708. *Studies on Unimolecular Chlorohydrocarbon Decompositions. Part II.** *

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The homogeneous thermal decompositions of ethyl chloride, ethylidene dichloride, and *iso*propyl chloride have been studied at low pressures. All three reactions are unimolecular, their rate constants being pressure-dependent below a certain critical pressure in each case. The order of reaction with ethylidene dichloride was perceptibly above 1 at the lowest pressures studied. The results have been examined from the point of view of the theories of Rice and Ramsperger, and are in accord with the idea that the transformation probability of an activated molecule is a function of the energy in excess of the minimum required for reaction.

THE marked differences between the homogeneous first-order decompositions of 1 : 2-dichloroethane (Barton and Howlett, *J.*, 1949, 155; Howlett, *Nature*, 1950, **165**, 860; *Trans. Faraday Soc.*, 1952, **48**, 25), the tetrachloroethanes (Barton and Howlett, *J.*, 1951, 2033), and 2 : 2'-dichlorodiethyl ether (Barton, Head, and Williams, *J.*, 1951, 2039) on the one hand, and those of ethyl chloride, 1 : 1-dichloroethane (Barton and Howlett, *J.*, 1949, 165), and the monochloro-propanes and -butanes (Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114; Barton, Head, and Williams, *loc. cit.*; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725; Howlett, to be published) on the other, leaves little alternative explanation for the mechanism of the latter reactions but that they are unimolecular processes. The evidence already presented in support of this contention includes lack of sensitivity towards small additions of oxygen and chlorine, and complete insensitivity to chain-inhibiting substances such as propylene. Furthermore, good first-order velocity constants are obtained right from zero time (showing absence of induction periods) and for large percentages of conversion, over considerable pressure ranges. It is well known, however, that any theory of unimolecular reactions, such as Lindemann and Hinshelwood's mechanism (*Trans. Faraday Soc.*, 1922, **17**, 598), demands the existence of a critical pressure region, below which the Maxwell–Boltzmann distribution of energies is not maintained. This should be manifest in a lowering of the rate constant and a change over towards second-order kinetics, and these two effects have been considered the most important qualitative characteristics of unimolecular reactions (cf. Ramsperger, *Chem. Reviews*, 1932, **10**, 27).

In the present investigation, therefore, three representatives of the apparently 100% unimolecular decompositions have been studied at low pressures, both to confirm our ideas on their mode of reaction and then, with their aid, to examine theories of unimolecular reactions. These theories, although well advanced, have mainly been applied to reactions such as the decompositions of nitrous oxide, dinitrogen pentoxide, and azomethane, which, as emphasised in a preliminary note (*Nature*, in the press; cf. Pease, *J. Chem. Physics*, 1939, **7**, 749), are not now considered to be simple unimolecular reactions.

EXPERIMENTAL

Materials and Apparatus.—Ethyl chloride, 1 : 1-dichloroethane, and *iso*propy lchloride were purified as described in previous publications. The following physical constants were measured : ethyl chloride, b. p. 12·4$_5$°; 1 : 1-dichloroethane, b. p. 57·3° (corr.), n_D^{20} 1·4170; *iso*propyl chloride, b. p. 34·8° (corr.), n_D^{20} 1·3782. Critical compilations of these constants are available in the relevant previous publication and in Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier, 1950.

In essentials, the apparatus employed was similar to that described by Barton and Howlett (*J.*, 1949, 155). The Pyrex-glass spoon gauges used have permitted readings to be taken to 0·01 mm. of mercury. All results reported refer to decompositions in a reactor of surface/volume ratio 2 cm.$^{-1}$, and whose surface has been aged by covering it with a carbonaceous film through storage in prolonged contact with the reaction products at 450—500°.

* Barton and Howlett, *J.*, 1949, 165, is considered to be Part I of this series.

Results.—Ethyl chloride. Barton and Head (*loc. cit.*) reported a recalculated velocity constant for this decomposition of $k = 10^{-14 \cdot 6} e^{-60,800/RT}$ sec.$^{-1}$, and this is unvarying (Barton and Howlett, *J.*, 1949, 165) over the pressure range 20—200 mm. In the present study, the pyrolysis of ethyl chloride has been examined at 456°. Fig. 1 shows the decomposition rate constant as a function of the initial pressure (p_0). At higher pressures (>8 mm.) the mean velocity constant (236 × 10^{-6} sec.$^{-1}$) agrees well with that found previously (235 × 10^{-6} sec.$^{-1}$). Below 8 mm. the rate constant falls below its high-pressure value. (In Figs. 1—4, the low-pressure velocity constants plotted, are the initial velocity constants calculated as first order.)

FIG. 1.

(*Note change of scale above 20 mm.*)

FIG. 2.

(*Note change of scale above 30 mm.*)
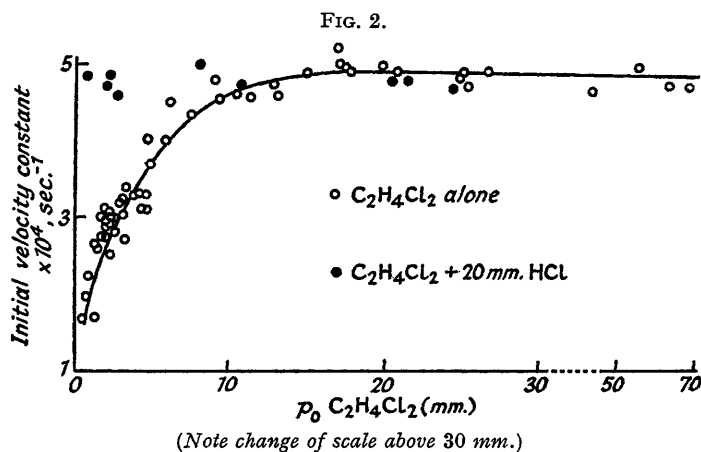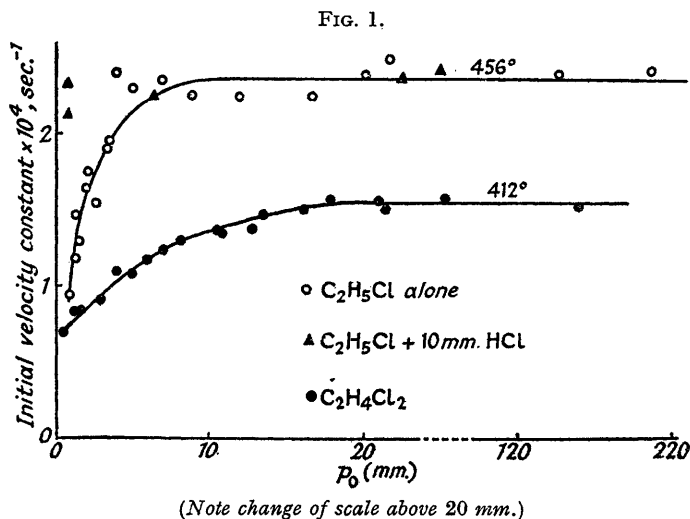
It is already known (Howlett, Thesis, London, 1948), that the reaction products, ethylene and hydrogen chloride, even when added in amounts equal to that of the decomposing substrate, have no effect upon the pyrolysis. It is established therefore that hydrogen chloride has no " chemical " catalytic influence upon the reaction. This has been confirmed in the present work, and it has also been shown (see Fig. 1) that the addition of about 10 mm. of hydrogen chloride restores the rate constant to the high-pressure value where the partial pressure of ethyl chloride is <8 mm. It was considered that with the present apparatus, the critical pressure was too low to allow a more quantitative study of the low-pressure region with ethyl chloride.

1 : 1-*Dichloroethane.*—The recalculated specific reaction rate (cf. Barton and Head, *loc. cit.*) for 1 : 1-dichloroethane pyrolysis in an unpacked reactor is constant over the range 20—200 mm. at $k = 10^{11 \cdot 65} e^{-48,300/RT}$ sec.$^{-1}$. The decomposition has been studied at 412°, 433°, and

449°. At higher pressures the mean rate constants were respectively 0·000157, 0·000488, and 0·00107 sec.$^{-1}$, in good agreement with those calculated from the equation above (0·000174, 0·000502, and 0·00107 sec.$^{-1}$). At each temperature studied, k begins to fall at pressures below 17—20 mm. This is illustrated in Figs. 1, 2, and 3. A notable feature of the kinetics below the critical pressure is that no fall in specific velocity is observed as reaction proceeds (with consequent lowering of the partial pressure of reactant). This implies that 1 mm. of vinyl chloride plus 1 mm. of hydrogen chloride are equal in efficiency for energy transfer to 1 mm. of dichloroethane (similar to the effect in azomethane decomposition noted by Ramsperger, *J. Amer. Chem. Soc.*, 1927, **44**, 1495). This fact is of considerable aid in determining the reaction order as a function of p_0. It was found that the decomposition remained virtually of first order down to 4 mm., below which the order began to rise noticeably and reached about 1·5 at 1 mm. The change over towards second-order kinetics has therefore been observed, but the pressure range over which accurate results could be obtained was insufficient to follow this effect to completion. As also shown in Fig. 2, additions of approx. 20 mm. of hydrogen chloride have no effect upon high-pressure results, but maintain the high-pressure constant below 17 mm. partial pressure of 1 : 1-dichloroethane.

FIG. 3.
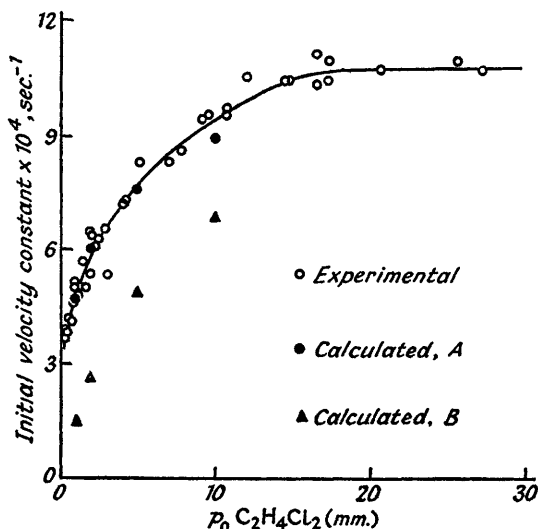
A number of co-decompositions of 1 : 1-dichloroethane (I) and 1 : 2-dichloroethane (II) have been carried out. Barton, Head, and Williams (*loc. cit.*) have discussed Ash and Brown's conclusions (" Records of Chemical Progress," 1948, p. 81) concerning the results of chlorine-atom attack upon the α- and β-hydrogen atoms in ethyl chloride, etc., in so far as they affect dehydrochlorination. The former authors have given good theoretical arguments for the correlation between structure and mode of decomposition given previously by Barton, Onyon, and Howlett (*Trans. Faraday Soc.*, 1949, **45**, 733). If this discussion is correct, (I) should be an inhibitor for the pyrolysis of (II), with little (if any) observable change in its own rate of decomposition. The co-decomposition has been studied at 446°, where the mean velocity constants for decomposition alone were found to be 0·00096 (0·00094) and 0·000334 (0·00034) sec.$^{-1}$ for (I) and (II), respectively. The figures in parentheses are those calculated from the published rate equations. In a number of experiments starting from 4 mm. of (I) + 20 mm. of (II), the observed rate of pressure increase was considerably less than the sum of the separate rates. Since inhibitors have no effect on the dehydrochlorination of (I), this proves that (I) is a fairly powerful inhibitor for the decomposition of (II). By assuming that (I) decomposed normally (see later) under these conditions, it is found that the rate of decomposition of (II) varies from about one-third of normal, with 4 mm. partial pressure of (I) present, to two-thirds of normal at 2 mm. of (I). These observations are facilitated because (I) reacts three times faster than even uninhibited (II). Attention was then turned to co-decompositions of 20 mm. of (I) + 4—9 mm. of (II). By assuming that, in these experiments, (II) decomposed at the maximally inhibited rate (Barton and Howlett, *J.*, 1949, 155), it was calculated that (I) decom-

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posed at a mean rate constant of 0·00101 sec.$^{-1}$. There was no obvious correlation of this figure with the partial pressure of (II). Thus little (if any) decomposition is induced in (I) by the addition of chlorohydrocarbon radicals or chlorine atoms. These co-decompositions, therefore, amply confirm the predictions referred to above.

isoPropyl chloride. The investigation with this compound was similar to that with ethyl chloride. Barton and Head (*loc. cit.*) give $k = 10^{13·4} e^{-50,500/RT}$ sec.$^{-1}$ for 2-chloropropane decomposition and show that the first-order constant is invariant over the initial pressure range 60—135 mm. Experiments have now been repeated at 406·6° (where Barton and Head find $k = 0·00159$ sec.$^{-1}$), the variation of k with p_0 being studied. The results are plotted in Fig. 4. Very good agreement is obtained at higher pressures with the previous results, and the pressure range of applicability for their first-order constant is considerably extended. The velocity constant falls below $p_0 = 4$ mm. It has also been shown that the high-pressure rate constant could be restored, even when the partial pressure of *iso*propyl chloride was less than 3 mm., by the addition of 3 mm. of hydrogen chloride, which has no effect upon the high-pressure constant (cf. Fig. 4).

FIG. 4.
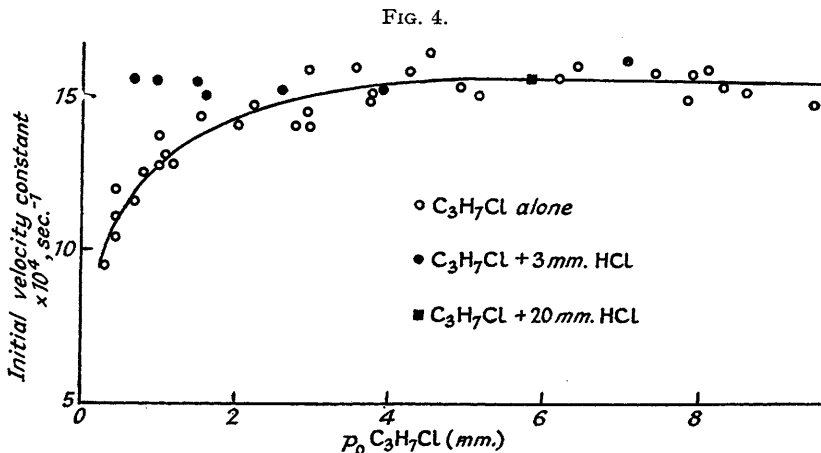
DISCUSSION

It is clear that Ramsperger's criteria for the unimolecular nature of a reaction are satisfied by the three reactions under consideration. Chloroethane, 1 : 1-dichloroethane, and 2-chloropropane pyrolyses all show a critical pressure region below which the velocity constant falls and the change over towards a second-order reaction has been established. We are therefore justified in using these reactions, particularly that of ethylidene dichloride, to examine the mathematical theory of unimolecular reactions. First, it is necessary to determine the number of degrees of freedom contributing towards the activation energy. Thus if $\frac{1}{2}n$ classical oscillators act as the energy reservoir, then the fraction of activated molecules at equilibrium is approximately

$$dN = \frac{e^{-[E+(\frac{1}{2}n-1)/RT]/RT}([E + (\frac{1}{2}n - 1)RT]/RT)^{(\frac{1}{2}n-1)}}{(\frac{1}{2}n - 1)!}$$

and n may be calculated by using Figs. 1, 2, 3, and 4 (cf. Hinshelwood, " Kinetics of Chemical Change," Oxford, 1940, p. 81). The calculation of the experimental values of dN requires a knowledge of the effective molecular collisional diameters. These have not been determined, but Vogel (*Ann. Physik*, 1914, **43**, 1234) determined gaseous viscosities of methane, the chloromethanes, and ethane. From this, the variation of molecular diameter with chlorination of methane may be calculated, and by assuming increases of the same magnitude starting from ethane, the effective molecular diameters of ethyl chloride and 1 : 1-dichloroethane are estimated to be 5·5 and 6·0 Å, respectively. Similarly, from the viscosity data compiled for propane (Partington, " Advanced Treatise on Physical Chemistry," Longmans, 1949, p. 861) the molecular diameter of *iso*propyl chloride is set

at 6·0 Å. The use of these quantities in the equation above gives values of 13—14, 6—7, and 12 classical oscillators contributing towards the activation energy for the decomposition of these three compounds respectively. The first of these is the only one calling for comment. It is less than the possible classical limit (18), but by employing a quantised model the specific heat, $C_v°$, of ethyl chloride may be shown to be about 27 cal. degree^{-1} mole^{-1} at 730° K (Howlett, to be published). A small error in determining such a large value of n arises since $E \gg \frac{n}{2} RT$ (Fowler and Guggenheim, " Statistical Thermodynamics," Cambridge, 1949, p. 521). The inclusion of a second term in the expansion of the integral of the distribution law gives $\frac{1}{2}n = 13$. It seems, therefore, that with ethyl chloride the critical-pressure calculation of n gives an answer which is about the limit of possibility.

Several communications on unimolecular reactions have appeared in recent years (Eley, *Trans. Faraday Soc.*, 1943, **39**, 168; Evans and Rushbrooke, *ibid.*, 1945, **41**, 621; Barrer, *ibid.*, 1948, **44**, 399) in which rate-constant equations are given for the alternative mechanisms (the Polanyi–Hinshelwood or the Kassel–Rice–Ramsperger hypotheses). Evans and Rushbrooke, however, have concluded that a distinction between the possible slow stages of a unimolecular process is, in general, not a useful one, and since Barrer's method is tedious to apply, it has seemed better to examine the 1 : 1-dichloroethane decomposition by means of the very useful treatments given by Rice and Ramsperger (*J. Amer. Chem. Soc.*, 1927, **49**, 1617) and Kassel (*J. Phys. Chem.*, 1928, **32**, 225). Thus we shall employ the form of the curve connecting p_0 and k to obtain information about the way in which conversion of activated molecules into reacting molecules depends upon the magnitude and location of the molecular energy. Rice and Ramsperger (*loc. cit.*) have shown that a graph of $1/k$ against $1/p_0$ yields a straight line if the transformation probability for a molecule is independent both of the energy in excess of the activation energy and of its location within the molecule—in effect the simplified Hinshelwood treatment—but a curved plot if this is not so. The curvature is greater the larger the number of internal degrees of freedom which may be contributing towards the activation energy. Fig. 5 shows such a graph for the results obtained with 1 : 1-dichloroethane at 449°. The marked curvature, in a direction such that the rate is maintained better at the lower pressures than is accounted for on the simple theory, indicates that a localised-energy theory, with transformation probability dependent upon the excess of energy, must be applied. By extrapolation of Fig. 5 to $1/p_0 = 0$, a value of 0·00115 sec.$^{-1}$ is obtained for $k\infty$, whereas the experimental result is that k is approximately constant above 20 mm. at 0·00107 sec.$^{-1}$. This discrepancy is, however, not serious in kinetic work. We can also deduce from Fig. 5 that the Arrhenius activation energy should be pressure-variant below the critical pressure. In a localised energy case, the Arrhenius activation energy for the low-pressure second-order reaction should be $\frac{1}{2}(n - 3)RT$ cal. mole.$^{-1}$ less than that of the high-pressure first-order reaction. Unfortunately, the second-order region has only been approached, so we cannot use this limiting conclusion to obtain an independent measure of n, but a plot of the apparent activation energy (obtained by comparing results at 449° and 412°) against p_0 shows a definite fall at low pressures. This is shown in Fig. 6 and indicates that $\frac{1}{2}n > 4$, thus confirming the point made by Fig. 5.

In order to apply Rice and Ramsperger's treatment, it is necessary to integrate the equation

$$k = \frac{k\infty}{kT\Gamma\left(\frac{n+1}{2}\right)} \int_0^\infty \frac{e^{-(\varepsilon - \varepsilon_0)/kT}\left(\dfrac{\varepsilon - \varepsilon_0}{kT}\right)^{(n-1)/2}}{1 + \dfrac{\beta}{p}\dfrac{(\varepsilon - \varepsilon_0)^{(n-1)/2}}{\varepsilon^{(n-2)/2}}} \, d(\varepsilon - \varepsilon_0)$$

where $\qquad \beta = k\infty \dfrac{\Gamma\left(\dfrac{n}{2}\right)}{\Gamma\left(\dfrac{n+1}{2}\right)} \sqrt{\dfrac{m}{\pi}} \dfrac{1}{4s^2} e^{\varepsilon_0/kT}$

deduced by them (their original symbolism is retained). This has been integrated graphic-ally for 1 : 1-dichloroethane at 449° as shown in Fig. 7. The values inserted were : $\varepsilon_0 = 47{,}600$ cal. mole^{-1} ($E_{\text{exp.}} - \boldsymbol{R}T$), $n = 13$, $s = 6 \times 10^{-8}$ cm., $k_\infty = 0{\cdot}00115$ sec.$^{-1}$; β, in units of mm. of Hg, is calculated to be $10^{10{\cdot}73}$. The outer curve of the graph corresponds to infinite pressure, succeeding curves being calculated for 10, 5, 2, and 1 mm., respectively. Qualitatively, it is seen that the greatest contribution to reaction comes from molecules having a moderate excess of energy (about 8 kcal. mole^{-1}, the equivalent of say 5 vibrational quanta/molecule) over the minimum necessary for activation, in agreement with Barrer's conclusion (*loc. cit.*) reached by use of the modified Polanyi–Hinshelwood hypothesis.
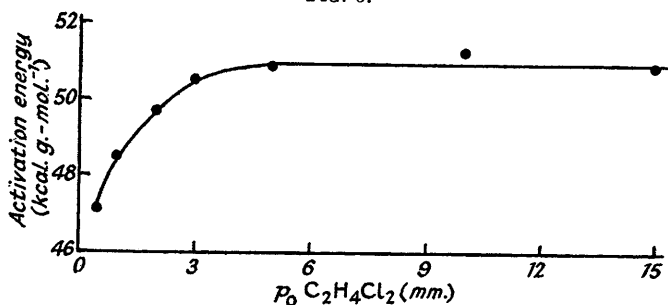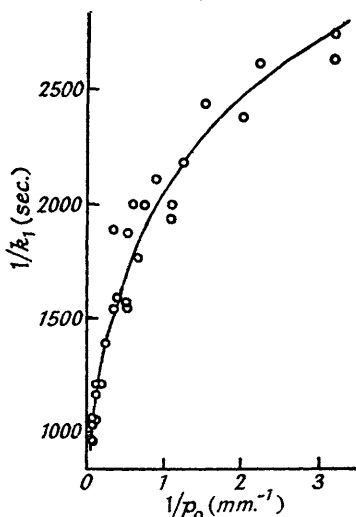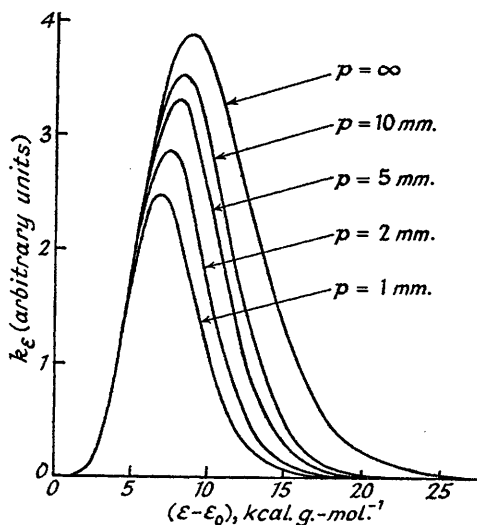
FIG. 6.

FIG. 5.

FIG. 7.

The areas under the curves are summed and plotted together with the experimental figures in Fig. 3 (there designated " Calculated, A "). As final evidence that the simple theory is inadequate to explain the results, Fig. 3 also shows the low pressure figures calculated (B) from this theory by using $k = k_\infty /(1 + \beta_1/p)$,

where $$\beta_1 = \frac{k_\infty \sqrt{m}(kT)^{(n-1)/2} \, e^{\varepsilon_0/kT} \Gamma(\tfrac{1}{2}n)}{4\sqrt{\pi} \, s^2 \, \varepsilon_0^{(n-2)/2}} = 6{\cdot}87 \text{ (mm. Hg units)}$$

Rice and Ramsperger's symbolism (*loc. cit.*) being used again. ε_0 is here 56,160 cal. mole^{-1} ($E_{\text{exp.}} + \tfrac{1}{2}(n - 2)\boldsymbol{R}T$), s, n, and k_∞ being as before.

The more complex theory clearly gives the truer explanation of the facts, despite the fact that the theory strictly applies to the concentration of the energy into a single square term. It seems likely that in hydrogen chloride elimination reactions at least two square terms would be involved, but Kassel (" The Kinetics of Homogeneous Gas Reactions,"

Chem. Catalogue Co., 1932, p. 102) has stated that variation in the form of the k–p_0 curve is practically negligible in these two cases.