	9.47
112.8	8.99	112.0	9.45
134.1	8.79	140'1	9.23

TABLE II

\* All runs at 669.0° K; k (from rate equation)  $8.85 \times 10^{-4}$  sec.<sup>-1</sup>. † All runs at  $713.5^{\circ}$  K; k (from rate equation)  $9.57 \times 10^{-4}$  sec.<sup>-1</sup>.

The reaction was shown to be substantially homogeneous by using a reactor packed with glass tubing in which the surface area/volume ratio had been increased by a factor of about four compared with the unpacked reactor. Here the mean velocity constant was increased by 12 % over that computed for the same temperature from the above rate equation.



FIG. 3.

Temp. (° K)	No. of Runs	Mean Velocity Constant (sec. <sup>-1</sup> )	Percentage Standard * Deviation of the Mean
2-Chloropropane			
640.6	7	$0.162 \times 10^{-3}$	0.2
646.7	5	0.238	١٠٥
651.2	6	0.311	0.6
657.5	6	0.475	1.3
665.1	14	0.706	0.2
669 <b>•</b> 0	9	0.001	0.6
674•9	12	1.225	o•8
679•7	9	1.203	0.6
1 : 2-Dichloropropane			
689.5	8	0.223	o•8
699.7	8	0.443	1.5
713.5	13	0.942	0.2
725.1	11	1.821	0.9
Experiments in Packe	d Reactor.		
2-Chloropropane	1		
659.7	10	0.222	0.4
1 : 2-Dichloropropane			
682.7	13	0.502	2.2
		1	1

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TABLE III

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A similar, but more superficial, study has been made with 1:2-dichloro-propane. The results are summarized in Table III and in Fig. 4. The relevant rate equation was found to be

$$k = 10^{13\cdot8} e^{-54,900/\mathbf{R}T} \text{ sec.}^{-1}$$

Since the reaction was only examined at four temperatures we prefer not to attach any error limits to this equation. Packing the reactor in the same way as for 2-chloropropane led to the result shown in Table III, which represents an increase of 23 % over the rate calculated from the above rate equation. It must be concluded that the decomposition was substantially homogeneous.

Effect of Propylene.—In previous parts of this series  $^{1}$  and elsewhere  $^{11}$  we have shown that propylene constitutes a powerful inhibitor for those decompositions of chlorinated hydrocarbons which proceed by a chain mechanism. The effect of adding propylene to decomposing 2-chloro- and I: 2-dichloro-propanes was therefore studied. As with ethyl chloride,<sup>1</sup> I: 1-dichlorethane <sup>1</sup> and *tert.*-butyl chloride,<sup>2</sup> propylene had no influence on the rate of decom-position. This is illustrated in Table IV where the 2-chloropropane initial

2-Chloropropane *		1:2-Dichloropropane †		
$\frac{\text{Pressure of } C_3H_6 \times 100}{\text{Init. Press. of 2-Chloropr.}}$	k (sec. <sup>-1</sup> )	$\frac{\text{Pressure of } C_8H_6 \times 100}{\text{Init. Press. of } 1:2\text{-Dichloropr.}}$	$k \; (sec.^{-1})$	
0 ‡ 2·6 6·7 13·5 25·8	$4.76 \times 10^{-4}$ 4.62 4.75 4.94 4.65	0 ‡ 1.6 3.2 5.3 11.2	$4.78 \times 10^{-4}$ 4.68 4.65 4.65 4.67 4.57	
77.0	4.47	13.4	4.63	

TABLE IV

\* All expt. corrected to  $658 \cdot 2^{\circ}$  K; k (from rate equation)  $4.75 \times 10^{-4}$  sec.<sup>-1</sup>. † All expt. corrected to  $701 \cdot 2^{\circ}$  K; k (from rate equation)  $4.86 \times 10^{-4}$  sec.<sup>-1</sup>. Average value for normal runs carried out during these experiments.

pressure was 82 mm., and where the 1 : 2-dichloropropane initial pressure varied from 103 to 130 mm.

Effect of Chlorine and Oxygen .- Small amounts of chlorine and oxygen are powerful inducing agents for the decomposition of 1 : 2-dichlorethane.<sup>10, 12</sup> As the data summarized in Table V (for chlorine) and Table VI (for oxygen)

2-Chloropropane *		1:2-Dichloropropane †	
$\frac{\text{Pressure of } Cl_2 \times 100}{\text{Init. Press. of 2-chloropr.}}$	k (sec1)	$\frac{\text{Pressure of } Cl_2 \times 100}{\text{Init. Press. of } 1:2\text{-Dich loropr.}}$	$k (\text{sec.}^{-1})$
0.1 0.5 0.9 1.4 0 <sup>+</sup>	4.78 × 10 <sup>-4</sup> 4.63 4.99 Rapid—non-linear 5.63	0.2 0.5 1.5 3.3 0 ‡	$6.06 \times 10^{-4}$ 6.01 5.81 5.73 5.79

TABLE V

\* All expt. corrected to  $658\cdot 2^{\circ}$  K; k (from rate equation)  $4\cdot75 \times 10^{-4}$  sec.<sup>-1</sup>. † All expt. corrected to  $704\cdot7^{\circ}$  K; k (from rate equation)  $5\cdot90 \times 10^{-4}$  sec.<sup>-1</sup>. ‡ Normal run with no addition of chlorine, carried out immediately after the chlorine experiments were completed. The marked increase in rate with 2-chloropropane may mean that larger amounts of chlorine destroy the reactor coating and thus re-introduce the fast heterogeneous decomposition.

<sup>11</sup> To be published.

12 Barton, Nature, 1946, 157, 626.

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show, these two elements, in small amounts and in coated reactors, have no significant effect on the rates of decomposition of 2-chloropropane and of 1:2-dichloropropane. In every case the initial pressure was in the range 65 to 135 mm.

2-Chloropropane *		1:2-Dichloropropane †		
Pressure of $O_2 \times 100$ Init. Pressure of 2-chloropr.	k (sec1)	$\frac{\text{Pressure of } O_2 \times 100}{\text{Init. Pressure of } 1:2\text{-Dichloropr.}}$	k (sec.~1)	
0·2 0·5 1·6 2·6 5·0 0 ‡	4.70 × 10 <sup>-4</sup> 4.79 4.84 5.13 Poor first 5.78 f order plots 5.02	0.2 0.3 0.7 1.7 3.6 0 ‡	$5.31 \times 10^{-4}  5.33  5.31  5.22  5.08  5.32 $	

TA	BL	Æ	VI

\* All expt. corrected to 658.2° K; k (from rate equation) 4.75  $\times$  10<sup>-4</sup>.

† All expt. corrected to  $703 \cdot 2^{\circ}$  K; k (from rate equation)  $5 \cdot 43 \times 10^{-4}$ .

<sup>‡</sup> Normal run with no addition of oxygen, carried out immediately after the oxygen expt. were completed.

### Discussion

The decompositions of 2-chloropropane and of I:2-dichloropropane correspond by all experimental criteria with the similar reactions of ethyl chloride, I:I:1-dichlorethane I and *tert*.-butyl chloride.<sup>2</sup> Thus they are not inhibited by propylene, show no induction periods and are substantially homogeneous. Furthermore their rate equations have non-exponential terms (see further below) which are within a power of ten of  $Io^{13}$ , the value generally accepted as normal. Neither reaction, under the experimental conditions used here, was induced by the addition of chlorine or oxygen.<sup>\*</sup> By the arguments given previously I, I both reactions must be unimolecular in mechanism.



FIG. 5.

<sup>13</sup> Gregg and Mayo, Faraday Soc. Discussions, 1947, 2, 328; cf. Fairclough and Hinshelwood, J. Chem. Soc., 1937, 538, 1573; Cremer, Experientia, 1948, 4, 349; Bamford and Dewar, Nature, 1949, 163, 256; Moelwyn-Hughes, Kinetics of Reactions in Solution (Oxford University Press, 1933), p. 167; (1947 edition), p. 294.

edition), p. 294. \* Cullis, Hinshelwood and Mulcahy (*Proc. Roy. Soc. A*, 1949, **196**, 160) noted that 50 mm. of 2-chloropropane decomposed at  $343^{\circ}5^{\circ}$  C at 0.27 mm./min. This corresponds to a first-order velocity constant of  $9 \cdot 0 \times 10^{-5}$  sec.<sup>-1</sup>, which

### TABLE VII \*

Substance Decomposed	Reaction Products	log <sub>10</sub> A	E (kcal./mole)
(a) Normal Non-Exponential	Terms		
$\begin{array}{c} C_2H_5Cl^1 \\ (CH_3)_2CHCl \\ (CH_3)_3CCl^2 \\ CHCl_2 . CH_3^{1} \dagger \\ CH_3 . CHCl . CH_2Cl \\ (CH_3)_3C (OH)^{14} \\ (CH_3)_2(C_2H_5)C(OH)^{14} \\ (CH_3)_3C . OAc^{15} \\ (CH_3)_3C . O . CO . CH_2CH_3^{16} \\ Cyclopentene^{17} \end{array}$	$\begin{array}{l} C_2H_4 + HCl\\ CH_3 . CH : CH_2 + HCl\\ (CH_3)_2C : CH_2 + HCl\\ CH_2 : CHCl + HCl\\ CH_2 : CHCl + HCl\\ (CH_3)_2C : CH_2 + H_2O\\ Amylenes + H_2O\\ (CH_3)_2C : CH_2 + CH_3 . CO_2H\\ (CH_3)_2C : CH_2 + CH_3 . CH_2 . CO_2H\\ (CH_3)_2C : CH_2 + CH_3 . CH_2 . CO_2H\\ Cyclopentadiene + H_2 \end{array}$	$\begin{array}{c} 14.6 \pm 0.25 \\ 13.4 \pm 0.2 \\ 12.4 \pm 0.2 \\ 11.8 \pm 0.3 \\ 13.8 \\ 14.68 \\ 13.51 \\ 13.34 \\ 12.79 \\ 13.04 \end{array}$	$\begin{array}{c} 60.8 \pm 0.8 \\ 50.5 \pm 0.7 \\ 41.4 \pm 0.6 \\ 48.3 \pm 0.9 \\ 54.9 \\ 65.5 \\ 60.0 \\ 40.5 \\ 39.16 \\ 58.8 \end{array}$
(b) Abnormal Non-Exponential $CH_3 \cdot CH(OAC)_2^{-18}$ $CH_3 \cdot CH(OCCH_2CH_3)_2^{-19}$ $C_3H_7 \cdot CH(OAC)_2^{-19}$ $C1 \cdot CO_2 \cdot C_2H_5^{-20}$ $C1 \cdot CO_2 \cdot CH(CH_3)_2^{-21}$	$Terms \\ CH_3 . CHO + Ac_2O \\ CH_3 . CHO + (CH_3CH_2CO)_2O \\ C_3H_7 . CHO + Ac_2O \\ C_2H_5CI + CO_2 \\ (CH_3)_2CHCI + CH_3CH : CH_2 \\ + HCI + CO_2 \\ \end{cases}$	10·3 10·4 10·5 10·7 9·5	32·9 32·9 32·9 29·4 26·4

\* It seems established that the thermal decompositions of paraldehyde (Coffin, Can. J. Res., 1932, 7, 75) and of related trimeric aldehydes *(idem., ibid.,* 1933, 9, 603; Bell and Burnett, Trans. Faraday Soc., 1938, 34, 420) are simple unimolecular reactions. In spite of this they have not been considered in Table VII, for their transition states are not, presumably, four-membered as in the other compounds discussed. The non-exponential terms of such thermal depolymerizations are in the region of 1013. We have also not included the thermal decomposition of trichloromethyl chloroformate (Ramsperger and Waddington, J. Amer. Chem. Soc., 1933, 55, 214).

† The rate equation for I: I-dichlorethane is slightly different from that given previously 1 for the same reason as in the preceding footnote. Again we are indebted to Dr. K. E. Howlett for making the necessary calculations.

It has been observed <sup>13</sup> that for a related series of rate processes a plot of the logarithm of the non-exponential term of the rate equation against the corresponding energy term often gives a straight line. Whatever the theoretical significance of such relationships may be, it was clearly of interest to examine the application of this correlation to the series ethyl chloride, 2-chloropropane (isopropyl chloride), tert.-butyl

is nearly three times greater than that computed from the rate equation found in the present paper. Since a clean-walled reactor was used it seems likely that the reaction observed by Cullis, Hinshelwood and Mulcahy was mainly heterogeneous. It also seems probable that the marked oxygen-catalyzed decomposition of 2-chloropropane, noted by these authors, was heterogeneous in origin. We have found that relatively large quantities of oxygen do catalyze the reaction, but the catalytic activity of the coated reactor walls, as judged by the rates of subsequent runs, is markedly increased in the process.

<sup>14</sup> Schultz and Kistiakowsky, J. Amer. Chem. Soc., 1934, 56, 395.
 <sup>15</sup> Rudy and Fugassi, J. Physic. Chem., 1948, 52, 357.

<sup>16</sup> Warwick and Fugassi, *ibid.*, 1948, **52**, 1314. <sup>17</sup> Vanas and Walters, J. Amer. Chem. Soc., 1948, **70**, 4035.

<sup>18</sup> Coffin, Can. J. Res., 1931, 5, 636.
<sup>19</sup> Idem., ibid., 1932, 6, 417.
<sup>20</sup> Choppin, Frediani and Kirby, J. Amer. Chem. Soc., 1939, 61, 3176; Choppin and Kirby, ibid., 1940, 62, 1592.

<sup>21</sup> Choppin and Compere, *ibid.*, 1948, 70, 3797.

chloride, which differ structurally in a regular manner.\* As Fig. 5 shows an excellent straight line is thereby obtained.

It is perhaps helpful at this stage in our investigations to summarize very briefly some of the more important literature with regard to unimolecular decomposition reactions. The latter can for the most part be divided into two types: (a) molecules which decompose to give two (or more) molecules by a single chemical transformation; (b) molecules which decompose to give two radicals which then undergo a further series of reactions, very rapid compared with the rate of initial rupture of the molecule. Representative examples of the first type are further subdivided, as in Table VII into (a) reactions which have normal nonexponential terms, and (b) reactions where this term is abnormally low. The reactions included in both (a) and (b) must be regarded as proceeding through a cyclic four-membered transition state, exemplified by (I) for ethyl chloride and (II) for *tert*.-butyl alcohol.



It has been suggested <sup>21, 22</sup> that reactions which involve transition states of this type having improbable configurations should have relatively large negative entropies of activation and thus rate equations with abnormally low non-exponential terms. However, this view cannot ex-plain the absence of such anomalies for the compounds listed in the first part of Table VII. A possible explanation given by Rice and Gershinowitz <sup>23</sup> for the tert.-butyl alcohol dehydration is that the reaction proceeds in two steps, the first a migration of hydrogen from carbon to oxygen, the second a rupture of the oxygen-carbon bond. Apart from energetic considerations it seems to us that this mechanism is unlikely, since the requirement 24 of cis-stereochemistry in elimination reactions of the type discussed here cannot be explained easily on such a basis. Although reactions of both types (a) and (b) are elimination reactions, they do differ from each other in one respect. In type (a) reactions a linkage is formed whereas in type (b), a  $\Sigma = 0$  linkage is produced. C = C system is present in the transition Correspondingly the state of type (a) but not in that of type (b).

The interpretation of the kinetics of reactions classified under type (b) and the proof of the absence of radical chains in their mechanisms is always difficult. Consequently it has been felt that discussion as for type (a) reactions is not justified at the present juncture. It is of interest in this connection, however, that recent work by Szwarc,<sup>25</sup> using a technique whereby these difficulties are largely eliminated, indicates that

\* The rate equation for ethyl chloride,  $k = 10^{14.6 \pm 0.25} e^{-60,800 \pm 800/RT} _{\rm Sec.^{-1}}$  is slightly different from that given previously.<sup>1</sup> In the previous calculation of the best straight line by the least squares method the same statistical weight was given to each *mean* velocity constant. Dr. K. E. Howlett, to whom we are indebted, has now repeated the calculation giving the same statistical weight to *every* observed velocity constant and has further calculated the error limits by the method described previously.<sup>2</sup>

<sup>22</sup> Daniels, Ind. Eng. Chem., 1943, **35**, 504; Glasstone, Laidler and Eyring, The Theory of Rate Processes (McGraw-Hill Book Co., New York, 1941), pp. 295-297.

pp. 295-297.
 <sup>23</sup> J. Chem. Physics, 1935, 3, 479.
 <sup>24</sup> Barton, J. Chem. Soc., 1949, 2174.
 <sup>25</sup> Szwarc, J. Chem. Physics, 1948, 16, 128; 1949, 17, 431.

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the non-exponential terms for the initial rupture of certain hydrocarbon molecules into two radicals are close to  $10^{13}$ .

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