# 859. *Studies on Unimolecular Chlorohydrocarbon Decompositions. Part III.**

By K. E. Howlett.

A marked relationship between the Arrhenius parameters, $A$ and $E$, is observed for the rate-constant equations for unimolecular pyrolysis of the monochloroalkanes. This is examined quantitatively from the activated-complex and the energy-accumulation theories of reaction. The thermal decomposition of *iso*butyl chloride is shown to be a homogeneous unimolecular dehydrochlorination for which $k = 10^{14 \cdot 02}\ e^{-56850/\boldsymbol{R}T}$. The correlations predicted from the alternative explanations of unimolecular processes are tested by application to this reaction and to the decompositions of *tert.*-butyl and *n*-propyl chlorides. The better agreement is found with the idea that the slow stage of a unimolecular reaction consists of the concentration of energy transforming activated molecules into reacting molecules. The anomalous values of $A$ and $E$ for pyrolysis of ethylidene dichloride compared with those of the monochloroalkane decompositions are discussed.

Barton and Head (*Trans. Faraday Soc.*, 1950, **46**, 114) and Barton, Head, and Williams (*J.*, 1951, 2039) have drawn attention to the marked correlation which exists between the parameters, $A$ and $E$, of the Arrhenius rate-constant equation for the homogeneous unimolecular decompositions of the simple monochloroalkanes. A fair range of the variables shows a direct, approximately linear relation between $\log_{10} A$ and $E$. Somewhat analogous correlations in other series of reactions have been observed, and such behaviour has been critically discussed before (see, *e.g.*, Evans and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1333; Fairclough and Hinshelwood, *J.*, 1937, 538, 1573, and references there cited; Gregg and Mayo, *Discuss. Faraday Soc.*, 1947, **2**, 328; Cremer, *Experientia*, 1948, **4**, 349; Bamford and Dewar, *Nature*, 1949, **163**, 256; Christiansen, *Acta Chem. Scand.*, 1949, **3**, 61; Bernstein, *J. Chem. Physics*, 1952, **20**, 524) but no example investigated is a homogeneous gaseous reaction. Indeed, Szwarc (*Chem. Reviews*, 1950, **47**, 108) has denied the significance of correlation in this instance.

In the series under discussion, very poor agreement is found between the experimental activation energies and those calculated by means of the empirical equation proposed by Fugassi and Warrick (*J. Phys. Chem.*, 1942, **46**, 630). These authors have sought to describe the activation energy for a reaction where two bonds are broken, in terms of the vibration frequency and bond energy of the weakest bond ruptured. Table 1 gives the values of $\bar{\nu}$ and $D$(C–Cl) (including the zero-point energy) employed in these calculations, and shows the inadequacy of this treatment as applied to typical eliminations of hydrogen chloride.

Table 1.

| Substance | $D$(C–Cl) (kcal./g.-mol.) | $\bar{\nu}$, cm.$^{-1}$ | $E$ (calc.) (kcal./g.-mol.) | $E$ (obs.) |
|---|---|---|---|---|
| EtCl | 80·4 | 650 | 52·4 | 60·8 |
| Pr$^{i}$Cl | 77·9 | 612 | 49·7 | 50·5 |
| Bu$^{t}$Cl | 75·3 | 570 | 46·7 | 41·4 |

The purpose of this paper is to examine the observations amongst dehydrochlorination reactions from the point of view of the mechanism of unimolecular reactions. The reaction model must therefore be defined. It is useful to regard unimolecular processes as consisting of the three steps, collisional activation, energy concentration in a particular location, and passage over the energy barrier (mechanical dissociation or rearrangement) to products (cf. references in Part II *). Eley (*Trans. Faraday Soc.*, 1943, **39**, 168) has suggested that a distinction between the possible slow stages of this scheme, steps 2 or 3, might be obtained experimentally from the sign of d$E$/d$T$ when $\log_{10} A > 13$, although admittedly the difficulty of assessing an accurate value for $E$ over a limited temperature range is great. This

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* Part II, 1952, 3695.

test can only be applied to the four unimolecular dehydrochlorinations of ethyl, *n*-butyl and *iso*butyl chlorides (see Experimental section) and of 1 : 2-dichloropropane, for which the calculated values of the entropy of activation are positive. The last example is unsuitable for discriminative work owing to the small temperature range over which the decomposition has been studied. In the other three cases the Arrhenius activation energies have been recalculated over the upper and lower halves of the temperature ranges investigated. The results are inconclusive, $dE/dT$ being respectively positive, 0, and negative, and giving a mean figure of +10 cal./deg. g.-mol.

The decompositions of ethyl, *n*- and *iso*-propyl, and *n*- and *tert.*-butyl chlorides were therefore first considered from the activated-complex theory, their rate equations being rewritten in the form $k_r = e(\boldsymbol{k}T/\boldsymbol{h})e^{-E_{exp.}/\boldsymbol{R}T}e^{\Delta S^\ddagger/\boldsymbol{R}}$ (Glasstone, Laidler, and Eyring, "Theory of Rate Processes," McGraw-Hill, 1941). The transmission coefficient has been neglected, but would make no difference to the conclusions, provided its variation is not large. Quantum-mechanical calculations indicate that, in the absence of other interactions, eliminations of this type will proceed through a four-centre planar transition state (cf. *e.g.*, Penney, "Quantum Theory of Valency," Methuen, 1935, p. 82; Barton, *J.*, 1949, 2174). Thus, in the activated state, the carbon atoms which will become doubly bound and their associated groups resemble an eclipsed ethane structure, so that the two permanently bound pairs of substituents are also at the position of closest approach. The rotation of alkyl-substituted methyl groups about C–C bonds is more energetically hindered than that of unsubstituted groups (Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140; Howlett, *J.*, 1951, 1409). These restrictions might therefore increase the activation energy or lower the non-exponential term by affecting the entropy of activation. Comparison with the known rate equations shows that no correlation can be traced with the former possibility. Further, a simple statistical effect might be operative, somewhat analogous to that cited by Szwarc concerning the pyrolyses of *p*-xylene and toluene (*J. Chem. Physics.*, 1948, **16**, 128). The chlorine atom in the monochloroalkanes can eliminate with a variable number of hydrogen atoms, *e.g.*, 2 in *n*- and 9 in *tert.*-butyl chloride. If this is significant, then this statistical factor should be included in the rate equation. $\Delta S^\ddagger$ has been calculated for the operation of the first, and of both these effects in monochloroalkane pyrolyses and is compared with the transition-state non-bonded interactions in Table 2. Correlation may exist between both $\Delta S^\ddagger$ cols. and col. 4.

TABLE 2.

| Substance | $\Delta S^\ddagger$ | Modified $\Delta S^\ddagger$ | Non-bonded interactions |
|---|---|---|---|
| EtCl | 4·5 | 3·1 | 2 H---H |
| Pr$^n$Cl | −0·73 | −1·7 | 1 H---H + 1 H---Me (or Et) |
| Pr$^i$Cl | −0·79 | −3·5 | |
| Bu$^n$Cl | 1·8 | 0·85 | |
| Bu$^t$Cl | −5·1 | −9·3 | 2 H---Me |

Turning to the alternative explanation of unimolecular reactions—that step 2 is rate determining—an interesting parallel may be observed by applying the mathematical theory of Rice and Ramsperger (see Part II). For each of the decompositions treated in Part II, the number of square terms contributing towards the activation energy has been determined. Thus the fractional contribution towards the rate constant for any specified molecular energy in excess of $E$ may be calculated. The necessary integrations have been carried out for 1 : 1-dichloroethane at 412°, *iso*propyl chloride at 406·6°, and ethyl chloride at 456°. Comparison of the first curve with that given previously for the same compound at 449° shows that the $(\varepsilon - \varepsilon_0)$ value at maximum $k_\varepsilon$ lies at an approximately constant value (8·5 kcal./g.-mol. at 412°, 9 at 449°). The results for the various reactions may therefore be compared, despite the fact that they refer to different temperatures and rates.

For any one decomposition it is found that the contribution of the partial rate constant $k_\varepsilon$ increases with $(\varepsilon - \varepsilon_0)$ up to moderate energy excesses, because the decreased time $t$ (Fairclough and Hinshelwood, *loc. cit.*) between activation and spontaneous reaction outweighs the decreased probability of such a high energy state. For large energy excesses, of course, when $t$ is very small and capable of little further variation, the extreme improbability of the state ensures that the contribution to reaction again approaches zero. Thus when comparing different decompositions, it is reasonable to suppose that, up to a limit, the non-exponential terms will vary directly with the values of $(\varepsilon - \varepsilon_0)$ at maximum $k_\varepsilon$. The three reactions already studied show just this correlation (Table 3).

TABLE 3.

| | $Me\cdot CHCl_2$ | $Pr^iCl$ | EtCl |
|---|---|---|---|
| $\log_{10} A$ ............................................. | 11·65 | 13·5 | 14·7 |
| $(\varepsilon - \varepsilon_0)$ (kcal./g.-mol.) at max. $k_\varepsilon$ .............. | 9 | 15 | 18·5 |

In order to discriminate between these alternative explanations, the decomposition of *iso*butyl chloride, and low-pressure pyrolyses of *tert.*-butyl chloride and *n*-propyl chloride, have been investigated.

## EXPERIMENTAL

*Apparatus and Materials.*—The apparatus used has been described in Part II (*loc. cit.*). The three chlorides were prepared by standard methods from the corresponding alcohols and purified by treatment with sulphuric acid, fractional crystallisation, and distillation (cf. Barton, Head, and Williams, *loc. cit.*). The following physical constants were measured: *iso*butyl chloride, b. p. 68·5° (corr.), $n_D^{20}$ 1·3982; *tert.*-butyl chloride, b. p. 50·7° (corr.), $n_D^{20}$ 1·3844; *n*-propyl chloride, b. p. 46·5° (corr.), $n_D^{25}$ 1·3851.

## RESULTS

iso*Butyl Chloride.*—It is first necessary to establish that pyrolysis of *iso*butyl chloride leads to dehydrochlorination, although this result is expected (Howlett, Thesis, London, 1948). The decomposition has been studied over the temperature range 361·5° to 475° and a number of long-term experiments, of duration $>20$ times that required for half decomposition, have shown that, at various temperatures, the final pressure is close to twice that initially admitted (see Table 4). At the end of each of these runs, the pressure in the system fell to zero on connecting the reactor to a small, evacuated liquid-air trap. Titration of the condensate with standard alkali indicated 85—100% of the theoretical quantity of hydrogen chloride. Better quantitative agreement cannot be expected in this case (cf. Mayo and Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339; Howlett, *J.*, 1951, 1409), and the absence of hydrogen in the products shows that only dehydrochlorination occurs.

TABLE 4.

| Temp. | $p_0$, mm. | $p_t/p_0$ | Temp. | $p_0$, mm. | $p_t/p_0$ |
|---|---|---|---|---|---|
| 417° | 23·7 | 2·01 | 450° | 3·07 | 2·00 |
| 429 * | 4·77 | 1·98 | 450 | 5·55 | 2·03 |
| 431 | 4·96 | 2·08 | 452 * | 30·4 | 2·06 |
| 438 * | 63·2 | 1·97 | 463 | 3·45 | 2·00 |
| 444 * | 20·3 | 2·00 | 474 | 2·77 | 2·03 |

* Packed reactor.

Fig. 1 shows that at various temperatures, first-order kinetics are followed to a considerable percentage of reaction, and Table 5 shows that the rate constant at 450° is invariant with initial pressure above $p_0 = 3$ mm., and also unchanged by the addition of propene. Propene is well known as a strong inhibitor of radical-chain dehydrochlorinations.

TABLE 5.

| $p_0$, mm. | $10^5k$, sec.$^{-1}$ | $p_0$, mm. | $10^5k$, sec.$^{-1}$ | $p_0$, mm. | $p_{C_3H_6}$, mm. | $10^5k$, sec.$^{-1}$ |
|---|---|---|---|---|---|---|
| 3·07 | 70 | 9·33 | 70 | 9·60 | 1·75 | 73 |
| 3·75 | 65 | 21·0 | 70 | 9·00 | 3·45 | 70 |
| 4·91 | 69 | 43·9 | 73 | 9·72 | 5·6 | 70 |
| 9·20 | 74 | — | — | 9·74 | 8·2 | 69 |

The homogeneity of the reaction is demonstrated by the negligible increase in the rate constant, obtained by carrying out the decomposition in a reactor packed to a 10-fold increase in surface : volume ratio over that in the unpacked reaction vessel. These results are illustrated, together with the results obtained in an " empty " reactor in the Arrhenius plot, Fig. 2. The pyrolysis of *iso*butyl chloride is therefore a clean homogeneous unimolecular dehydrochlorination. Table 6 lists the observed rate constants for decompositions in both empty and packed reactors. From the results given in Fig. 2 it may be calculated by the method of least squares, giving equal weight to each experiment, that $k = 10^{14\cdot02}\ e^{-56850/RT}$ for the pyrolysis of *iso*butyl chloride in an unpacked reactor, the walls of which are covered with a carbonaceous film. For decompositions of initial pressure <3 mm. this equation is inapplicable because in this region the rate constant is a function of the pressure (see Fig. 3).

Fig. 1.

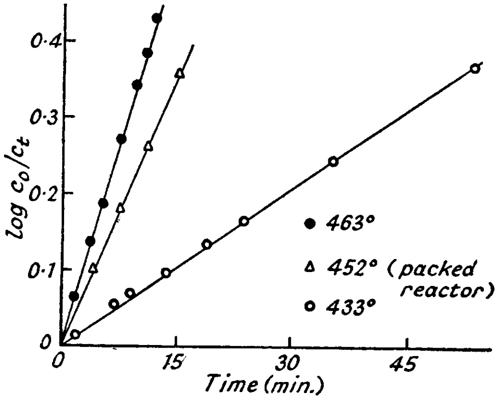


Fig. 2.

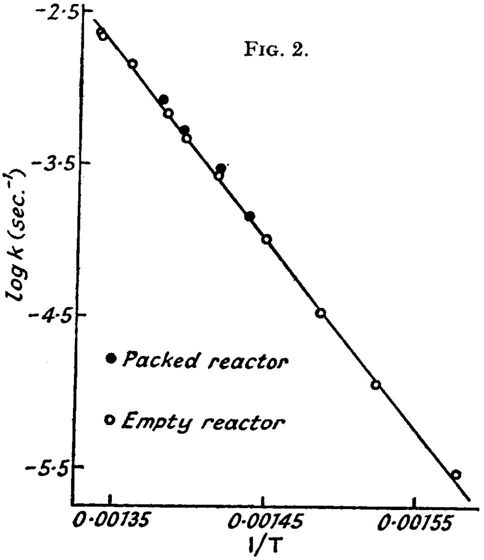
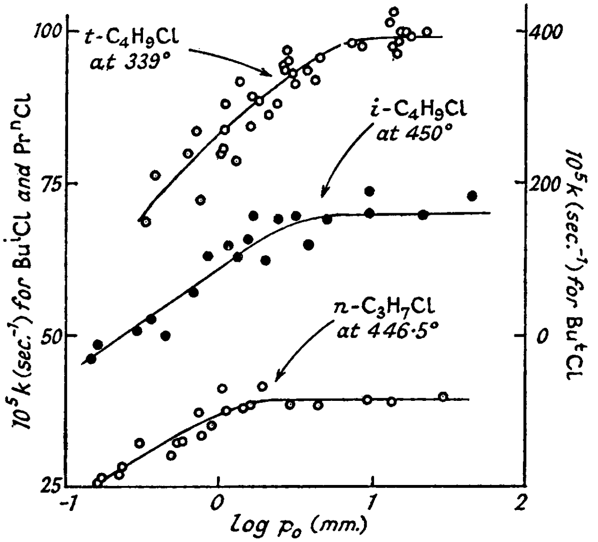


Fig. 3.



tert.-*Butyl Chloride and* n-*Propyl Chloride*.—Barton and Onyon (*Trans. Faraday Soc.*, 1949, **45**, 725) and Barton, Head, and Williams (*loc. cit.*) have given the rate equations $k = 10^{12\cdot4}$ $e^{-41400/RT}$ and $10^{13\cdot45}\ e^{-55000/RT}$ for *tert.*-butyl and *n*-propyl chloride respectively. These rate constants refer to decomposition from initial pressure >50 mm. In the present study, the decomposition of *tert.*-butyl chloride has been examined at 339° and that of *n*-propyl chloride at 446·5°, in an attempt to find critical pressure regions in the $k$–$p_0$ graphs. In each case good agreement has been obtained with the previous work at high pressures (the velocity constants

TABLE 6.

| Temp. | No. of runs | $10^5k$, sec.$^{-1}$ | Temp. | No. of runs | $10^5k$, sec.$^{-1}$ |
|---|---|---|---|---|---|
| *Unpacked reactor.* | | | | | |
| 361·5° | 2 | 0·30 | 444° | 3 | 47·4 |
| 384 | 2 | 1·17 | 450 | 15 | 69·7 |
| 400 | 5 | 3·42 | 463 | 8 | 145 |
| 417 | 6 | 10·3 | 474 | 7 | 214 |
| 433 | 7 | 26·8 | 475 | 3 | 230 |
| *Packed reactor.* | | | | | |
| 422·5 | 3 | 15·0 | 444·5 | 4 | 53·6 |
| 432 | 4 | 30·5 | 452 | 5 | 82·8 |

calculated from the rate equations are respectively 0·00417 and 0·00055 sec.$^{-1}$). The results are shown in Fig. 3, which also depicts the results obtained with *iso*butyl chloride at 450°. The transitional regions found are *ca.* 6 mm. (Bu$^t$Cl), 1—1·5 mm. (Pr$^n$Cl), and 3 mm. (Bu$^i$Cl).

## DISCUSSION

The values of $\log_{10} A$ and $E$ for decomposition of *iso*butyl chloride lie close to the straight line correlating these quantities given by Barton, Head, and Williams (*loc. cit.*) for other chlorohydrocarbon pyrolyses. *iso*Butyl chloride cannot, however, be fitted to the correlation of Table 2. The chlorine atom in this compound can be eliminated with only the tertiary hydrogen atom, and the activated complex would have 2 H---Me non-bonded interactions. Both entries for $\Delta S^\ddagger$ in Table 2 for this compound are $+1{\cdot}65$ E.U. in contrast to the values of *ca.* $-5$ or $-9$ expected if *iso*butyl chloride conformed to the suggested explanation of $\log_{10} A$ in terms of entropy of activation effects due to non-bonded interactions, and to the number of β-hydrogen atoms.

Better agreement is found with the second correlation. From the critical-pressure regions reported above, the numbers of classical oscillators contributing towards the activation energies are 10 (Bu$^t$Cl), 14½ (Pr$^n$Cl) and 14 (Bu$^i$Cl). By assuming in each case that the transformation probability of an activated molecule is a function of its energy content (cf. Part II), the appropriate integrations of Rice and Ramsperger's equation have been performed, and $(\epsilon - \epsilon_0)_{\max.\,k_\epsilon}$ values of 11·5, 19·5, and 19·5 kcal./g.-mol. respectively found. Thus all six unimolecular dehydrochlorinations examined from this point of view show a reasonably systematic variation in $(\epsilon - \epsilon_0)_{\max.\,k_\epsilon}$ with $\log_{10} A$, whilst 1 : 1-dichloroethane is inconsistent with the others when $\log_{10} A$ is plotted against $E$. This consistency of one correlation coupled with an anomaly in the other can be appreciated if a reaction of high activation energy tends to accumulate this energy from a large number of square terms, and *vice versa.* The participation of a large number of square terms shifts the maximum in the $k_\epsilon$–$(\epsilon - \epsilon_0)$ curve to higher energy values, so that while the chlorohydrocarbon is of constant type, *i.e.*, one C–Cl bond in an otherwise paraffinic molecule, correlation of $\log_{10} A$ with $(\epsilon - \epsilon_0)_{\max.\,k_\epsilon}$ implies correlation with $E$. When, however, the vibrational modes immediately adjacent to the reaction centre arise partly from an additional C–Cl bond, the anomalous behaviour is not surprising, for it has frequently been suggested (Rice, *Z. physikal. Chem.*, 1930, *B*, **7**, 226; Glasstone, Laidler, and Eyring, *op. cit.*, p. 287; Barrer, *Trans. Faraday Soc.*, 1948, **44**, 399) that the efficiency of energy transfer in a "vibrational collision" will vary with the nature of the two oscillators concerned. 1 : 1-Dichloroethane, with a larger number of low frequency vibrators near the reaction centre than (say) ethyl chloride, may thus be expected to show a different looseness of coupling between those oscillators which are the chief contributors towards the activation energy. If this is so, then the effective values of $n$ and $t$ (which determine $\log_{10} A$) at constant $E$, will be different for the decompositions of compounds of type $>$CH·CCl$_2$– and for those of the series $>$CH·CCl–.

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