HETEROLYSIS AND THE PYROLYSIS OF ALKYL HALIDES IN THE GAS PHASE

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Contents

I. Early Work in the Field

The middle twenties saw the development of experiments designed to test theories of the kinetics of gas-phase reactions. The first study of the kinetics of the pyrolysis of an alkyl halide was reported by Glass and Hinshelwood[1] in 1929. These workers were interested in demonstrating homogeneous catalysis of a gas-phase reaction, and they chose the system isopropyl ether–isopropyl iodide. They showed that the reaction

$$C_3H_7I = C_3H_6 + C_3H_8 + I_2 \qquad (1)$$
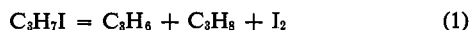
proceeded at a measurable rate in the temperature range 300–350°. No quantitative kinetic data were, however, reported for this reaction. Systematic work on the kinetics of the pyrolysis of alkyl halides in clean glass vessels was initiated by Lessig,[2] in the laboratory of Farrington Daniels. Of the substances investigated, ethyl bromide seemed to hold out the most hope of

being an uncomplicated gas-phase reaction. The stoichiometry was firmly established as

$$C_2H_5Br = C_2H_4 + HBr \qquad (2)$$

and the rate of reaction was shown to be independent of the surface-to-volume ratio of the reaction vessel and to follow the first-order kinetic law. Bromine was found to increase the rate of reaction. A rough estimate of the activation energy yielded a value of 50 kcal mole^{-1}. In the latter stages of the reaction, it was noted that the reverse reaction caused departures from the simple first-order behavior. Among the other substances investigated were ethylene bromide, ethylene, isopropyl and *t*-butyl chlorides, and ethyl iodide.
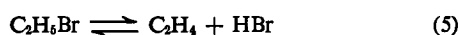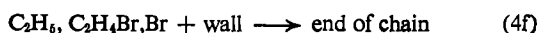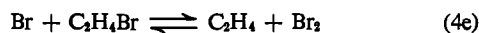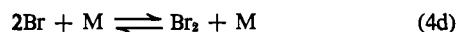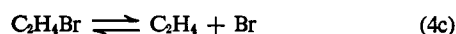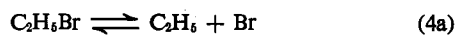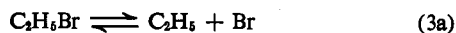
The second paper from this laboratory by Vernon and Daniels[3] dealt with a more detailed study of the ethyl bromide decomposition. It was found that in clean glass reaction vessels, traces of air had a marked accelerating effect upon the reaction. The unimolecular dissociation was accompanied by a bimolecular reverse reaction, and four different methods were used for calculating the rate constant (k_1) from the experimental results. k_1 starts to decrease (as a function of p_0) at about 100 mm. Above this pressure the rate constants were well represented by $k_1 = 3.85 \times 10^{14} \exp(-54{,}500/RT)$ sec^{-1}. The data were used to test current theories of unimolecular reactions.

Prior to the next communication,[4] Brearley, *et al.*,[5] had noted in the case of *t*-butyl chloride that more reproducible results were obtained if the vessel were seasoned by leaving the products in the vessel in order to deposit a carbonaceous coating. Fugassi and Daniels[6] noted that hydrogen atoms added from a discharge tube did not accelerate the rate of decomposition of ethyl bromide. Daniels and Veltman[4] reported that their data were well represented by $k_1 = 1.16 \times 10^{14} \exp(-53{,}200/RT)$ sec^{-1} at pressures above 130 mm, when the catalytic effect of the walls is destroyed by a carbonaceous coating. The rate is markedly enhanced in clean Pyrex or upon packing the vessel with clean Pyrex glass. In these studies of the ethyl bromide decomposition, it was noted that at low pressures induction periods were present. Bromine was found to increase the rate of reaction, the rate being proportional to the square root of the bromine concentration. Nitric oxide did not retard the decomposition, but traces of mercury did. Finally decomposing ethyl bromide caused acetaldehyde to decompose at 350°, at which temperature it is normally stable.[7]

(1) J. V. S. Glass and C. N. Hinshelwood, *J. Chem. Soc.*, 1815 (1929).
(2) E. T. Lessig, *J. Phys. Chem.*, 36, 2325 (1932).

(3) E. L. Vernon and F. Daniels, *J. Amer. Chem. Soc.*, 55, 922 (1933).
(4) F. Daniels and P. L. Veltman, *J. Chem. Phys.*, 7, 756 (1939).
(5) D. Brearley, G. B. Kistiakowsky, and C. H. Stauffer, *J. Amer. Chem. Soc.*, 58, 43 (1936).
(6) P. Fugassi and F. Daniels, *ibid.*, 60, 771 (1938).
(7) J. G. Roof and F. Daniels, *ibid.*, 62, 2912 (1940).

Daniels and Veltman[4] discussed three mechanisms: radical nonchain (3), radical chain (4), and molecular (5).

$$C_2H_5Br \rightleftharpoons C_2H_5 + Br \quad (3a)$$

$$Br + C_2H_5Br \rightleftharpoons C_2H_4Br + HBr \quad (3b)$$

$$C_2H_5 + C_2H_4Br \rightleftharpoons C_2H_5Br + C_2H_4 \quad (3c)$$

$$C_2H_5Br \rightleftharpoons C_2H_5 + Br \quad (4a)$$

$$Br + C_2H_5Br \rightleftharpoons C_2H_4Br + HBr \quad (4b)$$

$$C_2H_4Br \rightleftharpoons C_2H_4 + Br \quad (4c)$$

$$2Br + M \rightleftharpoons Br_2 + M \quad (4d)$$

$$Br + C_2H_4Br \rightleftharpoons C_2H_4 + Br_2 \quad (4e)$$

$$C_2H_5, C_2H_4Br, Br + wall \longrightarrow end \ of \ chain \quad (4f)$$

$$C_2H_5Br \rightleftharpoons C_2H_4 + HBr \quad (5)$$

In mechanism 4, (a) is the initiation step, (b) and (c) are the propagation steps, and (d), (e), and (f) are possible chain-ending steps. The bromine-catalyzed reaction could be explained in terms of (d), (b), and (e). The authors conclude that the reaction mechanism involves long chains (4), a view suggested by Semenov.[8]

In 1936, Brearley, et al.,[5] reported that t-butyl and t-amyl chlorides decomposed by the unimolecular route, the Arrhenius equations being $k_1 = 1.9 \times 10^{14} \exp(-46,000/RT)$ sec^{-1} and $k_1 = 4.5 \times 10^{14} \exp(-46,000/RT)$ sec^{-1}, respectively. The rate constant ratio was 2.35. No direct tests were made to establish the unimolecular nature of the decomposition, however. As was pointed out earlier, these authors emphasized the importance of seasoning the reaction vessels to ensure reproducibility of the runs. Kistiakowsky and Stauffer[9] investigated the rates of addition of hydrogen chloride and hydrogen bromide to isobutylene and also reported the rate of unimolecular pyrolysis of t-butyl bromide. The Arrhenius equation for the latter reaction was $k_1 = 10^{13.3} \exp(-45,500/RT)$ sec^{-1}.

Arnold and Kistiakowsky[10] investigated the gas-phase pyrolysis of ethylene iodide. At the lower temperatures of the range studied, there was a large heterogeneous component of the reaction; this was not noticeable at the higher temperatures. The rate equation followed was
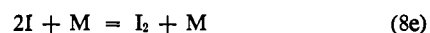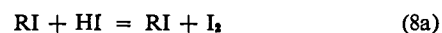
$$-\frac{d}{dt} [C_2H_4I_2] = k_1[C_2H_4I_2] + k_2[C_2H_4I_2][I_2]^{1/2} \quad (6)$$

indicating the presence of both a first-order and an iodine-catalyzed reaction. Ogg[11a] reported the rates of reaction of hydrogen iodide with methyl, ethyl, and n-propyl iodides. The rate expression derived from the results was

$$-\frac{d}{dt} [I_2] = k_2[RI][HI] + k_1[RI] \frac{[HI]}{[HI] + [I_2]} \quad (7)$$

the first term representing a bimolecular reaction and the second the consequence of the unimolecular dissociation of the

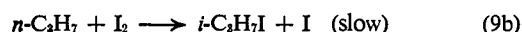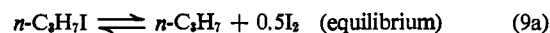iodide into an alkyl radical and an iodine atom. The following mechanism was suggested

$$RI + HI = RI + I_2 \quad (8a)$$

$$RI = R + I \quad (8b)$$

$$R + HI = RH + I \quad (8c)$$

$$R + I_2 = RI + I \quad (8d)$$

$$2I + M = I_2 + M \quad (8e)$$

(a) accounting for the first and (b)–(e), on the assumption that (b) is rate controlling, for the second term in the rate equation

Ogg and Polanyi,[11b] while looking for gas-phase racemization of sec-butyl iodide, reported the decomposition of the racemic form of this compound as following the same kinetic law as found for ethylene iodide over the temperature range 238–276°. The rate constant for unimolecular dissociation was given as $k_1 = 8.9 \times 10^{11} \exp(-39,420/RT)$ sec^{-1}. It is interesting to note that homogeneous racemization was observed and that this was explained in terms of a Walden inversion caused by iodine atoms. Racemization was also produced by a heterogeneous mechanism on a clean glass surface.
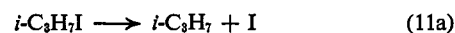
The pyrolysis of n-propyl, n-butyl,[12] isopropyl,[13] and t-butyl iodides[14] was examined by Jones and Ogg. In the case of n-propyl iodide, the suggested mechanism was
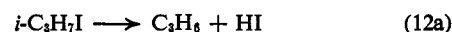
$$n\text{-}C_3H_7I \rightleftharpoons n\text{-}C_3H_7 + 0.5I_2 \quad (equilibrium) \quad (9a)$$

$$n\text{-}C_3H_7 + I_2 \longrightarrow i\text{-}C_3H_7I + I \quad (slow) \quad (9b)$$

$$i\text{-}C_3H_7I \longrightarrow 0.5C_3H_8 + 0.5C_3H_6 + 0.5I_2 \quad (fast) \quad (9c)$$

leading to the rate equation

$$-\frac{d}{dt} [C_3H_7I] = k[C_3H_7I][I_2]^{1/2} \quad (10)$$

in accord with observation. The Arrhenius equation was $k_2 = (1.79 \times 10^8)T^{1/2} \exp(-12,600/RT)$ mole^{-1} cc sec^{-1} for reaction 9b. Difficulty was experienced in interpreting the results for n-butyl iodide.[12] In the case of isopropyl iodide,[13] the reaction was of the first order and $k_1 = 1.59 \times 10^{13} \exp(-42,900/RT)$ sec^{-1}. Two mechanisms were suggested

$$i\text{-}C_3H_7I \longrightarrow i\text{-}C_3H_7 + I \quad (11a)$$

$$i\text{-}C_3H_7 + i\text{-}C_3H_7I \longrightarrow C_3H_8 + C_3H_6I \quad (11b)$$

$$C_3H_6I \longrightarrow C_3H_6 + I \quad (11c)$$

$$2I + M \rightleftharpoons I_2 + M \quad (11d)$$

and

$$i\text{-}C_3H_7I \longrightarrow C_3H_6 + HI \quad (12a)$$

$$C_3H_7I + HI \longrightarrow C_3H_8 + I_2 \quad (12b)$$

the latter being molecular. No clear-cut decision between the two was possible on the basis of the evidence. While the former compounds undergo homogeneous decomposition, t-butyl iodide was observed to decompose heterogeneously.[14] Jones[15] subsequently studied the pyrolysis of isobutyl iodide and found it to follow a similar rate law (eq 10) to that proposed for n-propyl iodide. A similar mechanism (9) was proposed and k_2, the rate constant for bimolecular attack of the isobutyl radical on iodine, was given as $k_2 = (3.39 \times 10^9)T^{1/2} \exp(-12,500/RT)$ mole^{-1} cc sec^{-1}.

(8) N. Semenov, "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935, p 450.

(9) G. B. Kistiakowsky and C. H. Stauffer, J. Amer. Chem. Soc., 59, 165 (1937).

(10) L. B. Arnold and G. B. Kistiakowsky, J. Chem. Phys., 1, 166 (1933).

(11) (a) R. A. Ogg, J. Amer. Chem. Soc., 56, 526 (1934); (b) R. A. Ogg and M. Polanyi, Trans. Faraday Soc., 31, 482 (1935).

(12) J. L. Jones and R. A. Ogg, Jr., J. Amer. Chem. Soc., 59, 1931 (1937).

(13) J. L. Jones and R. A. Ogg, Jr., ibid., 59, 1939 (1937).

(14) J. L. Jones and R. A. Ogg, Jr., ibid., 59, 1943 (1937).

(15) J. L. Jones, ibid., 60, 1877 (1938).

Butler and Polanyi,[16] using a flow system, investigated the C–I bond dissociation energies of a series of organic iodides. The results were interpreted in terms of two primary reactions

$$C_nH_{2n+1}I \longrightarrow C_nH_{2n+1} + I \qquad (13)$$

$$C_nH_{2n+1}I \longrightarrow C_nH_{2n} + HI \qquad (14)$$
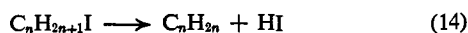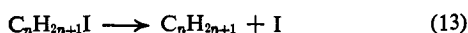
In a subsequent paper, Butler, et al.,[17] extended the work to a wider range of compounds.

Meisner and Schumacher[18] reported the gas-phase pyrolysis of methyl bromide, in the temperature range 480–520°. The reaction was homogeneous and resulted in the formation of carbon, hydrogen bromide, and methane, the latter two in the approximate ratio of 2:1. The kinetic behavior was complex, the ratio of final to initial pressure being about 1.4. On the basis of the evidence Whittingham[19] suggested the mechanism

$$CH_3Br \longrightarrow CH_2 + HBr$$
$$CH_2 + CH_2 \longrightarrow C + CH_4 \qquad (15)$$
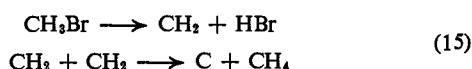
The major point, however, that emerged from the study is the enhanced stability of methyl bromide compared with ethyl bromide.

The pyrolyses of ethylene[20] and ethylidene bromide[21] were studied in the temperature range 300–400°. In the former case, clean glass vessels were used, and it was concluded that the reaction was heterogeneous. The stoichiometry was well represented by

$$C_2H_4Br \longrightarrow C_2H_4Br + HBr \qquad (16)$$

the reverse reaction being negligible. An activation energy of about 30 kcal mole^{-1} was reported. The same over-all reacstion was observed for ethylidene bromide, and the Arrhenius equation, $k_1 = 1.57 \times 10^{11} \exp(-40,900/RT)$ sec^{-1}, fitted the results. Both reactions, however, showed induction periods, which varied in a rather unpredictable fashion.

This represented the position of organic halide pyrolysis up to the end of the Second World War. The following mechanisms had been proposed for the decompositions, (i) heterogeneous, (ii) radical nonchain, (iii) radical chain, and (iv) unimolecular, although no very clear indication was apparent as to which mechanism obtained in any given case. The importance of seasoning of the reaction vessels had been emphasized and this represented a major step forward. With this background in view, it is proposed to review the progress made in this field from 1945 up to the present time.

II. Experimental Methods

A. THE STATIC METHOD

This was the method originally used by Lessig.[2] For the gas-phase reaction

$$A \longrightarrow bB + cC + \ldots \qquad (17)$$

if the initial pressure of A is p_0 and p is the pressure of A which has decomposed at time t, the total pressure (P) is given by

Figure 1. A static apparatus for measuring the rates of gas-phase reactions.[27] Reproduced by permission of the Editor of the *Journal of the Chemical Society*.

$$P = p_0 - p + (b + c + \ldots)p = p_0 + [(\Sigma r) - 1]p \qquad (18)$$

where $(a + b + \ldots) = \Sigma r$, and the pressure of substrate remaining at time t is

$$p_0 - p = \frac{p_0(\Sigma r) - P}{(\Sigma r) - 1} \qquad (19)$$

Hence if the reaction is studied at constant volume, measurement of the rate of pressure increase will accurately reproduce the rate of reaction. Since hydrogen halides attack mercury, an all-glass system is necessary, and Lessig[2] adapted a glass diaphragm gauge described by Karrer, et al.[22] Swinbourne[23] adapted a design due to Newton.[24] A typical apparatus is shown in Figure 1. In the case of a physical method being used to determine reaction rates, it is desirable to verify that the method gives a true representation of rate of reaction. This can be done in the present instance by comparing the percentage reaction as determined from pressure measurements with that determined by titration of the hydrogen halide produced. Such a plot in the case of cyclohexyl bromide[25] is shown in Figure 2.

In many cases, of which the sec-butyl halides provide the simplest example, more than one olefin may be produced in the reaction

$$\begin{array}{l} \nearrow c\text{-}2\text{-}C_4H_8 \\ sec\text{-}C_4H_9X \longrightarrow t\text{-}2\text{-}C_4H_8 + HX \qquad (20) \\ \searrow 1\text{-}C_4H_8 \end{array}$$

Samples of the products may then be taken at various times during the reaction and the olefin ratios determined by vapor phase chromatography.[26]

The importance of seasoning the reaction vessel has already been emphasized. This may be done as already described[5] by leaving the products of reaction in contact with the vessel. Alternatively, allyl bromide, which in the course of pyrolysis deposits a carbonaceous coatings,[27] may be decom-

(16) E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, 39, 19 (1943).

(17) E. T. Butler, E. Mandel, and M. Polanyi, *ibid.*, 41, 298 (1945).

(18) H. P. Meisner and H. J. Schumacher, *Z. Physik. Chem.*, A185, 435 (1939).

(19) G. Whittingham, *Discussions Faraday Soc.*, 2, 175 (1947).

(20) T. Iredale and A. Maccoll, *Nature*, 140, 24 (1937).

(21) P. T. Bennett and A. Maccoll, *J. Proc. Roy. Soc. N. S. Wales*, 74, 257 (1941).
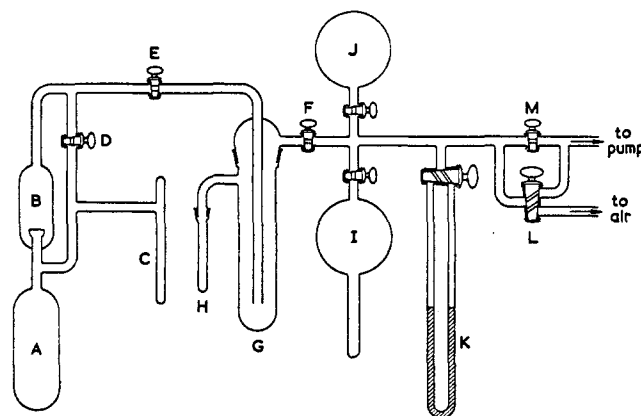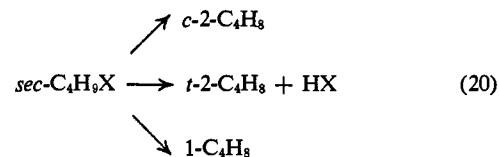
(22) S. Karrer, E. H. Wulf, and O. R. Johnson, *Ind. Eng. Chem.*, 14, 1015 (1922).

(23) E. S. Swinbourne, *Aust. J. Chem.*, 11, 314 (1958).

(24) T. W. Newton, *J. Chem. Phys.*, 18, 797 (1950).

(25) J. H. S. Green and A. Maccoll, *J. Chem. Soc.*, 2449 (1955).

(26) A. Maccoll and R. H. Stone, *ibid.*, 2756 (1961).

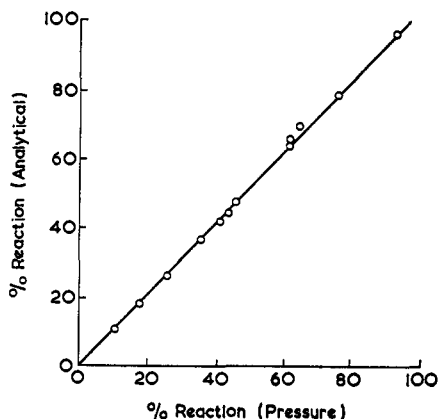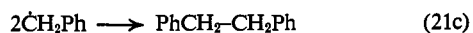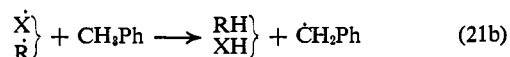(27) A. Maccoll, *ibid.*, 965 (1955).

Figure 2. Confirmation of stoichiometry (cyclohexyl bromide, after Green and Maccoll[25]). Reproduced by permission from "Studies on Chemical Structure and Reactivity,"[J. H. Ridd,[Ed., Methuen and Co. Ltd., London, 1966.

Figure 3. A flow apparatus for measuring rates of gas-phase reactions.[31] Reported by permission of the Editor of the *Journal of Chemical Physics*.

posed in the vessel.[25] The carbon coating is believed to eliminate surface reactions by covering the catalytically active glass surface.[28] Holbrook[29] has made electron spin resonance studies of surfaces seasoned by allyl bromide, *cis*-butene-2, and ethyl chloride and has shown that the former gives a strong esr signal, whereas the other two give no signal. Bridge and Holmes,[30] however, have shown that allyl bromide coated surfaces do not catalyze the elimination of hydrogen bromide from isopropyl and *n*-butyl bromides.

B. THE FLOW METHOD

After the early work on the iodides,[16,17] the next application of this method to the organic halides was made by Szwarc.[31] Here the substrate is carried through the reaction vessel by toluene vapor which acts as an atom or radical trap. The apparatus is shown in Figure 3. In the case of halides not possessing a β-carbon–hydrogen bond, the following reaction scheme obtains.

$$R-X \longrightarrow \dot{R} + \dot{X} \qquad (21a)$$

$$\left.\begin{array}{c} \dot{X} \\ \dot{R} \end{array}\right\} + CH_3Ph \longrightarrow \left.\begin{array}{c} RH \\ XH \end{array}\right\} + \dot{C}H_2Ph \qquad (21b)$$

$$2\dot{C}H_2Ph \longrightarrow PhCH_2\text{–}CH_2Ph \qquad (21c)$$

Thus the ratio $[HX]/[(PhCH_2)_2]$ should be unity. Rate constants for the first-order dissociation can be calculated from

$$k_1 = -\frac{1}{t}\ln\left(1 - \frac{x}{a}\right) \simeq \frac{x}{at} \qquad (22)$$

where t is the residence time in the reaction vessel and $x \ll a$. Blades and Murphy[32] have applied this technique to an investigation of the pyrolyses of ethyl, *n*-propyl, and isopropyl bromides. A comparison of their results with those of other
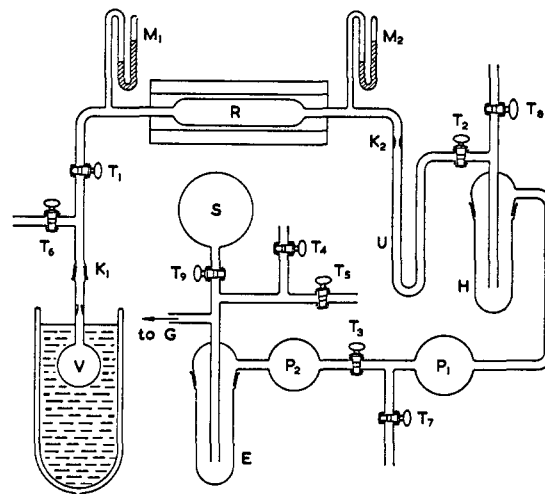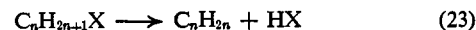
workers is shown in Table I.[33-35] No bibenzyl was observed, indicating that

$$C_nH_{2n+1}X \longrightarrow C_nH_{2n} + HX \qquad (23)$$

was faster than (21a–c). This agreement is excellent, considering the different temperature ranges over which the experiments were done, indicating a common mechanism and a constancy of Arrhenius parameters over a temperature range of about 350°.

Denbigh[36] first pointed out the advantages of the stirred-flow type of reactor. This was applied to a study of gas-phase reaction (the pyrolysis of di-*t*-butyl peroxide) by Mulcahy and Williams.[37] The advantages of the stirred-flow reactor (Figure 4) are that vigorous stirring brings about a uniform temperature in the reaction vessel and also the mixing is complete. To determine the rate constant, once the steady state is reached, only a linear equation has to be solved. This greatly simplifies the kinetic problem in the case of a complex decomposition, involving concurrent or consecutive reaction steps. Mulcahy and Williams derive the equation

$$k_1 = \frac{n_pRT}{xPV}\left\{\frac{x(n_0 + n_c) + (x - 1)n_p}{xn_0 - n_p}\right\} \qquad (24)$$

for a first-order reaction of stoichiometry

$$A \longrightarrow xP$$
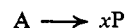
In (24), n_0 is the rate of influx of reactant, n_p the rate of efflux of product, and n_c the flow of carrier gas. Good agreement was obtained by these authors with Arrhenius parameters recorded for the di-*t*-butyl decomposition in static and in laminar flow vessels.

Herndon, *et al.*,[38] have used this method to determine the relative rates of dehydrochlorination of a number of alkyl halides.

(28) J. S. Shapiro, E. S. Swinbourne, and B. C. Young, *Aust. J. Chem.*, 17, 1217 (1964).

(29) K. A. Holbrook, *Proc. Chem. Soc.*, 418 (1964).

(30) M. R. Bridge and J. L. Holmes, *J. Chem. Soc., B*, 713 (1966).

(31) M. Szwarc, *J. Chem. Phys.*, 16, 128 (1948); M. Szwarc and B. N. Ghosh, *ibid.*, 17, 744 (1949).

(32) A. T. Blades and G. W. Murphy, *J. Amer. Chem. Soc.*, 74, 6219 (1952).

(33) P. J. Thomas, *J. Chem. Soc.*, 1192 (1959).

(34) A. Maccoll and P. J. Thomas, *ibid.*, 5033 (1957).

(35) A. Maccoll and P. J. Thomas, *ibid.*, 979 (1955).

(36) K. G. Denbigh, *Trans. Faraday Soc.*, 40, 352 (1944).

(37) M. F. R. Mulcahy and D. J. Williams, *Aust. J. Chem.*, 14, 534 (1961).

(38) W. C. Herndon, J. M. Sullivan, M. B. Henley, and J. M. Marion, *J. Amer. Chem. Soc.*, 86, 5691 (1964); W. C. Herndon, M. B. Henby, and J. M. Sullivan, *J. Phys. Chem.*, 67, 2842 (1963).

Table I

Rates of Reaction by Different Techniques

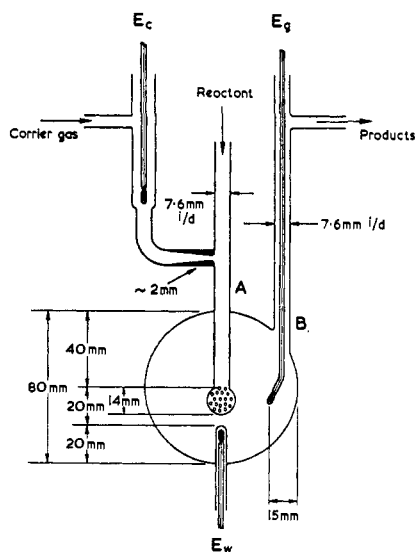| Compound	Static				Flow[82]		
	Log A	E, kcal mole^{-1}	Ref	Temp, °C	Log A	E, kcal mole^{-1}	Temp, °C
EtBr	13.45	53.9	33	380–430	12.86	52.3	530–630
n-PrBr	12.80	50.7	34	350–390	13.00	50.7	500–600
i-PrBr	12.62	47.8	35	310–350	12.60	47.7	500–600

Figure 4. A stirred-flow reactor for measuring rates of gas-phase reactions.[37] Reproduced by permission of the Editor of the *Australian Journal of Chemistry*.

C. THE SHOCK TUBE

Tsang[39–41] has applied the single-pulse shock tube to a comparative study of the rates of pyrolysis of a number of alkyl halides. The advantages of the shock tube are that a much larger temperature range can be covered and that, since the heating is homogeneous and the reaction times are short, heterogeneous effects are not present. The apparatus is shown n Figure 5. This author used the reflected shock wave and calculated the temperature from the velocity of the incident shock wave. The dwell time was taken to be the time between the arrival of the reflected shock wave and the onset of the expansion wave. In the first and third papers, a comparative technique is used in that a pair of substrates is simultaneously shocked and the rate constants are calculated from

$$k_1 = \frac{1}{t} \ln \frac{c_i}{c_f} \qquad (25)$$

where t is the dwell time, and c_i and c_f are the initial and final concentrations of substrate. A plot of log k_1^a against log k_1^b leads to a straight line, provided both decompositions follow the Arrhenius equation. Thus if $k_1^a = A_a e^{-E_a/RT}$ and $k_1^b = A_b e^{-E_b/RT}$, then it is easily shown that

$$\log k_1^a = \frac{E_a}{E_b} \log k_1^b + \log A_a - \frac{E_a}{E_b} \log A_b \qquad (26)$$

(39) W. Tsang, *J. Chem. Phys.*, 40, 1171 (1964).
(40) W. Tsang, *ibid.*, 40, 1498 (1964).
41) W. Tsang, *ibid.*, 41, 2487 (1964).

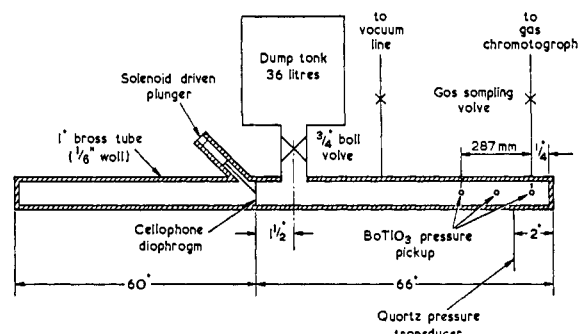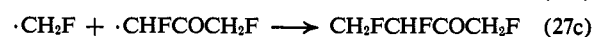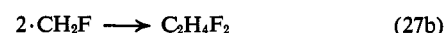Figure 5. A single-pulse shock tube.[40] Reproduced by permission of the Editor of the *Journal of Chemical Physics*.

a knowledge of the temperature not being necessary to derive one Arrhenius equation if the other is known. Using isopropyl bromide as a standard,[39] the Arrhenius equations were calculated for *t*-butyl chloride and bromide. In the third paper,[41] a further series of alkyl halides was investigated. In the second paper of the series[40] four *t*-butyl compounds were investigated using calculated temperatures, and the conclusion was drawn that the temperature in the shock front was probably 10–25° lower than that calculated.

A comparison of results obtained by the static and the shock tubes is shown in Table II.[42–44] Once again the agreement is very satisfactory, especially bearing in mind the large differences in the temperature ranges used in the two techniques.

D. CHEMICAL ACTIVATION[45]

If a chemical species is energized in the course of its production by chemical reaction, it will display characteristics of a nonequilibrium energy distribution with respect to the ambient temperature. In the alkyl halide field, Pritchard, *et al.*,[46] observed vinyl fluoride in the photolysis products of 1,3-difluoroacetone. The suggested mechanism was

$$CH_2FCOCH_2F \xrightarrow{h\nu} CH_2F\cdot + \cdot COCH_2F$$
$$\cdot COCH_2F \longrightarrow CO + \cdot CH_2F$$
$$\cdot CH_2F + CH_2FCOCH_2F \longrightarrow CH_3F + \cdot CHFCOCH_2F \qquad (27a)$$
$$2\cdot CH_2F \longrightarrow C_2H_4F_2 \qquad (27b)$$
$$\cdot CH_2F + \cdot CHFCOCH_2F \longrightarrow CH_2FCHFCOCH_2F \qquad (27c)$$
$$2\cdot CHFCOCH_2F \longrightarrow (CHFCOCH_2F)_2 \qquad (27d)$$
$$2\cdot CH_2F \longrightarrow CHF=CH_2 + HF \qquad (27e)$$
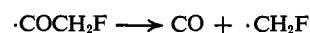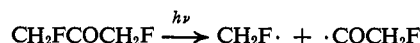
(42) N. Capon and R. A. Ross, *Trans. Faraday Soc.*, 62, 1560 (1966).
(43) D. H. R. Barton and A. J. Head, *ibid.*, 46, 114 (1950).
(44) S. C. Wong, Ph.D. Thesis, University of London, 1958.
(45) B. S. Rabinowitch and M. C. Flowers, *Quart. Rev.* (London), 122 (1964).
(46) G. O. Pritchard, M. Venugopalan, and T. F. Graham, *J. Phys. Chem.*, 68, 1786 (1964).

Table II

Rates of Reaction by Different Techniques

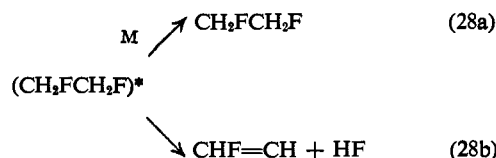| Compound	Log A	$E,$ kcal mole^{-1}	Temp, °C	Ref	Log A	$E,$ kcal mole^{-1}	Temp, °C
		Static				Dynamic[40,41]	
EtCl	13.46	56.6	420–500	42	13.16	56.4	550–730
i-PrCl	13.40	50.5	370–410	43	13.64	51.1	480–680
t-BuCl	13.72	45.0	290–330	44	13.73	44.7	480–680

Reaction 27e may be further written

$$\text{(CH}_2\text{FCH}_2\text{F)*} \nearrow \text{CH}_2\text{FCH}_2\text{F} \qquad (28a)$$

$$\searrow \text{CHF=CH} + \text{HF} \qquad (28b)$$

indicating a competition between deactivation by collision and elimination. As the pressure is reduced (28b) becomes of greater importance compared with (28a). Benson and Haugen[47] have shown how the above results could be analyzed to yield an activation energy for the thermal elimination reaction. Thus according to the RRK theory[48] of unimolecular decomposition, the rate constant is given as a function of energy by

$$k = A\left(1 - \frac{E_0}{E}\right)^{n-1} \qquad (29)$$

where E_0 is the critical energy necessary for decomposition, n is the number of effective oscillators, and A is the preexponential term in the Arrhenius equation. Provided E can be calculated, then for a given value of n, E_0 may be estimated.

Setser, *et al.*,[49] have reported the decomposition of activated chloroalkanes, produced by the recombination of radicals formed by abstraction by methylene. These authors photolyzed a mixture of ketene and diazomethane, a reaction known to produce singlet methylene, in the presence of methyl chloride. The proposed reaction scheme is

$$2\text{CH}_2 + \text{CH}_3\text{Cl} \longrightarrow \text{CH}_3\cdot + \cdot\text{CH}_2\text{Cl} \qquad (30a)$$

$$2\cdot\text{CH}_3 \longrightarrow \text{C}_2\text{H}_6 \qquad (30b)$$

$$\cdot\text{CH}_3 + \cdot\text{CH}_2\text{Cl} \longrightarrow \text{CH}_3\text{CH}_2\text{Cl} \qquad (30c)$$

$$2\cdot\text{CH}_2\text{Cl} \longrightarrow \text{CH}_2\text{ClCH}_2\text{Cl} \qquad (30d)$$

The activated species formed in scheme 30 then undergo reaction by a mechanism similar to (28). Addition of oxygen to the system, with which alkyl radicals react rapidly while singlet methylene does not, virtually eliminated reactions 30b–d. This observation showed that the methylene reacts by abstraction, rather than by insertion. As is expected from (30) and (28), there is an increase in the production of C_2H_4 and $\text{C}_2\text{H}_3\text{Cl}$, the elimination products, as the pressure is lowered.

More recent work in the field will be discussed in the following section.

III. The Experimental Results (Molecular Reactions)

A. FLUOROALKANES

The direct investigation of the pyrolysis of alkyl fluorides containing a β-carbon–hydrogen bond in a static or dynamic system has not yet been achieved.[49a] In the case of the static system, difficulties arise probably owing to the penetration of the surface coating by hydrogen fluoride and its subsequent attack upon the glass walls of the reaction vessel. However, Pritchard, *et al.*[46] (section II.D), have shown how chemical activation methods may be used.

Of the methane derivatives, the fluoroform decomposition has been investigated by shock-tube techniques,[50] the decomposition of activated CHTF_2 has been accorded the scheme[51]

$$\text{(CHTF}_2\text{)*} \nearrow \text{CHF} + \text{TF} \qquad (31)$$

$$\searrow \text{CTF} + \text{HF}$$
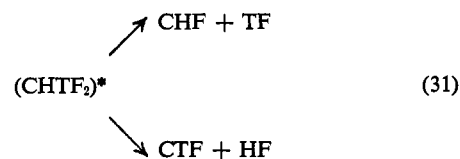
and two groups of workers[52,53] have examined the pyrolysis of difluorochloromethane. (In the case of this compound, it is hydrogen chloride which is eliminated.) In all cases a fluoro- or difluorocarbene has been postulated as the initial product of decomposition, indicating α elimination.

In analyzing the results of Pritchard, *et al.*, Benson and Haugen[47] estimated the energy of $\text{C}_2\text{H}_4\text{F}_2$ to vary from 85.4 at 29° to 93.5 kcal mole^{-1} at 308°. Using the RRK theory, this gave the action energy for elimination from ethylene fluoride as 62 ± 3 kcal mole^{-1}. In subsequent communications[54–57] Pritchard and his coworkers have applied this analysis to a series of polyfluorides. The results are set out in Table III. Of particular interest is the observation of α elimination in the case of CD_3CHF_2, leading to HF formation, as distinct from the DF produced by β elimination. There is also a suggestion of HD being split out.

(47) S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1965).

(48) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co. Inc., New York, N. Y., 1960.

(49) D. W. Setser, R. Littrell, and J. C. Hassler, *J. Amer. Chem. Soc.*, **87**, 2062 (1965).

(49a) However, A. F. Trotman-Dickenson mentions (*Discussions Faraday Soc.*, 44, 289 (1967) that his group has observed the homogeneous elimination of hydrogen halides from 2-chloroethyl fluoride.

(50) A. P. Modia and J. E. La Graffe, *J. Chem. Phys.*, **44**, 3375 (1966); E. Tschukow-Rouse and J. E. Marte, *ibid.*, **42**, 2049 (1965).

(51) Y. N. Yang and F. S. Rowland, *J. Amer. Chem. Soc.*, **88**, 626 (1966).

(52) F. Gozzo and C. R. Patrick, *Nature*, **202**, 80 (1964); *Tetrahedron*, **22**, 3329 (1966).

(53) J. W. Edwards and P. A. Small, *ibid.*, **202**, 1329 (1964); *Ind. Eng. Chem., Fundam.*, **4**, 396 (1965).

(54) G. O. Pritchard and R. L. Thommarson, *J. Phys. Chem.*, **71**, 1674 (1967).

(55) J. T. Bryant, B. Kirtman, and G. O. Pritchard, *ibid.*, **71**, 1960 (1967).

(56) J. T. Bryant and G. O. Pritchard, *ibid.*, **71**, 3439 (1967).

(57) M. J. Perona, J. T. Bryant, and G. O. Pritchard, *J. Amer. Chem. Soc.*, **90**, 4782 (1968).

Table III

Energies of Activation for Fluoroalkanes

Compound	n	E_0, kcal mole^{-1}	E, kcal mole^{-1}	Temp, °C	Ref
CH$_3$CH$_2$F	10	59	85.4–92.4	0–297	54
CH$_2$FCH$_2$F	12	59	85.4–93.5	0–308	54
CH$_3$CHF$_2$	11	53	85.4–92.7	0–287	56
CH$_2$FCHF$_2$	13	59	85.4–96.5	0–377	55
CD$_3$CHF$_2$	12	53^a	85.4–92.7	0–283	57
	12	64^b			

^{a} For β elimination. ^{b} For α elimination.
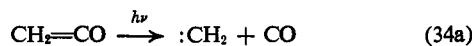
Trotman-Dickenson, *et al.*, have made activated alkyl fluorides by (i) reactions of radicals with fluorine,[58] (ii) combination of radicals, and (iii) insertion of methylene. Typical processes are shown below involving (i) the thermal fluorination of ethane

$$C_2H_6 + F_2 = (C_2H_5F)^* + F \quad (32a)$$

$$(C_2H_5F)^* = C_2H_4 + HF \quad (32b)$$

$$(C_2H_5F)^* + M = C_2H_5F + M \quad (32c)$$
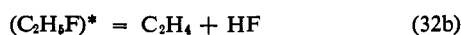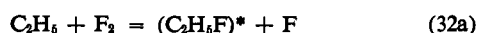
(ii) the photolysis of equimolar mixtures of acetone and 1,3-difluoroacetone

$$(CH_3)_2CO \xrightarrow{h\nu} 2\dot{C}H_3 + CO \quad (33a)$$

$$(CH_2F)_2CO \xrightarrow{h\nu} 2\dot{C}H_2F + CO \quad (33b)$$

$$\dot{C}H_3 + \dot{C}H_2F \longrightarrow (CH_3CH_2F)^* \quad (33c)$$
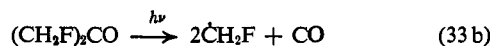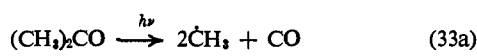
and (iii) the photolysis of ketene in the presence of methyl fluoride, neopentane, and oxygen

$$CH_2{=}CO \xrightarrow{h\nu} :CH_2 + CO \quad (34a)$$

$$:CH_2 + CH_3F \longrightarrow (CH_3CH_2F)^* \quad (34b)$$

$$:CH_2 + C_5H_{12} \longrightarrow (C_6H_{14})^* \quad (34c)$$

By this means activated ethyl fluoride with energy content of 69 (i), 85 (ii), and 115 (iii) kcal mole^{-1} was produced. Assuming $n = 12.5$, the RRK theory was used to derive rate constants on the assumption that $A = 10^{13.5}$ sec^{-1} leading to an activation energy of 51 kcal mole^{-1}. The authors point out that this is a *lower* limit, since the RRK method underestimates the rate of reaction of molecules with low energies. In the discussion, Trotman-Dickenson reports the use of the RRKM theory to yield a revised value of the action energy of 58 kcal mole^{-1}. Results are shown in Table IV. In addition, values of k_e/k_s (rate constant for elimination/rate constant for stabilization) were listed for a number of compounds and the relative rates of elimination estimated.

Table IV

**Energies of Activation for Fluoroalkanes**

Compound	C$_2$H$_5$F	CH$_2$F-CH$_2$F	CH$_3$CH$_2$-CHF$_2$	CH$_3$CF$_2$-CH$_3$	CH$_3$CF$_2$-Cl
Method	a–c	b, c	b, c	b, c	b
n	12.5	14	21	21	15.5
E, kcal mole^{-1}	51	52	54	43	58

(58) J. A. Kerr, A. W. Kirk, B. V. O'Grady, D. C. Phillips, and A. F. Trotman-Dickenson, *Discussions Faraday Soc.*, 44, 263 (1967).

Chemical activation thus provides a very powerful tool for investigating the behavior of fluoroalkanes, so far inaccessible to the more conventional kinetic methods. The one criticism, however, that may be leveled is its dependence on the theory of unimolecular processes.

B. CHLOROALKANES

The pyrolysis of methyl chloride has been examined by Shilov and Sabirova.[59] These authors reject the possibility of α elimination to form methylene

$$CH_3Cl = :CH_2 + HCl$$
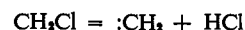
Noticeable decomposition was only observed around 800°. This would suggest that α elimination may be discounted in the case of those halides which possess a β-carbon–hydrogen bond, and which normally pyrolyze in the temperature range 230–450°. The Arrhenius parameters of the alkyl chloride decompositions reported in the literature are set out in Table V.[60-93]

As has been mentioned earlier (section II.B), Herndon *et al.*,[38] have investigated the relative rates of elimination of a number of alkyl chlorides using a stirred-flow reactor. The

(59) A. E. Shilov and R. D. Sabirova, *Russ. J. Phys. Chem.*, 33, 1365 (1959).

(60) D. H. R. Barton and A. J. Head, *Trans. Faraday Soc.*, 46, 114 (1950).

(61) D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 165 (1949).

(62) H. Hartmann, H. G. Bosche, and H. Heydtmann, *Z. Phys. Chem.* (Frankfurt am Main), 42, 329 (1964).

(63) K. A. Holbrook and A. R. W. Marsh, *Trans. Faraday Soc.*, 64, 643 (1967).

(64) D. H. R. Barton, A. J. Head, and R. S. Williams, *J. Chem. Soc.*, 2039 (1951).

(65) H. Hartmann, H. Heydtmann, and G. Rinck, *Z. Phys. Chem.* (Frankfurt am Main), 28, 85 (1961).

(66) K. E. Howlett, *J. Chem. Soc.*, 4487 (1952).

(67) R. C. S. Grant and E. S. Swinbourne, *ibid.*, 4423 (1965).

(68) J. S. Shapiro and E. S. Swinbourne, *Can. J. Chem.*, 46, 1341 (1968); A. Maccoll and E. S. Swinbourne, *J. Chem. Soc.*, 149 (1964).

(69) A. Maccoll and R. H. Stone, *ibid.*, 2756 (1961).

(70) H. Heydtmann and G. Rinck, *Z. Phys. Chem.* (Frankfurt am Main), 30, 250 (1961).

(71) H. Heydtmann and G. Pinck, *ibid.*, 36, 75 (1963).

(72) E. S. Swinbourne, *J. Chem. Soc.*, 4668 (1960).

(73) E. S. Swinbourne, *Aust. J. Chem.*, 11, 314 (1958).

(74) C. J. Harding, A. Maccoll, and R. A. Ross, *Chem. Commun.*, 289 (1967).

(75) R. C. L. Bicknell and A. Maccoll, *Chem. Ind.* (London), 1912 (1961).

(76) R. C. L. Bicknell, Ph.D. Thesis, University of London, 1962.

(77) D. H. R. Barton, A. J. Head, and R. S. Williams, *J. Chem. Soc.*, 453 (1952).

(78) T. O. Bamkole, Ph.D. Thesis, University of London, 1964.

(79) M. R. Bridge, D. H. Davies, A. Maccoll, R. A. Ross, and O. Banjoko, *J. Chem. Soc., B*, 805 (1968).

(80) P. J. Thomas, *ibid.*, 136 (1961).

(81) R. L. Failes and V. R. Stimson, *Aust. J. Chem.*, 20, 1553 (1967).

(82) D. H. R. Barton and F. P. Onyon, *Trans. Faraday Soc.*, 45, 725 (1949).

(83) S. C. Wong, Ph.D. Thesis, University of London, 1958; A. Maccoll and S. C. Wong, *J. Chem. Soc.*, in press.

(84) R. L. Failes and V. R. Stimson, *Aust. J. Chem.*, 15, 437 (1962).

(85) B. Roberts, Ph.D. Thesis, University of London, 1961.

(86) P. J. Thomas, *J. Chem. Soc.*, 1238 (1967B).

(87) C. J. Harding, Ph.D. Thesis, University of London, 1968.

(88) D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 165 (1949).

(89) K. E. Howlett, *ibid.*, 3695 (1952).

(90) H. Hartmann, H. Heydtmann, and G. Rinck, *Z. Phys. Chem.* (Frankfurt am Main), 28, 71 (1961).

(91) D. H. R. Barton and F. P. Onyon, *J. Amer. Chem. Soc.*, 72, 988 (1950).

(92) K. E. Howlett, *J. Chem. Soc.*, 945 (1953).

(93) E. S. Swinbourne and B. C. Young, *ibid.*, 1181 (1967).

Table V

Arrhenius Parameters for Chloroalkane Pyrolyses

Compound	Temp range, °C	Log A/ sec⁻¹	E, kcal mole⁻¹	Ref
C₂H₅Cl	400–490	14.60	60.8	60, 61
	550–730	13.16	56.4	41
	420–500	13.46	56.6	42
	400–520	14.03	58.4	63
	410–470	13.51	56.6	62
n-C₃H₇Cl	420–480	13.45	55.0	64
	400–460	13.50	55.1	62
n-C₄H₉Cl	390–460	14.50	57.9	65
	430–470	14.00	57.0	64
	400–450	13.63	55.2	62
n-C₅H₉Cl	400–460	14.61	58.3	67
i-C₄H₉Cl	360–480	14.02	56.9	66
	390–450	13.81	55.3	62
neo-C₅H₁₁Cl	410–500	13.26	60.0	68
i-C₃H₇Cl	370–400	13.40	50.5	60
	480–680	13.64	51.1	41
sec-C₄H₉Cl	330–390	13.62	49.6	69
	320–390	14.00	50.6	70
	300–420	14.07	50.8	71
c-C₆H₉Cl	310–380	13.47	48.3	72
c-C₆H₁₁Cl	320–390	13.77	50.0	73
	350–480	13.88	50.2	38
sec-C₈H₁₇Cl	320–380	13.53	48.7	74
Bornyl chloride	320–390	13.99	50.6	75
Isobornyl chloride	310–350	14.78	49.7	76
Menthyl chloride	400–440	12.00	42.6	77
	310–350	11.93	42.4	78
neo-Menthyl chloride	310–350	11.04	40.9	78
C₆H₅CHClCH₃	310–380	12.60	44.8	79
p-F-C₆H₄CHClCH₃	330–380	12.99	45.6	79
p-Cl-C₆H₄CHClCH₃	330–380	12.24	44.1	79
p-Br-C₆H₄CHClCH₃	340–390	12.23	44.2	79
p-Me-C₆H₄CHClCH₃	300–340	14.10	47.7	79
m-Me-C₆H₄CHClCH₃	310–370	12.00	42.7	79
p-CN-C₄H₆CHClCH₃	340–390	12.54	47.0	79
CH₃OCHClCH₃	180–250	11.46	33.3	80
C₂H₅OCHClCH₃	160–220	10.52	30.3	81
t-C₄H₉Cl	270–350	14.20	46.0	5
	290–340	12.40	41.4	82
	290–330	13.77	45.0	83
	280–310	13.70	44.9	84
	480–680	13.74	44.7	39
	450–580	13.90	46.2	40
	270–350	14.41	46.6	85
t-C₅H₁₁Cl	270–330	14.65	46.0	5
	280–320	13.82	44.2	83
2-Cl-2,3-(CH₃)₂C₄H₇	270–310	13.38	42.3	83
2-Cl-2,3,3-(CH₃)₃C₄H₆	250–300	13.80	41.9	83
CH₃CH(Cl)CH = CH₂	350–390	13.34	48.5	86
CH₃CH(Cl)C(CH₃)=CH₂	320–360	13.28	46.9	86
(CH₃)₂CClCH=CH₂	240–310	13.30	42.6	87
(CH₃)₂C=CHCH₂Cl	240–310	12.03	38.3	87
CH₃CHCl₂	360–450	12.08	49.5	88
	350–450	11.65	48.3	89
	420–450	13.45	53.5	90
CH₃CCl₃	360–420	14.00	54.0	91
CH₃CH₂CHCl₂	380–440	12.76	51.2	92
CH₃CHClCH₂Cl	420–450	13.80	54.9	60
CH₃CCl₂CH₃	330–410	11.90	43.9	92
	320–380	14.52	51.4	93
CH₃CH₂CCl₂CH₃	310–370	14.49	50.2	93

Table VI

Relative Rates of Dehydrochlorination[38]

			Chloride			
Temp, °C	Cyclo-hexyl	2-Butyl	Cyclo-pentyl	exo-Nor-bornyl	1-Phenyl-ethyl	t-Butyl
300	1	0.85	1.20	0.67	7.8	100
500	1	1.12	0.93	0.77	6.9	71

results at 400 and 500° are set out in Table VI. A discussion of these results has been given by Hoffmann and the author.[94]

Erbe, *et al.*,[95] have reported on the Arrhenius parameters for the dehydrochlorination of a number of chloroalkanes.[95a] The results are set out in Table VII.

Table VII

Chloroalkane Pyrolyses[95]

Compound	Temp range, °C	Log A/ sec⁻¹	E, kcal mole⁻¹
1-Chlorodecane	380–430	14.1	55.7
3-Chlorodecane	330–380	12.29	45
4-Chlorodecane	310–350	11.94	43.4
3-Chloro-3-methylheptane	250–290	12.38	38
3-Chloro-3-methylundecane	230–290	11.3	36
1,6-Dichlorohexane	360–420	14.5	58
1,10-Dichlorodecane	350–410	13.35	53
1,2-Dichlorohexane	350–400	13.42	50
2,4-Dichlorohexane	320–380	12.63	46.2
2,2-Dichloroheptane	300–360	12.8	45
5,7-Dichlorodecane	310–370	14.25	49.5
6,7-Dichlorodecane	320–380	13.6	49.3
1,4,7-Trichloroheptane	340–380	12.3	45
3-Chlorohexene-2	250–320	10.75	34
2-Chloroheptene-1	370–408	13.6	55
4-Chloroheptene-3	380–430	14.0	57

Chemical activation studies have also been made on chloroalkanes.[49,96,97] Using abstraction reactions of Cl and H by methylene from the chloromethanes, chloroalkanes in the energy range 85–95 kcal mole⁻¹ have been produced, at 25°. The nonequilibrium rate constants for decomposition of a series of chloroalkanes are shown in Table VIII.

A necessary, though not sufficient condition for a reaction to follow a unimolecular mechanism is that the first-order rate coefficient should decrease as the initial pressure decreases, below a certain critical value. Further, it should return to its high-pressure value when an excess of inert gas is added. A number of chlorides have been investigated at low pressures. Thus Howlett[98,99] examined ethyl, *n*-propyl, isopropyl, iso-

(94) H. M. R. Hoffmann and A. Maccoll, *J. Amer. Chem. Soc.*, 87, 3774 (1965).

(95) F. von Erbe, T. Grewer, and K. Wehage, *Angew. Chem.*, 74, 985 (1962).

(95a) This paper was inaccurately described by *Chemical Abstracts* as a review article.

(96) J. C. Hassler, D. W. Setser, and R. L. Johnson, *J. Chem. Phys.*, 45, 3231 (1966).

(97) J. C. Hassler and D. W. Setser, *ibid.*, 45, 3237 (1966).

(98) K. E. Howlett, *J. Chem. Soc.*, 3695 (1952).

(99) K. E. Howlett, *ibid.*, 4487 (1952); see also H. Heydtmann, *Chem. Phys. Letters*, 1, 105 (1967).

Table VIII

Nonequilibrium Rate Constants for Chloroalkane Decomposition

	—Substrate system—					
	—CH_2Cl_2—		$CH_2Cl_2 + CF_4$		—CH_3Cl—	
	p,[a]	$10^8 k_1$,	p,	$10^8 k_1$,	p,	$10^8 k_1$,
Molecule	cm	sec	cm	sec	cm	sec
C_2H_5Cl	25	27	28	30	27	30
$1,2$-$C_2H_4Cl_2$	1.8	1.9	2.3	2.4	1.6	1.8
$1,1$-$C_2H_4Cl_2$	...	...	116	120	...	..
$1,1,2$-$C_2H_3Cl_3$	2.2	2.2	3.5	3.4	...	...

[a] Pressures at which k_g/k_t in (28) equals unity.

butyl, and *t*-butyl chlorides and 1,1-dichloroethane. Swinbourne[78] has reported the results for cyclohexyl chloride, and Roberts for *t*-butyl chloride.[85] Blades, *et al.*,[100] have reported results for chloroethene-1,1,2,2-d_4. Gill and Laidler[101] have applied the Slater theory[102] to ethyl chloride. In addition Wieder and Marcus[103] and Hassler and Setser[104] have applied the RRKM method[105] to certain chloroalkane decompositions.

Some studies have been made of the effects of deuteration on the rate constants. Thus Blades, *et al.*,[100] have examined the rate constants for pyrolysis of chloroethane-1,1,2,2-d_4. Their results were expressed as

$$k_H/k_D = 1.16e^{985/RT}$$

where k_H and k_D are the rate constants for the production of C_2D_4 and C_2HD_3, respectively.

C. BROMOALKANES

The early study of methyl bromide has already been referred to.[18, 19] Sehon and Szwarc[106] have applied the toluene flow technique to examine a series of bromomethanes. The results were interpreted in terms of the reaction

$$CH_xBr_{4-x} \longrightarrow CH_xBr_{3-x} + Br$$

no evidence being obtained for α elimination.

The results for the homogeneous gas-phase elimination of bromoalkanes are set out in Table IX.[107–121]

(100) A. T. Blades, P. W. Gilderson, and M. G. H. Wallbridge, *Can. J. Chem.*, **40**, 1526 (1964).
(101) E. K. Gill and K. J. Laidler, *Proc. Roy. Soc.* (London), A250, 121 (1959).
(102) N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.
(103) G. M. Wieder and R. A. Marcus, *J. Chem. Phys.*, **37**, 1835 (1962).
(104) J. C. Hassler and P. W. Setser, *ibid.*, **45**, 3246 (1966).
(105) R. A. Marcus and D. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1941); R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952); **43**, 2658 (1965).
(106) A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (London), A209, 110 (1951).
(107) A. T. Blades, *Can. J. Chem.*, **36**, 1043 (1958).
(108) G. D. Harden and A. Maccoll, *J. Chem. Soc.*, 1197 (1959).
(109) J. H. S. Green, A. Maccoll, and P. J. Thomas, *ibid.*, 184 (1960).
(110) N. N. Semenov, G. B. Sergeev, and G. A. Kaprilova, *Dokl. Akad. Nauk SSSR*, 105, 301 (1955).
(111) A. Maccoll and P. J. Thomas, *J. Chem. Soc.*, 2445 (1955).
(112) G. B. Sergeev, *Dokl. Akad. Nauk SSSR*, 106, 299 (1955).
(113) M. N. Kale, A. Maccoll, and P. J. Thomas, *J. Chem. Soc.*, 3016 (1958).
(114) M. N. Kale and A. Maccoll, *ibid.*, 5020 (1957).
(115) N. Capon, A. Maccoll, and R. A. Ross, *Trans. Faraday Soc.*, **63**, 1152 (1967).
(116) S. S. W. Price, R. Shaw, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3855 (1956).
(117) B. Stephenson, Ph.D. Thesis, University of London, 1957.
(118) G. D. Harden and A. Maccoll, *J. Chem. Soc.*, 2454 (1955).

Table IX

Arrhenius Parameters for Bromoalkane Pyrolysis

Compound	Temp range, °C	Log A/sec^{-1}	E, kcal mole^{-1}	Ref
C_2H_5Br	530–630	12.86	52.3	33
	380–430	13.45	53.9	33
	520–620	12.95	52.2	107
	470–670	13.19	53.7	41
n-C_3H_7Br	500–600	13.00	50.7	32
	350–390	12.90	50.7	34
	370–420	13.18	51.9	167
n-C_4H_7Br	370–420	13.18	50.9	34
i-C_4H_9Br	360–420	13.05	50.4	108
n-$C_5H_{11}Br$	370–420	13.09	50.5	109
n-$C_6H_{13}Br$	370–420	13.14	50.5	109
i-C_3H_7Br	500–600	13.60	47.7	32
	310–350	13.62	47.8	35
	350–500	12.74	47.0	110
sec-C_4H_9Br	300–350	12.63	43.8	111
	...	13.05	45.5	112
	330–400	13.53	46.5	113
c-C_5H_9Br	300–360	12.84	43.7	114
	300–360	11.9	41.4	116
$C_2H_5CHBrC_2H_5$	290–350	13.51	45.4	115
c-$C_5H_{11}Br$	300–350	13.52	46.1	25
$C_6H_5CHBrCH_3$	260–290	12.18	38.8	117
t-C_4H_9Br	240–290	13.3	40.5	9
	230–280	14.0	42.0	118
	430–630	13.5	41.5	40
	...	13.23	41.00	112
t-$C_5H_{11}Br$	220–270	13.6	40.5	119
$2,3$-$(CH_3)_2$-2-ClC_4H_7	210–260	13.54	39.0	120
4-Brompentene-1	300–350	12.94	44.7	53
CH_3CHBr_2	350–430	12.91	49.5	121

Tests of the unimolecular nature of bromide pyrolysis have not been extensive owing to difficulties of mixed mechanism (section V). However, Kale and the author[122] have demonstrated the pressure dependence of the first-order velocity coefficient for *sec*-propyl bromide. The effect of deuteration on the rate has been investigated by Blades[123] in the case of ethyl bromide-d_5, the Arrhenius parameters being log A/sec^{-1} = 13.32 and E = 54.80 kcal mole^{-1}. Good[121] has examined a series of deuterated isopropyl bromides and reports that the activation energies are independent of the number of deuterium atoms in the molecule, the effect, in contradiction to the work of Blades,[123] being on the A factors. Further Blades, *et al.*,[124] have examined ethyl-1,1,2,2-d_4 bromide and report $k_H/k_D = 0.502e^{2300/RT}$, the isotope effect falling to lower values as the initial pressure is decreased. Friedman, *et al.*,[125] have reported a ^{13}C isotope effect in the thermal decomposition of ethyl bromide. These authors concluded that, since the magnitude of the isotope effect is significantly lower than the values calculated for the rupture of a carbon–bromine bond,

(119) G. D. Harden, *ibid.*, 5024 (1957).
(120) G. D. Harden and A. Maccoll, *ibid.*, 5028 (1957).
(121) P. T. Good, Ph.D. Thesis, University of London, 1956.
(122) M. N. Kale and A. Maccoll, *J. Chem. Soc.*, 1513 (1964).
(123) A. T. Blades, *Can. J. Chem.*, **36**, 1043 (1958).
(124) A. T. Blades, P. W. Gilderson, and M. G. Wallbridge, *ibid.*, **40**, 1533 (1962).
(125) H. L. Friedman, R. B. Bernstein, and H. E. Gunning, *J. Chem. Phys.*, **23**, 109 (1955).

the decomposition is molecular in nature. Thomas and the author[126] have, however, pointed out that it was probable that the reaction was proceeding by a mixed unimolecular chain mechanism. This view was supported by the fact that the rates reported[125] were significantly faster than those observed by Daniels and Veltman for a process to which they ascribe a chain mechanism.[4]

D. IODOALKANES

Up until a decade ago, the situation with respect to the iodoalkanes was far from clear. Many of the observed reactions appeared to follow mechanisms involving iodine atoms (section I). However, some evidence existed in the literature[16,17] that hydrogen iodide might be eliminated. The compounds so far reported as undergoing molecular elimination are set out Table X.[127-133] No studies have been made of either the low-pressure behavior of the unimolecular rate coefficients or of the effects of deuteration upon the rate.

Table X
Arrhenius Parameters for Iodoalkane Pyrolysis

Molecule	Temp range, °C	Log A/sec^{-1}	E, $kcal\ mole^{-1}$	Ref
C_2H_5I	390–520	14.1	52.8	127
	330–390	13.66	50.0	128
	330–380	13.02	48.3	129
	...	14.24	51.0	130
i-C_3H_7I	290–360	14.46	48.2	131
	290–360	14.79	48.0	132
	270–300	12.96	43.5	133
	410–580	13.67	45.1	41
sec-C_4H_9I	290–330	15.20	47.9	132
t-C_4H_9I	380–490	13.73	38.0	41
	...	13.53	38.3	130
	...	12.52^a	36.4^a	b

^{a} These values were obtained from a study of the reverse reaction: HI + Ol → RI. ^{b} A. N. Bose and S. W. Benson, $J.\ Chem.\ Phys.$, 37, 1081 (1962).

IV. Heterogeneous Processes in the Pyrolysis of Haloalkanes

Most workers in the field of the kinetics of dehydrohalogenation have at some time or other inadvertently studied the heterogeneous process, if the reaction vessel had not been carefully seasoned. Barton and Onyon,[82] in their study of the homogeneous unimolecular decomposition of t-butyl chloride, also report on the heterogeneous mode of decomposition in clean glass vessels. In both packed ($S/V = 10$) and empty ($S/V = 3$) vessels, the first runs showed zero-order kinetics. The rates in both vessels were considerably higher than the unimolecular rate, those in the packed vessel being two to three times greater than those in the empty vessel. In a third

vessel packed with clean glass wool, rates at 220° were extremely fast. Barton, Head, and Williams[77] in their study of menthyl chloride show that in a clean glass-packed reactor, rate constants are about 25 times those in a seasoned vessel. Kaprilova[134] has shown that in the case of 1,2-dichloroethane, decomposing in clean glass reactors, chains start at the walls and end both homogeneously and also on the walls. The role of surfaces in the chain mode of decomposition will be discussed in the next section.

Shapiro, Swinbourne, and Young[135] have carried out a detailed investigation of dehydrochlorination on clean Pyrex glass in both packed and unpacked vessels. The results for a series of primary chlorides are set out in Table XI. Also included in the table are the rate constants for pyrolyses in a coated vessel and the rate constants for the heterogeneous process obtained by difference. In the case of ethyl chloride, which followed a first-order law, the activation energy for the heterogeneous reaction was 24 kcal mole^{-1}, considerably

Table XI
First-Order Rate Constants for Heterogeneous Pyrolysis (413°)

Compound	10^6k_1, sec^{-1} Clean vessel	Coated vessel	Hetero-geneous
C_2H_5Cl	3.2	2.6	0.6
n-C_3H_7Cl	8.9	6.0	2.9
i-C_4H_9Cl	15.1	8.8	6.3
neo-$C_5H_{11}Cl$	11.0	0.2	10.8

lower than for the molecular reaction (~56 kcal mole^{-1}). The authors report irreproducible behavior in the case of isopropyl chloride.

Schwab, Noller, and their co-workers[136-140] have made an extensive study of the decomposition of alkyl chlorides on a number of solid catalysts. Typical results on a titanium carbide surface are shown in Table XII. These authors suggest a polar transition state (akin to that proposed by Maccoll and Thomas[141] for the homogeneous gas-phase process) where

I
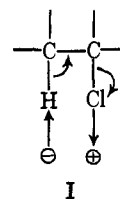
⊕ and ⊖ represent charged sites on the solid lattice. The most active catalysts were found to be those with a high electrostatic field strength associated with a surface interatomic

(126) P. J. Thomas and A. Maccoll, $J.\ Chem.\ Phys.$, 23, 1722 (1955).
(127) J. H. Yang and D. C. Conway, ibid., 43, 1296 (1965).
(128) A. N. Bose and S. W. Benson, ibid., 37, 2935 (1962).
(129) R. A. Lee, M.Sc. Thesis, University of London, 1959.
(130) Results of work by Dr. Choudary, kindly communicated by Dr. J. L. Holmes prior to publication.
(131) J. L. Holmes and A. Maccoll, $Proc.\ Chem.\ Soc.$, 175 (1957).
(132) J. L. Holmes and A. Maccoll, $J.\ Chem.\ Soc.$, 5919 (1963).
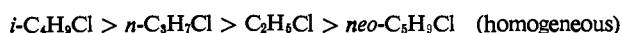(133) H. Teranishi and S. W. Benson, $J.\ Chem.\ Phys.$, 40, 2946 (1964).

(134) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," translated by M. Boudant, Princeton University Press, Princeton, N. J., 1959.
(135) J. S. Shapiro, E. S. Swinbourne, and B. C. Young, $Aust.\ J.\ Chem.$, 17, 1217 (1964).
(136) G. M. Schwab and A. J. Karatzas, $J.\ Phys.\ Colloid\ Chem.$, 52, 1053 (1948).
(137) G. M. Schwab and H. Noller, $Z.\ Elektrochem.$, 58, 762 (1954).
(138) H. Noller and K. Ostermeier, ibid., 60, 921 (1956).
(139) H. Noller and H. Wolff, $Z.\ Phys.\ Chem.$ (Frankfurt am Main), 13, 255 (1957).
(140) H. Noller and K. Ostermeier, $Z.\ Elektrochem.$, 63, 191 (1959).
(141) A. Maccoll and P. J. Thomas, $Nature$, 176, 392 (1955).

Table XII

The Decomposition of Chloroalkanes on a Titanium Carbide Surface

Chloroalkane	n-C$_3$H$_7$Cl	n-C$_4$H$_9$Cl	i-C$_3$H$_7$Cl	sec-C$_4$H$_9$Cl	t-C$_4$H$_9$Cl
Temp range, °C	410–440	...	280–310	230–250	150–180
E, kcal mole^{-1}	34	34	30	22	12

distance of about 2.6 Å. Campbell and Kemball,[142] on the other hand, have proposed in the case of the catalyses of ethyl chloride and ethyl bromide decompositions on an evaporated metal surface a dissociative adsorption. The metals studied were Pd, Pt, Ni, Fe, W, and Rh. Depending on the catalyst, rupture of either the carbon–halogen or carbon–hydrogen bond was assumed to occur.

Shapiro, et al.,[185] have favored a transition state like I for the reaction on clean glass surfaces, rather than the wall initiation suggested by the work of Kaprilova.[187] However, they do suggest a greater emphasis on the polarization of the carbon–chlorine bond. The value of the activation energy for the heterogeneous decomposition of ethyl chloride (24.1 kcal mole^{-1})[185] agrees excellently with the value of 24.5 kcal mole^{-1} reported by Schwab and Noller[187] for the same reaction on a silica surface. It is interesting to note the inversion of neopentyl chloride in the rate sequence of primary chlorides

$$i\text{-C}_4\text{H}_9\text{Cl} > n\text{-C}_3\text{H}_7\text{Cl} > \text{C}_2\text{H}_5\text{Cl} > neo\text{-C}_5\text{H}_9\text{Cl} \quad \text{(homogeneous)}$$

$$neo\text{-C}_5\text{H}_9\text{Cl} > i\text{-C}_4\text{H}_9\text{Cl} > n\text{-C}_3\text{H}_7\text{Cl} > \text{C}_2\text{H}_5\text{Cl} \quad \text{(heterogeneous)}$$

as between the homogeneous and heterogeneous mechanisms. In general, as these authors point out, the sensitivity to heterogeneous decomposition on a clean glass surface is greatest for tertiary halides; the secondary comes next and then finally the primary.

Holbrook and Rooney[143] have investigated the role of the surface in the pyrolysis of 2-chlorobutane. Interest was mainly focused upon the relative amounts of butene-1 and cis- and trans-butene-2. They conclude that both homogeneous and heterogeneous mechanisms occur in clean silica vessels.

Howlett[144] in his equilibrium studies on the system

$$t\text{-C}_4\text{H}_9\text{Cl} \rightleftharpoons i\text{-C}_4\text{H}_8 + \text{HCl}$$
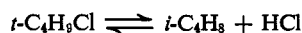
has shown that, in clean glass vessels packed with glass wool, equilibrium can be established at temperatures as low as 60°.
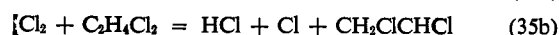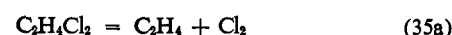
The pyrolysis of allyl chloride[145] is reported as having an appreciable heterogeneous component, even when the reaction is conducted over a heavily coated carbonaceous surface.

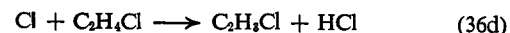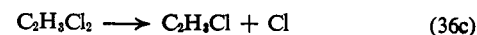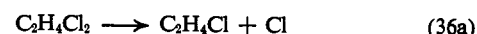## V. Radical Mechanisms in the Pyrolysis of Haloalkanes

A. CHLOROALKANES

The first chain mechanism reported in detail for the chloroalkanes was for the pyrolysis of 1,2-dichloroethane.[146] After an induction period, the length of which was dependent on the temperature, the reaction followed a first-order law and showed inhibition by small partial pressures of propene. The
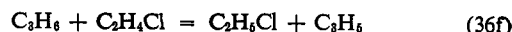
rate constant was expressed as $k_1 = 10^{10.81} \exp(-37,000/RT)$ sec^{-1}. The reaction was very sensitive to oxygen.[147] The authors proposed a chain scheme, leading to first-order kinetics, involving initiation by (35a) and (36b) and termination by (35c)

$$\text{C}_2\text{H}_4\text{Cl}_2 = \text{C}_2\text{H}_4 + \text{Cl}_2 \quad (35a)$$

$$[\text{Cl}_2 + \text{C}_2\text{H}_4\text{Cl}_2 = \text{HCl} + \text{Cl} + \text{CH}_2\text{ClCHCl} \quad (35b)$$

$$\text{Cl} + \text{CH}_2\text{ClCHCl} = \text{HCl} + \text{C}_2\text{H}_2\text{Cl}_2 \quad (35c)$$

Howlett[144] reinvestigated the reaction and proposed the scheme

$$\text{C}_2\text{H}_4\text{Cl}_2 \longrightarrow \text{C}_2\text{H}_4\text{Cl} + \text{Cl} \quad (36a)$$

$$\text{Cl} + \text{C}_2\text{H}_4\text{Cl}_2 \longrightarrow \text{C}_2\text{H}_3\text{Cl}_2 + \text{HCl} \quad (36b)$$

$$\text{C}_2\text{H}_3\text{Cl}_2 \longrightarrow \text{C}_2\text{H}_3\text{Cl} + \text{Cl} \quad (36c)$$

$$\text{Cl} + \text{C}_2\text{H}_4\text{Cl} \longrightarrow \text{C}_2\text{H}_3\text{Cl} + \text{HCl} \quad (36d)$$

This leads to the over-all rate constant $k = (k_a k_b k_c / k_d)^{1/2}$, and estimates were made of the elementary rate constants, which gave agreement with experiment. The inhibition produced by propylene

$$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_3\text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_3\text{H}_5 \quad (36e)$$

$$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_4\text{Cl} = \text{C}_2\text{H}_5\text{Cl} + \text{C}_3\text{H}_5 \quad (36f)$$

was explained in terms of (36e) and (36f) and led to the equation

$$\text{rate of decomposition} = \frac{k_a k_c}{k_e} \frac{[\text{C}_2\text{H}_4\text{Cl}_2]}{[\text{P}]} + \text{residual reaction} \quad (37)$$

which accurately represented the dependence of the rate on propylene pressure.

Barton and Onyon[82] and Howlett[148] laid down the general principles determining whether a chloroalkene would decompose homogeneously by the molecular or radical-chain mechanism. "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." They point out that, when ethyl chloride is attacked by a chlorine atom, the 1-chloroethyl radical (II) rather than the 2-chloroethyl radical (III) is produced. Similarly in 1,1-dichloroethane, IV is produced rather than V. This follows from the fact that

$$\overset{..}{\text{C}}\text{HClCH}_3 \quad \text{CH}_2\text{ClĊH}_2 \quad \dot{\text{C}}\text{Cl}_2\text{CH}_3 \quad \text{CHCl}_2\dot{\text{C}}\text{H}_2 \quad \dot{\text{C}}\text{HClCH}_2\text{Cl}$$

II   III   IV   V   VI

radical-chain chlorination of ethyl chloride and 1,1-dichloroethane gives predominantly 1,1-dichloroethane and 1,1,1-trichloroethane, respectively.[149] Radicals III, V, and VI can split off a chlorine atom to form a stable molecule; II and IV cannot without a hydrogen transfer. Thus ethyl chloride and 1,1-dichloroethane can act as their own inhibitors. On

(142) J. S. Campbell and K. Kemball, Trans. Faraday Soc., 57, 809 (1961).
(143) K. A. Holbrook and J. J. Rooney, J. Chem. Soc., 247 (1965).
(144) K. E. Howlett, ibid., 1409 (1951).
(145) A. M. Goodall and K. E. Howlett, ibid., 2596 (1954).
(146) D. H. R. Barton and K. E. Howlett, ibid., 155 (1949).

(147) D. H. R. Barton, ibid., 148 (1949); Nature, 157, 626 (1946).
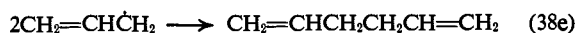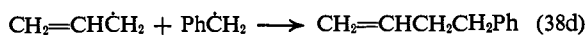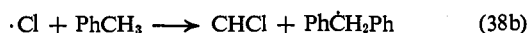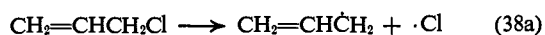(148) K. E. Howlett, Trans. Faraday Soc., 48, 25 (1952).
(149) W. E. Vaughan and F. F. Rust, J. Org. Chem., 5, 449 (1940).

the other hand, since propylene and the higher olefins are good inhibitors, 1- and 2-chloropropene and *t*-butyl chloride form products which are themselves inhibitors. Some predictions made on this basis are shown in Table XIII.[150–152] The agreement with the observed behavior is excellent.

Table XIII

Predicted Mode of Decomposition of Chloroalkanes[82]

Molecular	Unimolec- ular	Radical chain	Ref
C_2H_5Cl	X		60, 61
CH_3CHCl_2	X		88
CH_2ClCH_2Cl		X	146, 148
$CH_2ClCHCl_2$		X	150
CH_2ClCCl_3		X	151
$CHCl_2CHCl_2$		X	151
$CH_3CH_2CH_2Cl$	X		64
$CH_3CHClCH_3$	X		66
$CH_3CHClCH_2Cl$	X		60
$CH_3(CH_2)_2CH_2Cl$	X		66
$(CH_3)_3CCl$	X		82
$CH_2ClCH_2OCH_2CH_2Cl$		X	152
$C_6H_5CHClCH_3$	X		117
$C_6H_5CH_2CH_2Cl$		X	79

Shilov[153] has investigated the pyrolysis of allyl chloride in the temperature range 540–710° using toluene and benzene as carrier gases and also in the absence of a carrier. The decomposition followed first-order kinetics, but the rate coefficients were pressure dependent. In the presence of toluene k_1 is about half the value observed in the presence of benzene or with no carrier. Also [bibenzyl]/[HCl] ranges between 0.2 and 0.25. The gaseous products of reaction were 90% propylene and 10% allene. It is pointed out that the small amount of allene does not necessarily imply a molecular decomposition, since it could be formed by the decomposition of an allyl radical. The product ratio in the toluene experiments shows that reaction scheme 21, which predicts [bibenzyl]/[HCl] = 1, is inapplicable. Instead the author suggests reaction scheme 38 on the basis of which [bibenzyl]/[HCl] = 0.25 would be predicted. The author thus concludes that the reaction follows a radical nonchain mechanism and gives log
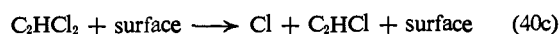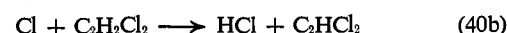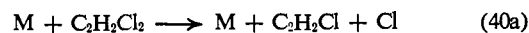
$$CH_2=CHCH_2Cl \longrightarrow CH_2=CH\dot{C}H_2 + \cdot Cl \qquad (38a)$$

$$\cdot Cl + PhCH_3 \longrightarrow CHCl + Ph\dot{C}H_2Ph \qquad (38b)$$

$$2Ph\dot{C}H_2 \longrightarrow PhCH_2CH_2Ph \qquad (38c)$$

$$CH_2=CH\dot{C}H_2 + Ph\dot{C}H_2 \longrightarrow CH_2=CHCH_2CH_2Ph \qquad (38d)$$

$$2CH_2=CH\dot{C}H_2 \longrightarrow CH_2=CHCH_2CH_2CH=CH_2 \qquad (38e)$$

$A = 13.17$ and $E = 59.3$ kcal mole⁻¹. This latter value would then be the homolytic bond dissociation energy of the carbon–chlorine bond, $D(CH_2=CHCH_2Cl)$. Goodall and Howlett[145] have also examined the decomposition in the temperature range 370–475° and report its decomposition to occur by simultaneous nonchain, chain, and heterogeneous processes to yield initially allene and hydrogen chloride. The allene rapidly polymerized in the temperature range studied. Porter

and Rust[154] have attempted to resolve the discrepancy between the two investigations by accurate product analyses.

The pyrolyses of some chloroethylenes have been reported by Goodall and Howlett.[155–157] Trichloroethylene decomposes by a mixed-chain and molecular mechanism,[155] in the temperature range 370–450°. The molecular component was reported as having $k_2 = 10^{12.08} \exp(-42,000/RT)$ sec⁻¹ mole⁻¹ l., the reaction being second order. For the chain component, bimolecular initiation was postulated

$$2CHClCCl_2 \longrightarrow Cl + C_2HCl_2 + C_2HCl_3 \qquad (39a)$$

$$2CHClCCl_2 \longrightarrow HCl + C_2HCl_2 + C_2Cl_3 \qquad (39b)$$
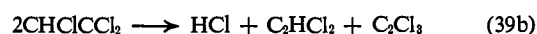
and the suggested scheme led to a kinetic equation in accord with observation. In the case of the 1,2-dichloroethylenes,[156,157] it is noted that the *cis–trans* conversion is very rapid in the temperature range studied (360–480°), and so the kinetics reported is for the equilibrium mixture. Again a molecular[156] and a radical-chain reaction[155] were observed. The former is considered to be a unimolecular reaction in the second-order region, and the activation energy varies from a limit of 52.7 kcal mole⁻¹, as infinite pressure is approached by extrapolation, to 42.5 kcal mole⁻¹ at 30 mm. The results are consistent with the theories of unimolecular reactions. In the chain mode of decomposition, the reaction varied from order 1.5 in a packed vessel to unity in an empty vessel. The reaction scheme suggested was

$$M + C_2H_2Cl_2 \longrightarrow M + C_2H_2Cl + Cl \qquad (40a)$$

$$Cl + C_2H_2Cl_2 \longrightarrow HCl + C_2HCl_2 \qquad (40b)$$

$$C_2HCl_2 + surface \longrightarrow Cl + C_2HCl + surface \qquad (40c)$$

$$M + C_2H_2Cl + Cl \longrightarrow M + C_2H_2Cl_2 \qquad (40d)$$

and this was able to account for the observed reaction order.

The pyrolysis of neopentyl chloride was reported by Swinbourne and Maccoll[68] to be a molecular elimination, involving a Wagner–Meerwein rearrangement leading to hydrogen chloride and methylpentenes. Anderson and Benson[158] suggested a possible chain mechanism. Shapiro and Swinbourne[68,159] reinvestigated the pyrolysis and reported a mixed unimolecular[68] and chain[159] mechanism. For the latter they report the Arrhenius equation log $k_{1.5} = 10^{13.55} \exp(-56,300/RT)$ l.¹/² mole⁻¹/² sec⁻¹, the reaction being of order 1.5. Of special interest was the observation of 1,1-dimethylcyclopropane in the products. A chain scheme was proposed, which involves first-order initiation, chlorine atoms as the main propagating species, and termination involving the combination of methyl and chloromethyl radicals.

Barton and Howlett[160] have discussed the use of acetaldehyde in the detection of chain reactions (*cf.* Roof and Daniels[7]). They show, in particular, that, whereas small amounts of acetaldehyde inhibit the decomposition of 1,2-dichloroethane, the decomposition of 1-chloroethane or 1,1-dichloroethane is unaffected by the presence of acetaldehyde. This behavior is, of course, consistent with the former reaction

(150) R. J. Williams, *J. Chem. Soc.*, 113 (1953).
(151) D. H. R. Barton and K. E. Howlett, *ibid.*, 2053 (1951).
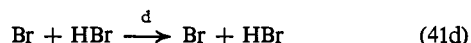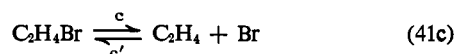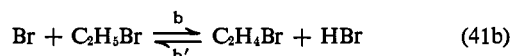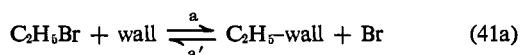(152) D. H. R. Barton, A. J. Head, and R. J. Williams, *ibid.*, 2039 (1951).
153) A. Shilov, *Dokl. Akad. Nauk SSSR*, 98, 601 (1954).

(154) L. M. Porter and F. F. Rust, *J. Amer. Chem. Soc.*, 78, 5571 (1956).
(155) A. M. Goodall and K. E. Howlett, *J. Chem. Soc.*, 2599 (1954).
(156) A. M. Goodall and K. E. Howlett, *ibid.*, 2640 (1956).
(157) A. M. Goodall and K. E. Howlett, *ibid.*, 3092 (1956).
(158) K. H. Anderson and S. W. Benson, *J. Chem. Phys.*, 39, 1673 (1963).
(159) J. S. Shapiro and E. S. Swinbourne, *Can. J. Chem.*, 46, 1351 (1968).
(160) D. H. R. Barton and K. E. Howlett, *Trans. Faraday Soc.*, 45, 735 (1949).

proceeding by a chain mechanism, the latter two by uni-molecular mechanisms.

The interpretation of induction periods in reactions proceeding by a chain route has been discussed by Barton and Howlett,[151] and Howlett has developed an approximate method for relating the induction period to the rate of buildup of the stationary route.[161] Goodall and Howlett[167] have also applied the method in the case of 1,2-dichloroethylene.

B. BROMOALKANES

Peri and Daniels[162] returned to the problem of the ethyl bromide pyrolysis in 1950, in a study of the exchange of radioactive Br_2, DBr, and radioactive HBr and DBr with ethyl bromide during the pyrolysis of the latter. They showed that there was no direct exchange of Br_2 with ethyl bromide. The Br of HBr exchanged in the temperature range 180–310° according to a kinetic law which is the first order in ethyl bromide and zero order in HBr. The activation energy was about 30 kcal mole^{-1}, but the rate depended on the surface of the reaction vessel. The deuterium of DBr exchanged in the temperature range 258–306° with all five hydrogen atoms of ethyl bromide. The reaction was first order in both ethyl bromide and deuterium bromide and the activation energy was about 40 kcal mole^{-1}. It was concluded that bromine exchange was a wall reaction, while deuterium exchange involved wall initiation and termination. The specific mechanism was
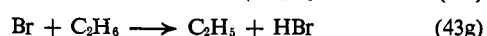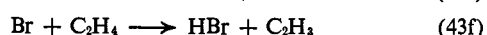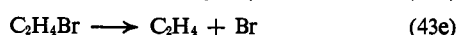
$$C_2H_5Br + wall \underset{a'}{\overset{a}{\rightleftharpoons}} C_2H_5\text{-wall} + Br \quad (41a)$$

$$Br + C_2H_5Br \underset{b'}{\overset{b}{\rightleftharpoons}} C_2H_4Br + HBr \quad (41b)$$

$$C_2H_4Br \underset{c'}{\overset{c}{\rightleftharpoons}} C_2H_4 + Br \quad (41c)$$

$$Br + HBr \overset{d}{\longrightarrow} Br + HBr \quad (41d)$$
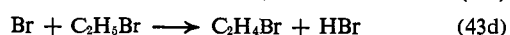
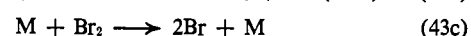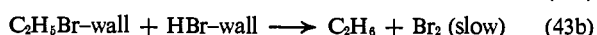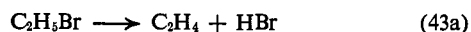from which it may be shown that the rate of deuterium exchange is given by

$$\frac{dc_D}{dt} = \frac{k_a k_b k_{b'}}{k_{a'} k_c} \left(\frac{c_{EtBr}}{c_{C_2H_5-wall}} \right) c_{C_2H_5Br} c_{DBr} \quad (42)$$

The term in the parentheses can be taken as constant and (42) then describes the observed kinetics. Bromination of the ethyl bromide, as was observed, was explained by the inclusion of the step 41(e).

$$Br_2 + C_2H_4Br \longrightarrow C_2H_4Br_2 + Br \quad (41e)$$

Goldberg and Daniels[163] as a result of further studies of the ethyl bromide system produced the following mechanism.

$$C_2H_5Br \longrightarrow C_2H_4 + HBr \quad (43a)$$

$$C_2H_5Br\text{-wall} + HBr\text{-wall} \longrightarrow C_2H_6 + Br_2 \text{ (slow)} \quad (43b)$$

$$M + Br_2 \longrightarrow 2Br + M \quad (43c)$$

$$Br + C_2H_5Br \longrightarrow C_2H_4Br + HBr \quad (43d)$$

$$C_2H_4Br \longrightarrow C_2H_4 + Br \quad (43e)$$

$$Br + C_2H_4 \longrightarrow HBr + C_2H_3 \quad (43f)$$

$$Br + C_2H_6 \longrightarrow C_2H_5 + HBr \quad (43g)$$

This led to the kinetic equation

$$-\frac{d}{dt}[C_2H_5Br] = k_a[C_2H_5Br] + k\frac{[HBr]}{[C_2H_4]}[C_2H_5Br] \quad (44)$$

Capon and Ross[164] have reported a reinvestigation of the ethyl bromide (and ethyl chloride) decompositions. By new experiments they confirmed the observation of Blades that the results of Goldberg and Daniels[163] were best explained on the basis of a kinetic equation of order 1.5. They also show that nitric oxide *increases* the rate of decomposition, contrary to the implication of Wojciechowski and Laidler[165] that nitric oxide has no effect on halide pyrolysis. When copyrolysis of ethyl chloride and ethyl bromide takes place, there is an interaction between the decompositions predominantly resulting in an increase in the rate of the ethyl chloride decomposition (sensitization). Hydrogen bromide and bromine both accelerate the decomposition of ethyl chloride and this is attributed to the initiation step (45) competing with

$$HBr + C_2H_5Cl + S \longrightarrow C_2H_6 + BrCl + S \quad (45a)$$

$$M + BrCl \longrightarrow Br + Cl + M \quad (45b)$$
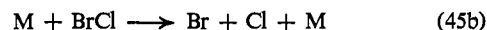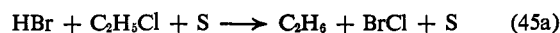
(35a) in the mechanism of Goldberg and Daniels.[163] Scheme 45 is based on the observation that the hydrogen bromide catalysis is surface dependent. Finally, the copyrolysis in the presence of cyclohexene proceeded at a rate which was simply the sum of the rates of unimolecular decomposition of ethyl chloride and ethyl bromide. It was concluded that while ethyl chloride decomposes by molecular elimination, ethyl bromide decomposes mainly by a chain mechanism, the maximally inhibited rate in the presence of inhibitors being that of molecular elimination.
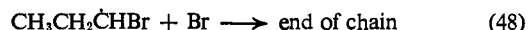
Semenov, *et al.*,[110] have reported that the decomposition of *n*-propyl bromide follows a kinetic law of order 1.5 and that the rate constant was expressible as $k_{1.5} = 10^{9.58} \exp(-42,000/RT)$ mm^{-1} sec^{-1}. In discussing these results Semenov[134] proposes a scheme which enables a stopping radical (CH_3-$CH_2\dot{C}HBr;S$) to be converted into a propagating radical ($\dot{C}H_2\dot{C}HCH_2Br;P$)[165a]

$$CH_3CH_2\dot{C}HBr + C_3H_7Br \longrightarrow CH_3\dot{C}HCH_2Br + C_3H_7Br \quad (46)$$
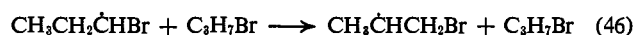
a similar step being proposed by Agius and Maccoll who reported $k_{1.5} = 10^{10.86} \exp(-33,800/RT)$ mole$^{-1/2}$ cc$^{1/2}$ sec^{-1}).[166] However, Semenov proposes

$$2CH_3CH_2\dot{C}HBr \longrightarrow \text{end of chain} \quad (47)$$

whereas Agius and Maccoll favor

$$CH_3CH_2\dot{C}HBr + Br \longrightarrow \text{end of chain} \quad (48)$$

Both chain-ending reactions lead to the observed kinetic law, if reactions 46 and 47 or 48 are introduced into the scheme corresponding to (4). Cross and Stimson[167] have recently studied the pyrolysis of *n*-propyl bromide and reported the reaction to be second order, with the rate constants given by $k_2 = 10^{18.1} \exp(-49,300/RT)$ sec^{-1} cc. mole^{-1}. Catalysis of the decomposition by both bromine and hydrogen bromide was observed. The mechanism suggested was

(161) K. E. Howlett, *Trans. Faraday Soc.*, 48, 35 (1952).
(162) J. B. Peri and F. Daniels, *J. Amer. Chem. Soc.*, 72, 424 (1950).
(163) A. E. Goldberg and F. Daniels, *ibid.*, 79, 1314 (1957).

(164) N. Capon and R. A. Ross, *Trans. Faraday Soc.*, 62, 1560 (1966).
(165) B. W. Wojciechowski and K. J. Laidler, *ibid.*, 59, 369 (1963).
(165a) S = stopping and P = propagating in the nomenclature of Agius and Maccoll.[166]
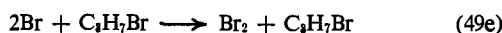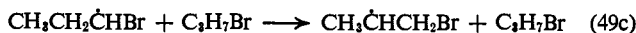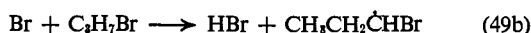(166) P. J. Agius and A. Maccoll, *J. Chem. Soc.*, 973 (1955).
(167) J. T. D. Cross and V. R. Stimson, *Aust. J. Chem.*, 21, 973 (1968).

$$HBr + C_3H_7Br \longrightarrow 2Br + \cdot C_3H_7 \qquad (49a)$$

$$Br + C_3H_7Br \longrightarrow HBr + CH_3CH_2\dot{C}HBr \qquad (49b)$$

$$CH_3CH_2\dot{C}HBr + C_3H_7Br \longrightarrow CH_3\dot{C}HCH_2Br + C_3H_7Br \qquad (49c)$$

$$CH_3\dot{C}HCH_2Br \longrightarrow C_3H_6 + Br \qquad (49d)$$

$$2Br + C_3H_7Br \longrightarrow Br_2 + C_3H_7Br \qquad (49e)$$

Such a scheme as (49) gives the correct kinetic equation, namely

$$-\frac{d}{dt}[C_3H_7Br] = k_1[C_3H_7Br] + k_2[C_3H_7Br]^2 \qquad (50)$$
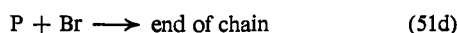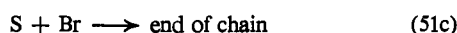
the first term representing the molecular decomposition of the substrate. As with ethyl bromide, the over-all reaction would thus appear to be stimulated by the molecular reaction. For the bromine catalysis, the initiation step (49a) is replaced by

$$Br_2 + C_3H_7Br \longrightarrow 2Br + C_3H_7Br \qquad (49f)$$
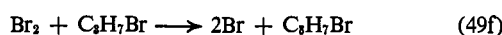
Scheme 49 also accounts for the catalysis by hydrogen bromide.

Green, Maccoll, and Thomas[109] have pointed out that since the probability of production of an S radical increases in the n-bromoalkanes as the length of the alkyl chain increases, the chain component of the over-all reaction should decrease. This is found to be so for the series n-propyl to n-hexyl bromides.

Wojciechowski and Laidler[165] discussed the mechanism of decomposition of a number of alkyl bromides. They assume surface initiation (51a,b) termination (49c,d)

$$RBr + surface \longrightarrow R + surface-Br \qquad (51a)$$

$$surface-Br \longrightarrow surface + Br \qquad (51b)$$

$$S + Br \longrightarrow end\ of\ chain \qquad (51c)$$

$$P + Br \longrightarrow end\ of\ chain \qquad (51d)$$

where S and P denote stopping and propagating radicals (L and T in their nomenclature). They further assume that the odd electron is most likely to be on the terminal carbon atom. By such a scheme they predicted that n- and isobutyl bromides should decompose according to a law of order 1.5, whereas sec-butyl and t-butyl bromides would follow a first-order law. No evidence exists for the former prediction, and the mechanism for the latter two reactions is widely accepted as being molecular. To test the prediction of Wojciechowski and Laidler, Capon, $et\ al.$,[115] have investigated the pyrolysis of 3-bromopentane, for which would be predicted a chain decomposition of order 1.5. The reaction was unimolecular, the Arrhenius parameters being comparable to those for other secondary bromide pyrolyses (Table IX).

C. IODOALKANES

Considerable clarification of the role of radical processes in the pyrolysis of organic iodides has been achieved by Benson and his school.[168] Early work (section I) had shown that alkyl iodides react rapidly with hydrogen iodide in the temperature range 240–300° while from 300 to 400° they pyrolyze according to

$$2RI \longrightarrow Ol + RH + I_2 \qquad (52)$$

where Ol represents an olefin of the same carbon number as R, with a small contribution from

$$RI \longrightarrow Ol + HI \qquad (53)$$

In distinction to the behavior of the alkyl iodides, unsaturated or conjugated iodides[169] appear to follow the simpler stoichiometry
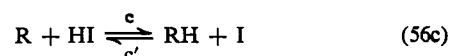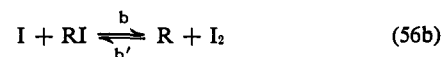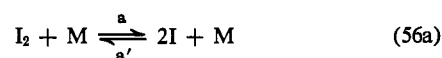
$$RI \longrightarrow R_2 + I_2 \qquad (54)$$
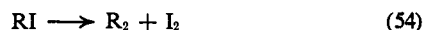
Iodine is also produced in the pyrolysis of ethylene iodide.[10,170] Benson, $et\ al.$, have approached the pyrolysis both directly[128,133] and through a study of the reverse reaction (addition of hydrogen iodide to olefins) and a knowledge of the equilibrium constant.[128,171]

Because of its importance in the mechanisms of pyrolysis of alkyl iodides, the kinetics of the reaction of hydrogen iodide with alkyl iodides will first be discussed. The early work of Ogg (section I) has been reinterpreted by Benson and O'Neal[172] and by Sullivan.[173] The over-all reaction is

$$RI + HI \longrightarrow RH + I_2 \qquad (55)$$
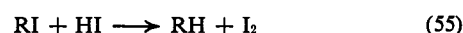
The former authors propose the scheme

$$I_2 + M \underset{a'}{\overset{a}{\rightleftharpoons}} 2I + M \qquad (56a)$$

$$I + RI \underset{b'}{\overset{b}{\rightleftharpoons}} R + I_2 \qquad (56b)$$

$$R + HI \underset{c'}{\overset{c}{\rightleftharpoons}} RH + I \qquad (56c)$$

which leads to the kinetic equation

$$\frac{d}{dt}[I_2] = \frac{k_b k_c K[RI][HI][I_2]^{1/2}}{k_{b'}[I_2] + k_c[HI]} \qquad (57)$$

where $K = [I]^2/[I_2]$. Equation 57 was used in conjunction with certain estimated values to compute the Arrhenius parameters of some of the elementary reactions in scheme 56. Sullivan, on the other hand, suggests initiation by

$$RI \longrightarrow R + I \qquad (56d)$$

and includes the further step

$$R + RI \longrightarrow R'I + RH \qquad (56e)$$

and on the basis of this scheme is able to derive the Arrhenius parameters of reaction 56b.

Flowers and Benson[174] have reinvestigated the reaction of methyl iodide with hydrogen iodide and have shown that it follows the rate law of eq 57. Further they show that the inclusion of steps 56d and e is unnecessary. They are able to measure k_b and also $k_c/k_{b'}$. By use of thermodynamic data, they are able to estimate the Arrhenius parameters for k_b, $k_{b'}$, and $k_{c'}$ (Table XIV). Hartley and Benson,[175] O'Neal and Benson,[176] and Golden, Rodgers, and Benson[177] have examined the corresponding reactions in the case of ethyl iodide, acetyl iodide, and allyl iodide, respectively. The parameters of the elementary reactions are also shown in Table XIV. Also shown in the table are the values for n-propyl iodide,[172] as determined by Benson and O'Neal from the

(168) S. W. Benson, $J.\ Chem.\ Phys.$, 38, 1945 (1963).

(169) A. Shaw, M.Sc. Thesis, University of Manchester, 1948.
(170) S. W. Benson and A. Amaro, $J.\ Chem.\ Phys.$, 36, 3464 (1962).
(171) A. N. Bose and S. W. Benson, $ibid.$, 37, 1081 (1962).
(172) S. W. Benson and E. O'Neal, $ibid.$, 34, 514 (1961).
(173) J. H. Sullivan, $J.\ Phys.\ Chem.$, 65, 722 (1961).
(174) M. C. Flowers and S. W. Benson, $J.\ Chem.\ Phys.$, 38, 882 (1963).
(175) D. B. Hartley and S. W. Benson, $ibid.$, 39, 132 (1963).
(176) H. E. O'Neal and S. W. Benson, $ibid.$, 37, 540 (1962).
(177) D. M. Golden, A. S. Rodgers, and S. W. Benson, $J.\ Amer.\ Chem.\ Soc.$, 88, 3196 (1966).

Table XIV

**Arrhenius Parameters[a] for Elementary Reactions
of Alkyl Iodides as Shown in Eq 56**

Parameter	CH_3I	C_2H_5I	n-C_3H_7I	C_3H_6I	CH_3COI
E_b	20.0	17.1	18.5	6.8	14.6
Log A_b	12.20	11.01	(11.30)	10.3	10.9
$E_{b'}$	0.4	0.2	...	0.0	0.0
Log $A_{b'}$	9.90	9.50	...	9.2	9.60
E_c	1.2	1.1	...	1.5	1.5
Log $A_{c'}$	9.40	8.92	8.64	8.7	9.13
$E_{c'}$	37.5	24.9	...	18.0	15.7
Log $A_{c'}$	11.60	11.22	11.21	10.3	10.3

[a] Units of E are kcal mole^{-1}; of A, l. mole^{-1} sec^{-1}.

work of Ogg. These studies convincingly show that, if hydrogen iodide is produced in iodide pyrolysis, it will rapidly react with the substrate to yield iodine and an alkane.

In his general discussion of the pyrolysis of alkyl iodides, Benson[168] suggests that the rate-determining step in the pyrolysis of alkyl iodides is always the formation of hydrogen iodide

$$I + RI \longrightarrow Ol + HI + I \qquad (58)$$
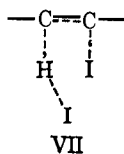
$$RI \longrightarrow Ol + HI \qquad (59)$$
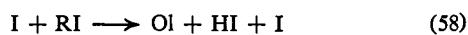
by either (58) or (59). In the case of (58), the rate law is

$$-\frac{d}{dt}[RI] = k_{1.6}[RI][I_2]^{1/2} \qquad (60)$$

whereas in the case of (59), the equation
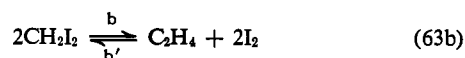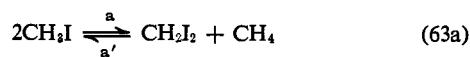
$$-\frac{d}{dt}[RI] = k_1[RI] \qquad (61)$$

is satisfied. Reaction 58 is of great interest, since the catalysis is postulated to proceed *via* the transition state VII.

$$
\begin{array}{c}
-C \!=\! C- \\
\quad | \quad\ | \\
\quad H \quad I \\
\quad\ \ \backslash \\
\quad\quad I \\
\text{VII}
\end{array}
$$

The fact that n-propyl iodide[12] decomposes according to (60) whereas isopropyl iodide[13, 131-133] follows (61) can be attributed to the fact that for the former, the iodine atom attack is on a secondary hydrogen atom, whereas for the latter it would be on a primary hydrogen atom. In the case of sec-butyl iodide,[11] iodine atom attack can take place fruitfully at a secondary hydrogen atom and so the rate law is a combination of (60) and (61), namely (62). Benson[168] also

$$-\frac{d}{dt}[sec\text{-}C_4H_9I] = k_1[C_4H_9] + k_{1.6}[sec\text{-}C_4H_9I][I_2]^{1/2} \qquad (62)$$

predicts that the course of the pyrolysis of methyl iodide

$$2CH_3I \underset{a'}{\overset{a}{\rightleftharpoons}} CH_2I_2 + CH_4 \qquad (63a)$$

$$2CH_2I_2 \underset{b'}{\overset{b}{\rightleftharpoons}} C_2H_4 + 2I_2 \qquad (63b)$$

and estimates the half-lives of the two processes.

In an investigation of the pyrolysis of ethyl iodide, Benson and Bose[128] show that the results are consistent with the rate-determining step being the unimolecular elimination of hydro-

gen iodide. However, they do not exclude the possibility that up to 20% of the over-all reaction might arise from radical disproportionation (64) following the cleavage of the

$$I + C_2H_5 \underset{b}{\overset{a}{\rightleftharpoons}} C_2H_4 + HI \qquad (64)$$
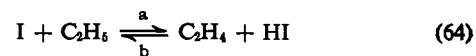
carbon and iodine bond. In a study of isopropyl iodide, Teranishi and Benson[133] show that the decomposition follows (56) and the mechanism is molecular, although up to 8% of an autocatalytic reaction might have been present.

The final approach to the problem of pyrolysis of alkyl iodides is through the study of the reverse reaction. This has been applied by Teranishi and Benson[133] to ethylene, by Bose and Benson to propylene[178] and isobutylene,[179] and by Nangia and Benson to butene-2.[180] In addition Nangia and Benson[181] have studied the kinetics of the dehydrogenation of propane and have derived parameters for Ol + HI → RI. The Arrhenius parameters are shown in Table XV.

Table XV

The Arrhenius Parameters for Ol + HI → RI

Olefin	C_2H_4[133]	C_3H_6[178,181]		2-C_4H_8[179]	i-C_4H_8[180]
E, kcal mole^{-1}	28.9	23.4	23.7	21.1[a]	18.0
Log A/l. mole^{-1} sec^{-1}	8.52	7.89	7.5	6.26	6.50

[a] This reaction has a molecular component.

In the case of butene-2 an iodine-catalyzed radical process is concurrent with molecular addition. The slow step in the former process is the reverse of (53). In all cases the over-all reaction is

$$2HI + RI \longrightarrow RH + I_2 \qquad (65)$$
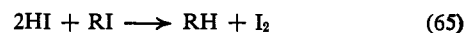
which is considered to be the result of the reverse of (53) followed by (55), except as mentioned in the case of the reaction of hydrogen iodide with butene-2.

The role of radical processes in the pyrolysis of alkyl iodides is thus very well documented.

VI. The Transition State in Molecular Gas-Phase Eliminations

A. THE DEVELOPMENT OF THE CONCEPT OF GAS-PHASE HETEROLYSIS

Prior to 1955 it was generally accepted that the unimolecular decomposition of alkyl halides proceeded through a four-centered transition state (VIII). In 1953, Green, *et al.*,[182]

$$
\begin{array}{c}
\diagdown \qquad \diagup \\
C \!=\! C \\
\diagup \ | \quad | \ \diagdown \\
H \!-\!-\!-\! X \\
\text{VIII}
\end{array}
$$
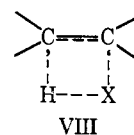
(178) A. N. Bose and S. W. Benson, *J. Chem. Phys.*, 37, 1081 (1962).
(179) A. N. Bose and S. W. Benson, *ibid.*, 38, 878 (1963).
(180) P. S. Nangia and S. W. Benson, *ibid.*, 41, 530 (1964).
(181) P. S. Nangia and S. W. Benson, *J. Amer. Chem. Soc.*, 86, 2773 (1964).
(182) J. H. S. Green, G. D. Harden, A. Maccoll, and P. J. Thomas, *J. Chem. Phys.*, 21, 178 (1953).

pointed out that for a series of alkyl bromides (i) $A \simeq 10^{13}$ sec^{-1} and (ii) in the decompositions of primary, secondary, and tertiary bromides, the activation energies were of the order of 50, 46, and 42 kcal mole^{-1}, respectively. The authors concluded that there was a clear correlation between the activation energy for elimination and the carbon–bromine bond strength. This was apparent from the fact that changing the carbon–bromine bond from primary to tertiary had a large effect on the rate, whereas changing the carbon–hydrogen bond from primary to tertiary had only a relatively small effect.

Thomas and the author[183] in 1955 modified this view, showing that, while little correlation existed between the activation energy for elimination and the homolytic bond dissociation energies $D(R–X)$, that is, the energy of the process

$$R–X \longrightarrow R\cdot + X\cdot$$
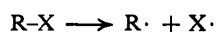
there was a clear correlation with the heterolytic bond dissociation energies $D(R^+X^-)$, that is, the energy of the process

$$R–X \longrightarrow R^+ + X\overset{..}{:}^-$$

It was pointed out that a possible explanation was that activation consisted primarily of an elongation, with polarization $(C^{\delta+}–X^{\delta-})$ of the carbon–halogen bond, with some assistance from a polarized $(C^{\delta-}–H^{\delta+})$ carbon–hydrogen bond. Evidence for only a slight participation of the latter came from the study by Thomas[33] of 4-bromopentene-1 which pyrolyzes at about the same rate as sec-butyl bromide despite the allylic weakening (homolytic) of the β-carbon–hydrogen bond.

From a consideration of the effects of α methylation and of α and β halogenation, the authors concluded that there was an analogy between gas-phase elimination and the solvolytic reactions of the corresponding substrates by the unimolecular mechanism (SN1 or E1) in polar solvents.[184] This was confirmed by the pyrolysis of 2-chloromethyl ethyl ether, which decomposes in a temperature range some 50° lower than the corresponding range for t-butyl chloride. Since the role of the polar solvent is to stabilize the highly polar transition state in solvolysis, it was suggested that in the gas phase the β-hydrogen atoms play somewhat the same role as that played by the solvent, in stabilizing the transition state. This was represented by

IX   or   X
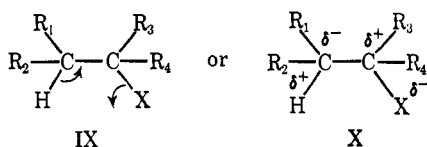
and the process could be represented energetically as shown in Figure 6. Curve a represents the potential energy for dissociation into R$^+$ and X$^-$ from an excited electronic state of R–X and curve b that for the dissociation into atoms from the ground state. Curve c represents the hypothetical stabilization of the R$^+$X$^-$ system by the β-hydrogen atom, eventually leading to the formation of an olefin and HX. As a result of the intersection of curves b and c, a splitting will occur leading to curve d which represents the reaction path. It was concluded "that important modification is needed in the current view that all gas reactions are in principle homolytic and accordingly require concepts of mechanism and structural effects
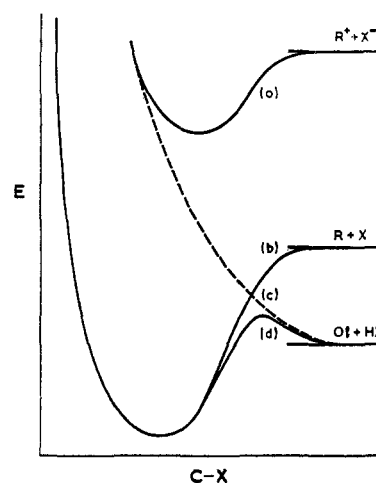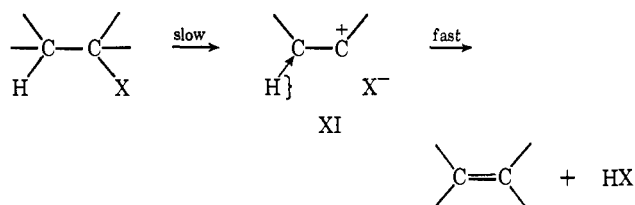

Figure 6. The reaction path in gas-phase elimination.

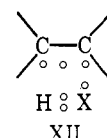which are strongly differentiated from those applying to heterolytic reactions in polar solvents."

The author further pursued the analogy between gas-phase elimination and unimolecular solvolyses in polar solvents at the Kekulé Symposium in 1958,[185] and the term quasi-heterolytic was coined to describe such gas-phase reactions. Ingold,[186] in reviewing the course of polar reactions in nonpolar media, favored "a rate controlling step involving halogen heterolysis but no hydrogen loosening of any kind." Gasphase elimination of hydrogen halides was represented as

which is essentially the same mechanism as for the E1 reaction in polar solvents. It was also shown that such an ionpair transition state could not be ruled out on energetic grounds.

The transition state in gas-phase elimination was further[187] discussed in 1962, and it was shown that for the α-methylated series of halides a linear relationship existed between the activation energy of elimination and the heterolytic bond dissociation energy. The behavior of carbonium ions in the gas phase (as observed in the mass spectrometer), in highly polar ion pairs (as observed in solvolysis), and in the ion pairs proposed for the transition state in gas-phase elimination was compared.

Benson and Bose[188] have suggested a semiion pair transition state for gas-phase elimination represented by

XII

(183) A. Maccoll and P. J. Thomas, Nature, 176, 392 (1955).
(184) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1963.

(185) A. Maccoll in "Theoretical Organic Chemistry," Butterworth & Co. (Publishers), Ltd., London, 1958.
(186) C. K. Ingold, Proc. Chem. Soc., 279 (1957).
(187) A. Maccoll in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962.
(188) S. W. Benson and A. N. Bose, J. Chem. Phys., 39, 3463 (1963).

On the basis of this model they were able to calculate activation energies in good agreement with experiment. Subsequently Benson and Haugen[189, 190] extended the treatment to other systems, and O'Neal and Benson[191] have shown how the model can also be used to predict the A factors.

B. THE ANALOGY WITH HETEROLYSIS IN POLAR SOLVENTS

The rate sequences shown below follow from the rate constant data in Tables V–X (an asterisk signifies chloroalkanes only).

(1) $(CH_3)_3CX \gg (CH_3)_2CHX \gg CH_3CH_2X$ $X = Cl, Br, I$
(2) $(CH_3)_3CCR_1R_2X > (CH_3)_2CHCR_1R_2X >$
      $CH_3CH_2CH_1CR_1R_2X > CH_3CR_1R_2X$ $X = Cl, Br$
(3) $CH_3CX_3^* > CH_3CHX_2 > CH_2CH_2X > CH_2XCH_2X$
                                           $X = Cl, Br$
(4) $CH_3CHClCH=CH_2 \simeq CH_3CHClCH_2CH_3$
      $CH_3CHBrCH_2CH=CH_2 \simeq CH_3CHBrCH_2CH_3$
(5) $(CH_3)_2CHX < C_6H_5CHXCH_3 < (CH_3)_3CX$ $X = Cl, Br$
(6) $p\text{-}CH_3\text{-}C_6H_4CHClCH_3 > p\text{-}F\text{-}MeC_6H_4CHClCH_3 >$
      $C_6H_5CHClCH_3 > p\text{-}Cl\text{-}C_6H_4CHClCH_3 >$
      $p\text{-}Br\text{-}C_6H_4CHClCH_3 > p\text{-}CN\text{-}C_6H_4CHClCH_3$
(7) $ROCHClCH_3 \ggg CH_2ClCH_3$ $R = CH_3, C_2H_5$
(8) $C_nH_{2n+1-x}D_xX < C_nH_{2n+1}X$
(9) $RCHClCOCH_3 < RCHClCH_3^{192}$ $R = CH_3, C_2H_5$
      $CH_3CHClCH_2COCH_3 > CH_3CHClCH_2CH_3^{192}$
(10) $c\text{-}C_5H_9X > c\text{-}C_6H_{11}X > CH_3CHXCH_2CH_3$ $X = Cl, Br$
(11) $RI > RBr > RCl$

In addition to sequences 1–11, Wagner–Meerwein rearrangements (12) have been observed in the gas phase[68, 75, 76] and gas-phase racemization[74] and isomerization[87] (13) investigated. Sequences 1–3 (except CH_2XCH_2X) and 5–6 (p-Me and p-F) show the effects of electron-releasing groups, while sequences 3 (CH_2XCH_2X), 6 (p-Cl, p-Br, p-CN), and 9 show the effects of electron-withdrawing groups. The former augment the rate of reaction and the latter diminish it, as is expected from the theory of solvolytic reactions in polar solvents.[184] In comparing the rate constant ratios for the gas phase and for solution, it must be remembered that the temperature range for the gas-phase studies is some 200–300° higher than that for the solution studies. This means that if, as appears reasonable from the data, the effect of substituents is largely on the activation energy, then the effect will be smaller the higher the temperature. A frequency distribution of log A values is shown in Figure 7 (data from Tables V, IX, and X). For a difference of activation energy of 5 kcal mole⁻¹, the rate constant ratios at a series of temperatures are shown below.

Temp, °C	0	100	200	300	400	500
k_A/k_B	10^4	850	200	80	40	25

Another difficulty lies in the choice of solvent with which to make the comparison. Winstein, et al.,[193] have discussed solvent effects in terms of competition between internal electron supply to the reaction center and solvent participation, that is, electron supply by the solvent. The less the latter occurs the more nearly limiting is the solvolysis in character. Thus it would appear that, if gas-phase eliminations are essentially polar in character, then this limiting behavior should be observed in the gas phase, where only internal electron supply
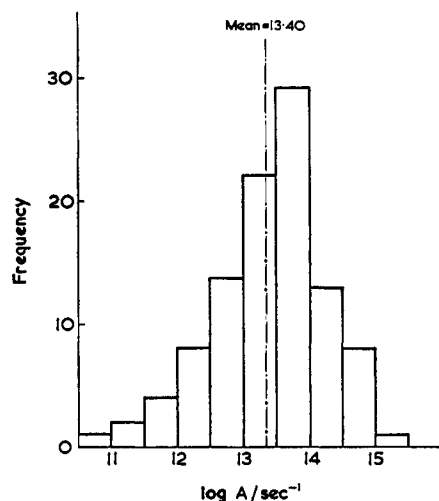

Figure 7. The distribution of log A values, taken from Tables V, IX and X.

is available. Further it would be expected that the analogy with solution reactions would be most pronounced in the case of solvents of high ionizing power and low nucleophilicity. The rate constant sequences 1–11, Wagner–Meerwein rearrangements (12), and gas-phase racemization and isomerization (13) will now be discussed in the light of the behavior of the corresponding substrates in polar solvents.

1. α-Methyl Substitution

Using the average Arrhenius parameters from Tables V, IX, and X, the rate constant ratios shown in Table XVI can be calculated at temperatures for which the isopropyl compound has a rate constant of 10^{-4} sec⁻¹.

Table XVI

Arrhenius Parameters and Rate Constant Ratios
for the α-Methylated Series

X		C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$
Cl	E, kcal mole⁻¹	57.8	50.8	45.0
	Log A/sec⁻¹	13.75	13.52	13.73
	Rate constant ratio (360°)	1	150	25,000
Br	E, kcal mole⁻¹	53.0	47.5	41.3
	Log A/sec⁻¹	13.11	13.32	13.51
	Rate constant ratio (325°)	1	160	46,000
I	E, kcal mole⁻¹	50.5	45.5	37.6
	Log A/sec⁻¹	13.76	13.81	13.26
	Rate constant ratio (285°)	1	102	35,400

Other series, e.g., n-propyl, sec-butyl, and t-amyl chlorides and bromides, may be examined in the same way, and the conclusion that α-methyl substitution has a large effect on the rate is further substantiated. To take another example, α,α-dimethylallyl chloride[87] decomposes at 300°, 110 times faster than α-methylallyl chloride.[86]

Hughes, et al.,[194] have investigated the solvolysis of SN2 blocked systems in 80% aqueous ethanol and estimate activa-

(189) S. W. Benson and G. R. Haugen, J. Amer. Chem. Soc., 87, 4036 (1965).
(190) S. W. Benson and G. R. Haugen, J. Phys. Chem., 70, 3336 (1966).
(191) H. E. O'Neal and S. W. Benson, ibid., 71, 2903 (1967).
(192) M. Dakubu, Ph.D. Thesis, University of London, 1965.
(193) S. Winstein, E. Grunwald, and H. W. Jones, J. Amer. Chem. Soc., 73, 2700 (1951).
(194) E. D. Hughes, C. K. Ingold, R. L. Martin, and O. F. Meigh, Nature, 166, 679 (1950).

tion energies for the primary, secondary, and tertiary compounds of 30.0, 26.7, and 23.3 kcal mole^{-1}. The ratios of the gas-phase activation energy to the solution activation energy in the case of the chlorides, bromides, and iodides are 1.93, 1.90, 1.96; 1.77, 1.78, 1.78; and 1.69, 1.70 and 1.64 for the primary, secondary, and tertiary compounds, respectively. This is a striking illustration of the almost quantitative nature of the proposed analogy. In the case of solvolysis of p-toluenesulfonates in formic acid, Winstein, et al.,[193] have shown that α-methyl substitution increases the rate by a factor of about 10^4, which is regarded as near-limiting behavior. If the gas-phase activation energies are used to calculate rate constant ratios at 25°, the rate increase for α-methyl groups comes out as $\sim10^4$. Again, the analogy would seem to be near quantitative.

2. β-Methyl Substitution

Averaged Arrhenius parameters and rate constant ratios for the primary β-methylated series at the temperature for which the rate constant for the ethyl compound is 10^{-4} sec^{-1} are shown in Table XVII. Values for n-propyl and isobutyl iodides are not available. Similar values are obtained for the secondary β-methylated series. A further example is the pair of compounds α-methylallyl chloride and α,β-dimethylallyl chloride, examined by Thomas.[86] In this case β-methylation augments the rate by 2.9 at 285°.

Table XVII

Arrhenius Parameters and Rate Constant Ratios for the Primary β-Methylated Series

X		C_2H_5	n-C_3H_7	i-C_4H_9
Cl	E, kcal mole^{-1}	57.8	55.1	56.1
	Log A/sec^{-1}	13.75	13.48	13.94
	Rate constant ratio (440°)	1	3.6	4.7
Br	E, kcal mole^{-1}	53.0	51.1	50.4
	Log A/sec^{-1}	13.11	13.03	13.05
	Rate constant ratio (400°)	1	3.4	7.3

The series of tertiary β-methylated chlorides studied by Wong[88] is of interest, since the three β-hydrogen atoms of t-butyl chloride have been progressively replaced. The Arrhenius parameters and relative rates are shown in Table XVIII.

Table XVIII

Arrhenius Parameters and Rate Constant Ratios for the Tertiary β-Methylated Series of Chlorides[88]

Chloride	E, kcal mole^{-1}	Log A/sec^{-1}	Rate const ratio (280°)
CH$_3$C(CH$_3$)$_2$Cl	45.0 (45.0)	13.77 (13.73)	1
CH$_3$CH$_2$C(CH$_3$)$_2$Cl	44.2 (45.1)	13.82 (14.24)	2.3
(CH$_3$)$_2$CHC(CH$_3$)$_2$Cl	42.3	13.38	4.7
(CH$_3$)$_3$CC(CH$_3$)$_2$Cl	41.9	13.80	18.0

It was thought better in calculating rate ratios to use the single set of results obtained by one worker than the average values (shown in parentheses) for t-butyl and t-amyl compounds.

An interesting conclusion to be drawn from these rate constant ratios is that β-methyl substitution is a second-order effect on the carbon–halogen bond rather than a first-order effect on the carbon–chlorine bond. This follows from the fact that, through the series shown in Table XVIII, the carbon–hydrogen bond changes from primary to secondary to tertiary and then back to primary, while the rate constant increases uniformly down the series.

Hughes, et al.,[194] have commented upon the relative insensitivity of the SN1 mechanism to β-methyl substitution. Winstein and Marshall[195] have investigated the solvolysis of the series of p-bromobenzenesulfonates corresponding to the chlorides listed in Table XVIII, in formic acid at 25°. The rate constant ratios found were 1:2.5:14.4:14.4, a series which bears a strong resemblance to that in Table XVIII. Here again the analogy is nearly quantitative.

3. α- and β-Halo Substitution

The most complete series illustrating the effects of α- and β-halo substitutions is for $C_2H_{6-x}X_x$. The results for the chlorides and bromides of this series are set out in Table XIX (data from Tables V and IX).
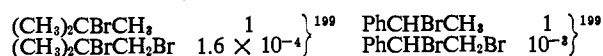
Table XIX

The Rate Constant Ratios for α- and β-Halo Substitution

CH_3CX_3	CH_3CHX_2	CH_3CHX	CH_2XCH_2X
		C=Cl (437°)	
32	8.2	1	0.55
		C=Br (416°)	
..	9.6	1	0.25

Another series (data from Table V) is CH$_3$CCl$_2$CH$_3$, CH$_3$CHClCH$_3$, and CH$_3$CHClCH$_2$Cl for which the rate constant ratios at 360° are 6:1:0.07. Again for CH$_3$CH$_2$CHCl$_2$ and CH$_3$CH$_2$CH$_2$Cl the ratio (440°) is 3.0:1 while for CH$_3$CH$_2$-CCl$_2$CH$_3$ and CH$_3$CH$_2$CHClCH$_3$ it is 3.6:1 (360°). The effect of α-halo substitution in augmenting the rate constant and of β-halo substitution in diminishing it is clearly seen. The data from the chemical activation experiments with fluoroalkanes lend general support to these observations, as reported in section III.A).

The corresponding effects in solvolysis are well documented. Thus Hine and Lee[196] have examined the series PhCH$_2$X, PhCHX$_2$, and PhCX$_3$ and found rate constant ratios 1:10:500 (X = Cl) and 1:2:200 (X = Br), illustrating the augmenting effect of α-halo substitution. The diminishing effect of β-halo substitution is shown by the following three pairs of compounds in solvent 80% ethanol (78°), 80% ethanol (25°), and ethanol

$$\begin{array}{ll} \text{(CH}_3\text{)}_2\text{CClCH}_3 & 1 \\ \text{(CH}_3\text{)}_2\text{CClCH}_2\text{Cl} & 2.5 \times 10^{-4} \end{array} \Big\}^{197,198}$$

$$\begin{array}{ll} \text{(CH}_3\text{)}_2\text{CBrCH}_3 & 1 \\ \text{(CH}_3\text{)}_2\text{CBrCH}_2\text{Br} & 1.6 \times 10^{-4} \end{array} \Big\}^{199} \quad \begin{array}{ll} \text{PhCHBrCH}_3 & 1 \\ \text{PhCHBrCH}_2\text{Br} & 10^{-3} \end{array} \Big\}^{199}$$

(195) S. W. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

(196) J. Hine and D. E. Lee, *ibid.*, **73**, 22 (1951).

(197) E. D. Hughes, *J. Chem. Soc.*, 255 (1935).

(198) H. C. Brown, M. S. Kharasch, and T. H. Choo, *J. Amer. Chem. Soc.*, **62**, 3435 (1940).
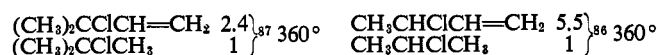
(199) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

at 55°, respectively. This behavior is interpreted as being due to mesomeric release overcoming inductive withdrawal in the case of α-halo substitution and inductive withdrawal in the case of β-halo substitution, of electrons at the α-carbon–chlorine bond which is undergoing reaction as shown in XIII and XIV.
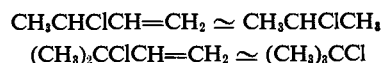
XIII   XIV
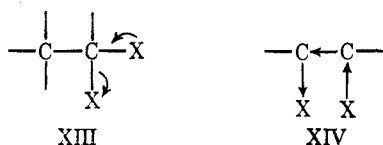
4. α- and β-Vinyl Substitution

The effect of α-vinyl substitution is seen by a comparison of the following pairs of substances

$$(CH_3)_2CClCH=CH_2 \quad 2.4 \atop (CH_3)_2CClCH_3 \quad 1 \Big\}_{87} 360° \qquad CH_3CHClCH=CH_2 \quad 5.5 \atop CH_3CHClCH_3 \quad 1 \Big\}_{86} 360°$$

In solvolysis, Vernon[200] has shown that

$$CH_3CHClCH=CH_2 \simeq CH_3CHClCH_3$$
$$(CH_3)_2CClCH=CH_2 \simeq (CH_3)_3CCl$$

Once again, the analogy is substantiated; in both the gas phase and in solution, the α-vinyl group is a little more effective than a methyl group in augmenting the rate.

β-Vinyl substitution has been investigated by Thomas[83] in the bromide series, namely for $CH_3CHBrCH_2CH=CH_2$ and $CH_2CHBrCH_2CH_3$. The observed rate constant ratio was 1.05:1 at 380°. In this case also, vinyl substitution has roughly the same effect as methyl substitution. However, an important conclusion from this study was that neither the allylic weakening of the β-carbon–hydrogen bond nor the incipient conjugation in the product olefin appeared to augment the role. This argued strongly against a homolytic transition state.

5. α- and β-Phenyl Substitution

The rate constant ratios shown in Table XX can be calculated

Table XX

Rate Constant Ratios for α- and β-Phenyl Substitution

CH_3-CHXCH_3	PhCHX-CH_3	$(CH_3)_2$-CXCH_3	CH_3CH_2-CH_2X	PhCH_2-CH_2X
X = Cl (α Series, 280°; β Series, 425°)				
1	28	113	1	1.8
X = Br (α Series, 280°; β Series, 385°)				
1	366	675	1	0.7

from the Arrhenius parameters shown in Tables V and IX. In the α-phenyl series, the effect of the phenyl group lies between that of one and two methyl groups. In the β-phenyl series, the β-phenyl group is about as effective as a methyl group in enhancing the rate of pyrolysis. In solvolysis, Hughes, et al.,[201] have shown that in dry ethanol, α-phenyl bromide undergoes an SN1 reaction 1.4 times as fast as does t-butyl
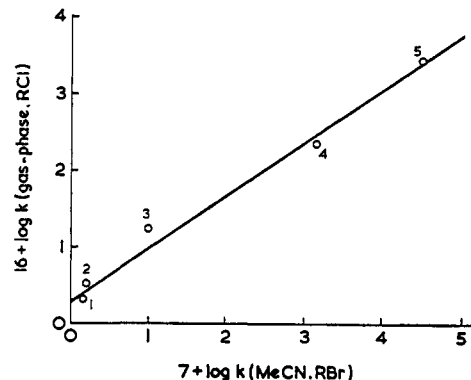

Figure 8. The logarithm of the rate of gas-phase elimination from chlorides as a function of the logarithm of the rate of unimolecular elimination from bromides in acetonitrile:[94] (1) sec-butyl, (2) cyclohexyl, (3) cyclopentyl, (4) α-phenylethyl, (5) t-butyl. Reproduced by permission of the Editor of the Journal of the American Chemical Society.

bromide. Again, Winstein and Fainberg[202] have shown that in 50% ethanol at 55°, the rate constant ratios are 1.2 and 2.4 in the cases of the chlorides and bromides, respectively. Thus an α-phenyl group is approximately equal to two methyl groups in augmenting the solvolysis rates. Winstein, et al.,[203] have studied ethyl and β-phenyl p-toluenesulfonates at 75° in formic acid; the β-phenyl compound reacts about twice as fast as the ethyl under those conditions. Comparing methyl and ethyl p-toluenesulfonates[198] it is found that the β-methyl group approximately doubles the rate of solvolysis. Thus in the β position, the phenyl group is about as effective as a methyl group in augmenting the rate.

Herndon, et al.,[38] have pointed out that α-phenyl ethyl chloride solvolyzes at about the same rate as t-butyl bromide in 80% aqueous ethanol, whereas in the gas phase t-butyl chloride pyrolyzes appreciably faster. Hoffmann and the author[94] have suggested that, since in 80% ethanol solvolysis of α-phenyl ethyl chloride possess a bimolcular as well as the predominantly unimolecular component, comparison is best made with a result obtained in a less nucleophilic solvent such as acetonitrile. Thus a plot of the logarithm of the rate constants for gas-phase elimination of a series of organic chlorides against the logarithm of the rate constant of the corresponding substrates undergoing unimolecular elimination in acetonitrile is linear (Figure 8). This would support the analogy in the case of a solvent with limiting behavior.[198]

6. The Effect of Substituents Remote from the Reaction Site

A subtle variation of a substrate can be effected by substitution in the phenyl ring in α-phenyl ethyl chloride. This technique has been exploited by Smith, et al.,[204,205] in the case of acetates. A study of substituted α-phenyl ethyl chlorides has been made by Bridge, et al.[79] The Arrhenius parameters, rate constant ratios (relative to X = H), and the constants of Brown and Okamoto[206] are shown in Table XXI. Although

(200) C. A. Vernon, J. Chem. Soc., 423 (1954).
(201) E. D. Hughes, C. K. Ingold, S. Masterman, and B. J. McNulty, ibid., 899 (1940).

(202) A. H. Fainberg and S. Winstein, J. Amer. Chem. Soc., 78, 2770 (1956); 79, 1597, 1602 (1957).
(203) S. Winstein, C. R. Lindegren, H. Marshall, and C. L. Ingraham, ibid., 75, 147 (1953).
(204) G. G. Smith, F. D. Bagley, and R. Taylor, ibid., 83, 3647 (1961).
(205) R. Taylor, G. G. Smith, and W. H. Wetzel, ibid., 84, 4817 (1962).
(206) H. C. Brown and Y. Okamoto, ibid., 80, 4979 (1958).

Table XXI

The Effect of X on the Pyrolyses of X-C₆H₄CHClCH₃

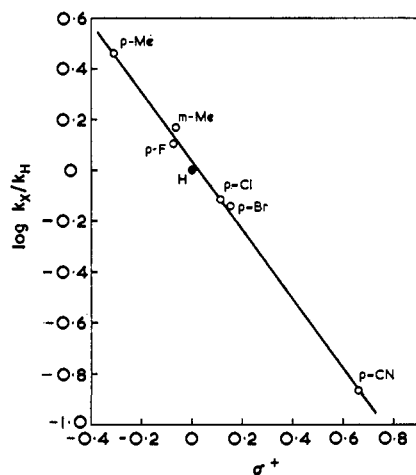| X	p-CH₃	p-F	m-CH₃	H	p-Cl	p-Br	p-CN
E, kcal mole^{-1}	14.10	12.99	12.00	12.60	12.24	12.23	12.54
Log A/sec^{-1}	47.7	45.6	42.7	44.8	44.1	44.2	47.0
k_X/k_H (335°)	2.89	1.27	1.46	1.00	0.77	0.72	0.14
σ^+	−0.311	−0.073	−0.066	0	+0.114	+0.150	+0.659

Figure 9. The Hammett–Brown–Okamoto plot (log k_X/k_H) against σ^+ for a series of substituted α-phenylethyl chlorides.[79]

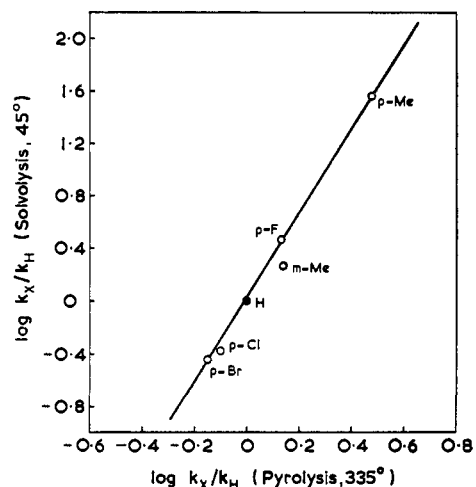**Figure 10.** A comparison of log k_X/k_H (solvolysis) and log k_X/k_H for a series of substituted α-phenylethyl chlorides.[79]

there appear to be random trends in the Arrhenius parameters, it is readily apparent that electron-releasing substituents (as measured by σ^+ values) augment the rate, whereas electron-withdrawing substituents diminish it. In fact, a linear relation exists between log (k_X/k_H) and σ^+ (Figure 9). Mechelynck-David and Fierens[207] and Yukawa, *et al.*,[208] in greater detail, have studied the solvolysis of certain of the compounds shown in Table XXI. A plot of the logarithm of the gas-phase rate constant against the logarithm of the solvolytic rate constant is shown in Figure 10. Here the analogy between gas-phase elimination and solvolysis in polar solvents is near quantitative. The value of ρ obtained from Hammett–Brown–Okamoto plot (Figure 9) is −1.36 (335°), indicating a moderate degree of polar character in the transition state. The value found for solvolysis is −4.95 (45°). It is not at all clear how to correct values determined at one temperature in order to compare them with values determined at another. Intuitively it might be reasonable to use a relationship such as $\rho_{T_2}/\rho_{T_1} = T_1/T_2$. If this is the case, ρ(gas phase) should be multiplied by $\simeq$1.9 to give $\rho = -2.6$ which is to be compared with $\rho = -4.95$ from the solvolysis studies.

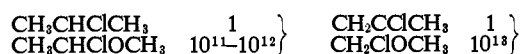### 7. The Effect of α-Methoxy Substitution

The most striking substitution so far studied is that of replacing an α-hydrogen atom by an alkoxy group. This was first done by Thomas[80] in the case of α-methoxyethyl chloride and later by Failes and Stimson[81] in the case of the α-ethoxy

compound. The Arrhenius parameters and rate constant ratios are shown in Table XXII. Also included in Table XXII

Table XXII

Substitution by Alkoxy Groups

Compound	Ethyl chloride	t-Butyl chloride	α-Methoxy-ethyl chloride	α-Ethoxy-ethyl chloride
E, kcal mole^{-1}	57.8	45.0	33.3	30.3
Log A/sec^{-1}	13.75	13.73	11.46	10.52
k/k_H (200°)	1	10^6	10^9	3 × 10^9
k/k_H (solvolysis)	1	10^7	10^{14}	3 × 10^{14}

are the rate constant ratios for solvolysis.[209] It should be noted that the large decrease in activation energy (25, 27 kcal mole^{-1}) is slightly compensated for by a decrease in the log A term. The effect of the α-methoxy group in solvolysis has been estimated by Ingold.[186] The values for two pairs of compounds are

$$\begin{array}{ll} CH_3CHClCH_3 & 1 \\ CH_3CHClOCH_3 & 10^{11}\text{--}10^{12} \end{array}\Big\} \qquad \begin{array}{ll} CH_2CClCH_3 & 1 \\ CH_2ClOCH_3 & 10^{13} \end{array}\Big\}$$

the ratio of the rate constants being given for 0°. This substitution shows the fantastic augmentation of the rate of pyrolysis brought about by one of the most strongly electron-releasing classes of substituents.

(207) C. Mechelynck-David and P. J. C. Fierens, *Tetrahedron*, 6, 232 (1959).

(208) Y. Yukawa, M. Sawada, and Y. Tsumo, *Bull. Chem. Soc. Japan*, 39, 2274 (1966).

(209) P. Bellinger, P. B. de la Mare, G. Kohnstam, and P. M. Presst, *J. Chem. Soc.*, 3641 (1955).

8. The Effect of Deuteration on the Rate of Elimination

Good,[121] by investigating a series of partially deuterated isopropyl bromides, was able to estimate the rate of pyrolysis of isopropyl-d_6 bromide as compared with isopropyl bromide. The observed ratio was $1:2.5$, and this did not seem to be greatly temperature dependent; that is, the effect of deuterium substitution was largely on the A factor. The most exhaustive study has been made by Blades, et al., who have reported the pyrolysis of chloroethane-1,1,2,2-d_4,[100] bromoethane-d_6,[123] and bromoethane-1,1,2,2-d_4.[124] The results are shown in Table XXIII. The rate constant ratios are 2.3 (440°), 2.4 (400°), and 2.8 (440°), respectively, the effect being largely on the activation energy. DePuy and King[210] have interpreted the results of the deuteration studies as implying a nearly broken β-carbon–hydrogen bond in the transition state. This would argue in favor of models IX or XII for the transition state.

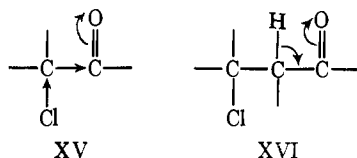### Table XXIII

The Effect of Deuteration on the Rate of Elimination

Compound	Log A_D/sec^{-1}	E_D, kcal mole^{-1}	Log (A_D/A_H)	$E_D - E_H$, kcal mole^{-1}
C_2D_5Br	13.32	54.8	...	...
C_2H_5Br	13.11	53.0	0.21	1.8
CHD_2CD_2Cl	...	...	−0.06	0.99
CHD_2CD_2Br	...	...	0.30	2.3

Shiner[211] has investigated the solvolysis of a series of deuterated t-amyl chlorides, containing two, six, and eight deuterium atoms per molecule, in 80% ethanol at 25°. The octadeuterio compound decomposed at a rate 0.4 times that of the hydrogen compound, the major effect being on the activation energy. A similar effect[212] was observed for 2,3-dimethyl-2-chlorobutane-3-d. Lewis and Boozer[213] have examined 2-pentyl bromide with deuterium atoms in the 1 or 3 positions. Once again a reduction in rate of solvolysis of the deuterium compound as compared with the hydrogen analog was observed.

9. The Effects of α- and β-Carbonyl Groups

Dakubu[192] has examined the compounds in Table XXIV. A carbonyl group α to the carbon–halogen bond diminishes the rate constant; in the β position it augments it. This is to be expected on the general theory of substituted effects,[184] for in the α position the effect will in the main be inductive withdrawal of electrons from the carbon–chlorine bond, whereas in the β position it can render the β-hydrogen atom more

XV   XVI

Table XXIV

The Arrhenius Parameters for Some Carboxylated Chloroalkanes

Compound	E, kcal mole^{-1}	Log A/sec^{-1}	Rate const ratio (390°)
$CH_3CHClCH_3$[a]	50.8	13.52	1
$CH_3CHClCOCH_3$	49.1	11.74	0.064
$CH_3CHClCH_2CH_3$	50.3	13.90	2.8
$CH_3CH_2CHClCOCH_3$	50.8	12.80	0.11

[a] Values from Table V.

acidic thus facilitating heterolysis. It is worthy of note in passing that, in the ester series, Emovon and the author have shown that a β-carbonyl group has a very large effect on the rate, increasing it by a factor of about 100, compared with the nonsubstituted compound.[214] This would suggest a much greater degree of β-hydrogen participation in the transition state for ester pyrolysis.

10. Cycloalkyl Halides

The Arrhenius parameters for cycloalkyl halide pyrolyses and for the corresponding sec-butyl compounds are shown in Table XXV (values from Tables V and IX). In both series the

Table XXV

The Arrhenius Parameters for Cycloalkyl Halide Pyrolyses

Compound	E, kcal mole^{-1}	Log A	Rate const ratio	
$CH_3CHClCH_2CH_3$	50.3	13.90	1	
c-C_5H_9Cl	48.3	13.47	1.8	360°
c-$C_6H_{11}Cl$	50.1	13.83	1	
$CH_3CHBrCH_2CH_3$	46.0	13.29	1	
c-C_5H_9Br	43.7	12.84	2.5	325°
c-$C_6H_{11}Br$	46.1	13.52	1.9	

Arrhenius parameters for the cyclohexyl compound are close to those of the corresponding sec-butyl compound, whereas for the cyclopentyl compounds there has been a small but significant drop in activation energy compared to that for the sec-butyl compounds. The rate sequence cyclopentyl > cyclohexyl > sec-butyl is well known from solvolytic studies of the SN1 mechanism.[215, 216] The analogy with the SN1 and E1 mechanisms of solvolysis in polar solvents is thus further substantiated.

11. The Effect of the Halogen on the Rate of Pyrolysis

The Arrhenius parameters in Table XVI may be used to calculate the rate constant ratios k_{Br}/k_{Cl} and k_I/k_{Cl}. The results of such a calculation are shown in Table XXVI. The sequence

(210) C. H. DePuy and R. W. King, Chem. Rev., 60, 431 (1960).
(211) V. J. Shiner, J. Amer. Chem. Soc., 75, 2925 (1953).
(212) V. J. Shiner, ibid., 76, 1603 (1954).
(213) E. S. Lewis and C. E. Boozer, ibid., 76, 791 (1954).

(214) E. U. Emovon and A. Maccoll, J. Chem. Soc., 227 (1964).
(215) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, J. Amer. Chem. Soc., 73, 212 (1951); J. D. Roberts and V. C. Chambers, ibid., 73, 5034 (1951).
(216) S. Winstein, B. K. Morse, H. W. Jones, J. Corse, D. Trefon, and H. Marshall, ibid., 74, 1127 (1952); P. B. de la Mare in "Progress in Stereochemistry," Vol. 1, W. Klyne, Ed., Butterworth & Co. (Publishers), Ltd., London, 1954, p 105.

Table XXVI

**Rate Constant Ratios for Varying Halogens (325°)**

Series	RCl	RBr	RI
Primary	1	13	475
Secondary	1	12	168
Tertiary	1 (1)	14 (44)	171 (106)

$k_{RI} > k_{RBr} > k_{RCl}$ is just that observed in unimolecular solvolysis,[184] the values observed for t-butyl chloride, bromide, and iodide being shown in parentheses in Table XXVI.

12. Wagner–Meerwein Rearrangements

Neopentyl chloride contains no β-carbon–hydrogen bond. If it is to eliminate by the unimolecular mechanism to form the isomeric methylbutenes, then a 1,2 methyl shift must occur. This was in fact observed.[68] However, later work[68] showed that about 40% of the total observed reactions leading to 2-methylbutene-1 and, to a lesser extent, 2-methylbutene-2 was unimolecular, there being a concurrent chain mechanism operating.[159]

Bornyl (XVII) and isobornyl chlorides (XVIII) have been shown[75,76] to yield camphene, tricyclene, and bornylene (which rapidly undergoes a retro-Diels–Alder process yielding trimethylcyclopentadiene). The rate enhancement, isobornyl: bornyl = 20:1 at 400°, is small compared with that observed in solvolysis ($\simeq 10^5$ at 25°), indicating that neighboring group assistance is energetically less favored in the gas phase than in solution.[184,217] Herndon, et al.,[88] reported that exobornyl chloride decomposes at 300°, slightly slower than does sec-butyl chloride. Here again, neighboring group assistance appears somewhat unfavorable.

(66)
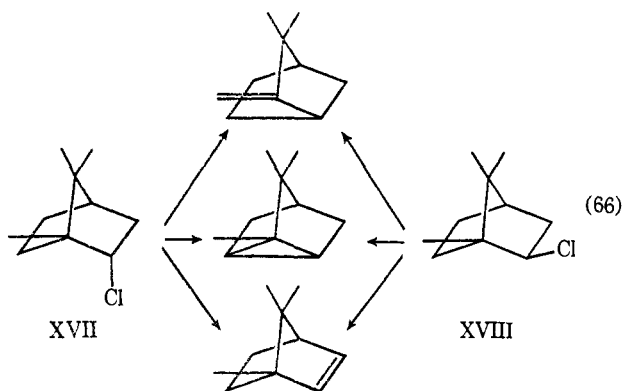
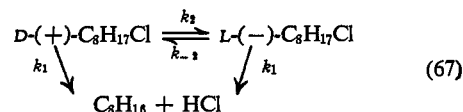### 13. Gas-Phase Racemization and Isomerism

A study was made of D-(+)-2-chlorooctane[94] with the object of ascertaining whether or not racemization occurred at a rate greater than that of elimination. Ingold[184] unmistakably demonstrated the role of dissociated carbonium ions in reactions proceeding by the unimolecular mechanism in polar solvents. In later work, Winstein and his school[218] elaborated

the scheme by introducing the idea of ion-pair return from the two discrete varieties of ion pairs: the contact (or intimate) ion pair R^+X^- and the solvent-separated ion pair $R^+ \| X^-$. The necessity for such a distinction arose from the fact that for many systems the polarimetric rate constant of a substrate was greater than the rate constant for substitution.

For the reaction scheme

$$D\text{-}(+)\text{-}C_8H_{17}Cl \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} L\text{-}(-)\text{-}C_8H_{17}Cl$$

with k_1 branches to $C_8H_{16} + HCl$ (67)

it can be shown that $\alpha_t/\alpha_0 = \exp[-(k_1 + 2k_2)t]$ where α_t and α_0 are the rotations at time t and time zero, respectively.[74] Similarly k_1 may be obtained from $k_1 = t^{-1} \ln p_0/(2p_0 - P_t)$, where p_0 and P_t are the initial pressure and the pressure at time t. Values of k_1 and $(k_1 + 2k_2)$ are compared in Table XXVII. It was not considered that the difference between the

Table XXVII

Comparison of Rate Constants from Pressure and Optical Rotation Data

Temp, °C	No. of runs	$10^4 (k_1 + k_2)$, sec^{-1}	No. of runs	$10^4 k_1$, sec^{-1}
358.2	5	4.60	40	4.49
338.5	5	1.39	11	1.32
326.5	3	0.61	8	0.60

values in columns 3 and 5 was significant. Thus it was concluded that $k_2 \ll k_1$. This view was substantiated by measuring the optical purity of the unreacted chloride. Values are shown in Table XXVIII, where f is the fraction of substrate consumed
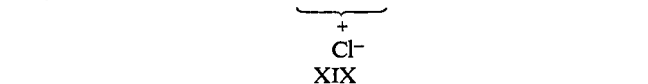
Table XXVIII

The Optical Purity of the Substrate

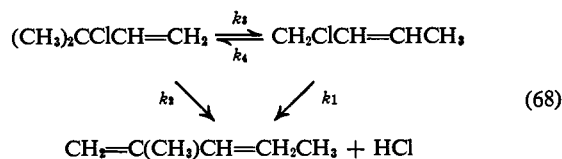| Time, sec	$(1 - f)$	α_t/α_0	$\alpha_t/\alpha_0(1 - f)$
1800	0.788	0.760	0.97
3600	0.622	0.605	0.97
5400	0.491	0.480	0.97
7200	0.387	0.395	1.02

at time t and $\alpha_t/\alpha_0(1 - f)$ is the optical purity of the substrate. Within experimental error, $k_2 = 0$. This supports the view that the transition state is best represented by an elongation of the carbon–halogen bond, with polarization. For racemization to occur, further separation would be necessary without the virtual halide ion selecting the hydrogen atom with which it is to eliminate, and this is apparently energetically unfavorable.

In solvolysis by the unimolecular mechanism in polar solvents, allylic systems are well known to rearrange via the mesomeric carbonium ion XIX.[219] In studying the pyrolyses of α,α- and γ,γ-dimethylallyl chlorides, Harding[87] found the reac-

$$CH_3CHClCH=CH_2 \rightleftharpoons CH_3CHCHCH_2 \rightleftharpoons CH_3CH=CH_2CH_2Cl$$

$$+$$
$$Cl^-$$
$$XIX$$

(217) P. Beltrame, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964); F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, 168, 65 (1951); S. Winstein, *J. Amer. Chem. Soc.*, 74, 1127 (1952).

(218) See S. Winstein, B. Appel, R. Baker, and A. Diaz in "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965.

(219) E. D. Hughes, *Trans. Faraday Soc.*, 37, 603 (1941); A. G. Catchpole and E. D. Hughes, *J. Chem. Soc.*, 4 (1948).

tion could be represented by

$$(CH_3)_2CClCH=CH_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} CH_2ClCH=CHCH_3$$

<div style="text-align:center">k_2 k_1 (68)</div>

$$CH_2=C(CH_3)CH=CH_2CH_3 + HCl$$

The rate constants satisfied the relationship $k_1 \simeq k_2 \gg k_3 \simeq k_4$. The Arrhenius equations for the isomerization rate constants were $\alpha\alpha \rightarrow \gamma\gamma$, $k_3 = 10^{8.68}\exp(-34,000/RT)$, and $\gamma\gamma \rightarrow \alpha\alpha$, $k_4 = 10^{11.08}\exp(-39,450/RT)$ sec^{-1}. The frequency factors, especially for reaction 3, were rather low. It is suggested that a 1,3 chlorine atom shift occurs, giving rise to the following mechanism

<div style="text-align:center">(69)</div>
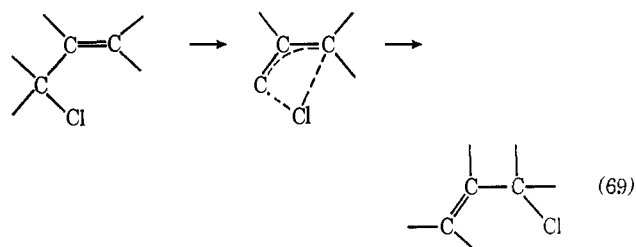
Comparison of these results with corresponding ones for the α- and γ-methyl compounds[220] shows that α or γ substitution has little effect on the rate of isomerization. Thus for the monomethyl series $10^4 k_3$ and $10^4 k_4 = 0.8$ and 0.5 sec^{-1}, respectively. In the dimethyl series the corresponding values are 1.5 and 3.2 sec^{-1}, respectively. The isomerism thus appears to proceed through an essentially homolytic transition state.

In the light of the evidence discussed above (see sections 1–13), it would appear that, while the analogy between gas phase elimination and unimolecular solvolysis in polar solvents is generally true, there are areas of discrepancy. These are in the main rather subtle areas, depending on the behavior of essentially free carbonium ions.

C. THE ION-PAIR THEORY

When a chemical bond breaks, it may do so either homolytically to yield a pair of radicals or heterolytically to yield a pair of ions.

$$R-X \longrightarrow R\cdot + X\cdot \qquad (70a)$$

$$R-X \longrightarrow R^+ + X^- \qquad (70b)$$
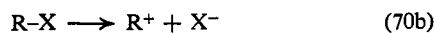
The energy of (70a) is the homolytic bond dissociation energy, $D(R-X)$; the energy of (70b) is the heterolytic bond dissociation energy, $D(R^+X^-)$. Both these quantities may be obtained from studies of the energetics of ionization using mass spectrometric techniques. Thus if $A(R^+)$ is the appearance potential of R^+, $I(R\cdot)$ is the ionization potential of the radical $R\cdot$, and $E(X)$ is the electron affinity of X, then (except when ion-pair production is observed in which case $A(R^+) = D(R^+X^-)$)

$$D(R - X) = A(R^+) - I(R\cdot) \qquad (71a)$$

and

$$D(R^+X^-) = A(R^+) - E(X) \qquad (71b)$$

Alternative methods are available for determining $D(R-X)$. Use can also be made of the relationship

$$D(R^+X^-) = D(R-X) + I(R\cdot) - E(X) \qquad (71c)$$

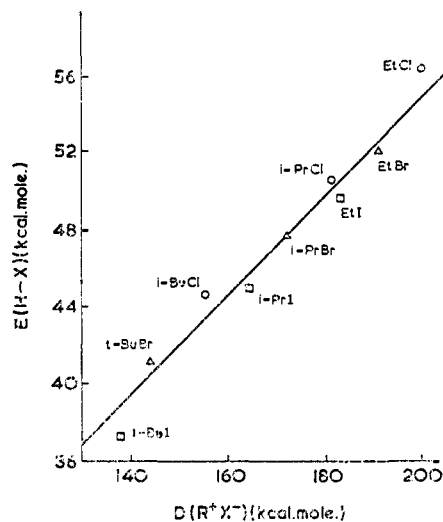(220) P. G. Rodgers, Ph.D. Thesis, University of London, 1966.

Figure 11. The activation energies for elimination plotted against the heterolytic bond dissociation energy. Reproduced by permission from "Studies on Chemical Structure and Reactivity," J. H. Ridd, Ed., Methuen and Co. Ltd., London, 1966.

Values of the homolytic and heterolytic bond dissociation energies have been published by Szabo and Berces[221] and by Benson and Bose.[188] The values are shown in Table XXIX,

Table XXIX

Homolytic and Heterolytic Bond Dissociation Energies

| | R | | |
X	C_2H_5	i-C_3H_7	t-C_4H_9
Cl	79, *200*	77, *181*	75, *155*
Br	65, *191*	63, *172*	61, *144*
I	52, *183*	50, *164*	48, *138*

the values in italics being the heterolytic bond dissociation energies. It is seen that α-methyl substitution has only a small effect on the homolytic bond dissociation energies but a large effect on the heterolytic bond dissociation energies. Similarly, changing the halogen has a large effect on the former, but only a small effect on the latter. The greater stabilization of the carbonium ion as compared with the radical by methyl substitution suffices to explain the first of these observations.

A plot of the activation energy for gas-phase elimination against heterolytic bond dissociation energies is shown in Figure 11. A reasonable straight line is observed. In fact, the activation energies, $E(HX)$, can be calculated from the simple relationship

$$E(HX) = 0.29D(R^+X^-) \qquad (72)$$

to within about 1 kcal mole^{-1}. The limitation of this method lies in the lack of experimental values for the heterolytic bond dissociation energies. However, it does provide a simple one-parameter equation for estimating the effect of α-methyl substitution in the alkyl halides. In justification of the ion-pair theory, the author showed[185] that such a transition state could

(221) S. G. Szabo and T. Berces, *Acta Chim. Acad. Sci. Hung.*, 22, 461 (1960).

not be excluded on purely energetic grounds. The activation energy can be estimated by use of

$$E(\text{HX}) = D(\text{R}^+\text{X}^-) - \frac{e^2}{r_t} \tag{73}$$

where r_t is the carbon–halogen distance in the transition state. Thus for ethyl bromide, $D(\text{Et}^+\text{Br}^-) = 184\,\text{kcal mole}^{-1}$, and, assuming $r_t = 2.5$ Å, the coulombic energy is $\simeq 130$ kcal mole^{-1} and so the activation energy is 54 kcal mole^{-1} to be compared with the experimental value of 53 kcal mole^{-1}. The value of r_t was arrived at by subtracting 0.2 Å from the covalent radius of carbon and adding the resultant value to the ionic radius of bromine. This probably overemphasized the orbital contraction of carbon, as has been pointed out by Benson and Bose,[188] who suggested that a critical extension of 3.4 Å would be more realistic.[221a] On this basis the coulombic energy would be 97 kcal mole^{-1}, making the activation energy 95 kcal mole^{-1}, greatly in excess of the observed value. This observation led Benson and Bose to suggest the semiion-pair model discussed in the next section. It had previously been pointed out[185] that the difference between the description of the transition state as an extension with polarization of the carbon–bromine bond and an intimate ion pair was largely verbal.

D. THE SEMIION-PAIR THEORY

Benson and Bose[188] suggested that (74) gives a better representation of the energy of the intimate ion pair than (73), where

$$E_c = \frac{-e^2}{r_t}\left(1 + \frac{\alpha_\pm}{r_t^3}\right) + \frac{B}{r_t^6} \tag{74}$$

$\alpha_\pm = \frac{1}{2}(\alpha_+ + \alpha_-)$, namely the mean polarizability of the ion pair, and B/r_t^9 represents the repulsive energy. E_c has a minimum with respect to r_t and

$$E_o(\text{min}) = -\frac{e^2}{9(r_t)_{\text{min}}}\left(8 + 5\frac{\alpha_\pm}{(r_t)^3{}_{\text{min}}}\right) \tag{75}$$

The authors note that $\alpha_\pm/(r_t^3)_{\text{min}}$ is always close to 0.13 and hence

$$E_c(\text{min}) \simeq -0.96e^2/(r_t)_{\text{min}} \tag{76}$$

Use of (76) gives the enthalpies of the ion-pair formation shown in Table XXX. The values in parentheses are obtained

Table XXX

The Enthalpy of Formation of Intimate Ion Pairs

R	Cl	Br	I
Et	101 (83)	94 (82)	80 (65)
i-Pr	82 (64)	79 (63)	71 (54)
t-Bu	56 (38)	51 (35)	50 (35)

by assuming a 15% contraction in the carbon–halogen distance in the transition state. The authors conclude that while "there is abundant evidence for a large charge separation in

the transition state, it is unlikely to be as great as that corresponding to an intimate ion-pair."

In view of this, the model XX for addition of HX to an olefin

XX
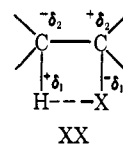
was suggested. On the basis of XX, (77) was deduced

$$E_c(\text{min}) = \Delta H^\circ + \frac{1}{2}(e^2\delta_1{}^2 r_{\text{HX}}{}^2/\alpha_{\text{HX}})(1 - \alpha_o\alpha_{\text{HX}}/2r_a{}^6) \tag{77}$$

where ΔH° is the enthalpy of dehydrohalogenation, r_{HX} and α_{HX} are the hydrogen–halogen distance and the polarizability of H–X in the transition state, α_o is the polarizability of the olefin in the transition state, and r_a is the distance between the hydrogen halide molecule and the olefin. On the basis of (77) values shown in Table XXXI for the activation energies of

Table XXXI

Activation Energies for Elimination Based on Eq 77

R	Cl	Br	I
		X	
Et	58 (58)	58 (53)	45 (51)
i-Pr	47 (51)	47 (48)	45 (46)
t-Bu	47 (45)	47 (41)	42 (38)

elimination are obtained, the experimental values being shown in parentheses. These values are of the correct order of magnitude but underestimate the effect of methyl substitution, which is the dominant effect.

The authors then consider an alternative model in which both the olefin and the hydrogen halide are initially polarized parallel to their reacting bonds by the equivalent of $\pm \frac{1}{2}e$ formed charges. The activation energy now is given by (78) and calculated values are compared with observed values

$$E_c(\text{min}) = \Delta H^\circ + \frac{e^2}{8}\left\{\frac{r_{\text{HX}}{}^2}{\alpha_{\text{HX}}} + \frac{r_{oo}{}^2}{\alpha_o} - \frac{3}{2}\frac{r_{\text{HX}}r_{oo}}{r_a{}^3}\right\} \tag{78}$$

in Table XXXII, the experimental values being given in parentheses.

Table XXXII

Activation Energies for Elimination Based on Eq 78

R	Cl	Br	I
		X	
C_2H_5	56 (58)	56 (53)	54 (51)
i-C_3H_7	52 (51)	52 (48)	50 (46)
t-C_4H_9	48 (45)	45 (41)	44 (38)

Once again, the effect of α-methyl substitution is underestimated by the model. This method was extended to include additions of halogens as well as halogen acids to olefins by Benson and Haugen[222] and to additions of halogens and halogen acids to acetylenes by the same authors.[223]
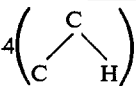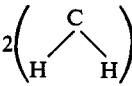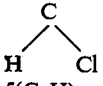
(221a) This assumes $r_c{}^+ = 1.4$ Å, which would appear to be a gross over-estimate. A value of 0.70 would appear more reasonable, giving $r_t = 2.7$ A.

(222) S. W. Benson and G. R. Haugen, *J. Amer. Chem. Soc.*, 87, 4036 (1965).

(223) S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, 70, 3336 (1966).

Table XXXIII

The Ethyl Chloride Reaction

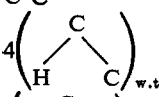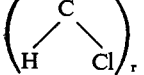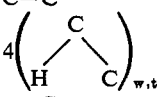| Ground state Vibrations	v, cm^{-1}	Entropy, cal deg^{-1} mole^{-1}	Transition state Vibrations	v, cm^{-1}	Entropy, cal deg^{-1} mole^{-1}
$4\left(\begin{smallmatrix}C\\C\quad H\end{smallmatrix}\right)$	1450	1.15	$\begin{smallmatrix}C\\H\quad C\end{smallmatrix}$	800	1
			$\begin{smallmatrix}C\\H\quad H\end{smallmatrix}$	1000	0.65
			$2\left(\begin{smallmatrix}C\\H\quad H\end{smallmatrix}\right)$	1450	0.56
$\begin{smallmatrix}C\\H\quad Cl\end{smallmatrix}$	400	2.1	$\begin{smallmatrix}C\\Cl\quad Cl\end{smallmatrix}$	280	2.8
5(C–H)	3000	0.0	4(C–H)	3000	0.0
			C·H	2200	0.05
C–C	1000	0.65	C÷C	1300	0.38
$4\left(\begin{smallmatrix}C\\H\quad C\end{smallmatrix}\right)_{w,t}$	1150	2.1	$4\left(\begin{smallmatrix}C\\H\quad C\end{smallmatrix}\right)_{w,t}$	1150	2.1
$\left(\begin{smallmatrix}C\\H\quad Cl\end{smallmatrix}\right)_r$	700	1.2	$\begin{smallmatrix}C\\H\quad Cl\end{smallmatrix}$	700	1.2
CH₃ (ir, 3.5 kcal mole^{-1})		5.8	(CH₂÷CH₂CH₃)$_t$	400	2.1
C–Cl	650	1.3			
		$S° = +14.3$			$(S^{\ddagger})° = +10.8$

O'Neal and Benson[224] have devised a method for calculating the Arrhenius A factors for four-centered reactions. In the ground state, motions of the heavy groups are represented by a carbon–carbon and carbon–chlorine stretch and by a C–C–Cl bend. Hydrogen motions relative to each other are described by four H–C–H bends (three in the methyl groups and one in the methylene group). The four (H–C–C)$_{w,t}$ bends account for the methyl and methylene wags and twists while the (H–C–Cl)$_r$ bend accounts for the methylene rocks. The barrier to the methyl rock is low, this motion being the hindered internal rotation. Certain assumptions (Table XXXIII) are made concerning the transition-state frequencies. The major entropy loss in the case of ethyl chloride comes from the freezing of the methyl rotation and leads to $\Delta S^{\ddagger} = -3.5$ cal mole^{-1} deg^{-1}. A correction is then made for reaction degeneracy, that is, the number of β-hydrogen atoms. In the case of ethyl chloride, this is 3 and so

$$(\Delta S^{\ddagger})' = (-3.5 + 2.3R \log 3) = -1.3 \text{ cal mole}^{-1}$$

This gives, using (79), $\log A = 13.3$. Values obtained in this

$$A = \frac{ekT}{h} \exp\{(\Delta S^{\ddagger})'/R\} \tag{79}$$

way are compared with the experimental values (in parentheses) in Table XXXIV. The values show little variation, which makes the assessment of the calculation difficult. "Calculated" values of the activation energies are also given in the paper, which are obtained by using the observed rate constants and the calculated A factors. It should, however, be pointed out that calculations are also made for six-centered transition states, and a general measure of agreement with experiment is reached in that the values for these reactions are on
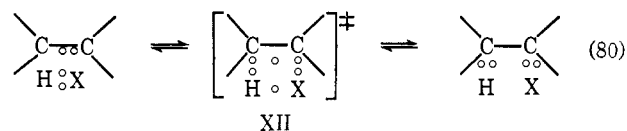
Table XXXIV

Calculated and Experimental Log A Values

R	X Cl	Br	I
Et	13.3 (13.8)	13.3 (13.1)	13.3 (13.8)
i-Pr	13.7 (13.5)	13.7 (13.3)	13.7 (13.8)
t-Bu	13.8 (13.7)	13.8 (13.5)	13.8 (13.3)

the whole lower than for the four-centered reactions. The addition reaction was represented as
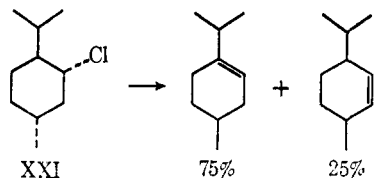

(80)

and the transition state by XII, which represents the semiion pair.

VII. The Products of Elimination

Barton[225] has pointed out that, on the basis of a planar four-centered transition state for gas-phase elimination from alkyl halides, such reactions must be stereospecific in requiring a cis configuration of the eliminated groups. He and his colleagues[77] have demonstrated this in the case of the pyrolysis of menthyl chloride (XXI), which forms predominantly menthene-3.

Maccoll and Bamkole[78] confirmed the product ratio and further showed that neomenthyl chloride pyrolyzes to give about 85% menthene-2, consistent with the cis requirement. Fur-

224) H. E. O'Neal and S. W. Benson, J. Phys. Chem., 7 1, 2903 (1967).

(225) D. H. R. Barton, J. Chem. Soc., 2174   949).

XXI   75%   25%


XXIV   XXV

ther the menthene-3 produced was essentially unracemized. However, as Harden and the author[108] pointed out, the 3:1 ratio observed in the case of menthyl chloride is just the ratio that would be expected in view of the fact that the hydrogen atom concerned in the elimination to form menthene-3 is tertiary, whereas the corresponding hydrogen in the case of menthene-2 is secondary.

The simplest monohalo compounds for which more than one olefin may be produced in the elimination are the *sec*-butyl halides. These compounds were first studied by Stone and the author,[69] and the percentage of butene-1 in the olefinic products from *sec*-butyl chloride, bromide, and iodide was respectively, 42, 34, and 17%. The former two values were obtained in the presence of added ammonia gas, in the hope of repressing the hydrogen halide catalyzed isomerization of butene-1 to butene-2. The ratio of *cis*-butene-2 to *trans*-butene-2 was very close to the equilibrium ratio. Heydtmann and Rinck[70] have reported a value of 43.5% butene-1 obtained in potassium chloride coated vessels, while Holbrook and Rooney[143] report the analyses of the olefin mixtures for a variety of surfaces. In particular they point out that an allyl bromide coating facilitates the *cis–trans* isomerization of the butene-2. Maccoll and Ross[226] have investigated the kinetics of the catalyzed isomerization of the butenes and have shown that for reaction 81 log k_2 = 11.86

$$CH_3CH_2CH=CH_2 \xrightarrow{HBr} CH_3—CH=CH—CH_3 \qquad (81)$$
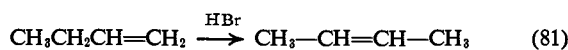
— 26,300/2.303 RT, with k_2 in units of mole^{-1} cc sec^{-1}, the reaction being investigated over a temperature range 310–380°. A transition state of the type XXII or XXIII was sug-

XXII   XXIII
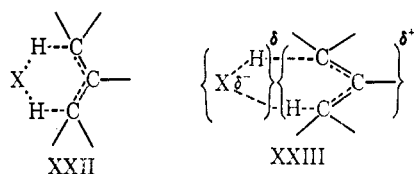
gested, Although it was not possible to decide between the two on the results reported, structure XXIII is clearly related to one proposed by the author and Stimson[227] to explain the hydrogen halide catalysis of the dehydration of alcohols. It is interesting to note that at 100% decomposition Heydtmann and Rinck[70] report the products of the pyrolysis of *n*-butyl chloride to be butene-1 (49%), *cis*-butene-2 (24%), and *trans*-butene-2 (27%) and explain their results in terms of a catalyzed isomerization.

It was argued[69] that, if coplanarity was a requirement of the transition state, then the *trans*-butene-2 should predominate over the *cis* as can be seen from the projections XXIV and XXV, as XXIV leading to the *trans* olefin is less sterically hindered than XXV leading to the corresponding *cis* compound. Heydtmann and Rinck[70] did in fact observe a slight preference for the *trans* olefin when the reaction was studied in
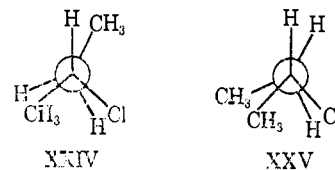
potassium chloride coated vessels, as compared with the allyl bromide carbon coated vessels used by Maccoll and Stone.[69]

The direction of elimination leading to the olefin with the greater number of alkyl substituents on the double bond is known as Saytzeff-oriented elimination, This is characteristic of the E1 mechanism of elimination.[184] For more highly substituted alkyl halides, pyrolysis tends to yield predominantly the Saytzeff product, thus further supporting the analogy proposed in section VI.B. DePuy and King[228] have extensively reviewed *cis* elimination in organic reactions.

VIII. The Present State of the Field

General agreement would appear to exist as regards a moderately polar transition state for alkyl halide pyrolysis. However, separation of the virtual halide ion is not sufficient to allow for racemization of an optically active halide.[74] The isomerism of allylic systems has been observed[87,229] but is still under investigation. In many other respects there is an almost quantitative analogy between gas-phase elimination and the reactions of the corresponding substrate by the unimolecular mechanism in polar solvents.

Recently, a six-centered elimination of hydrogen chloride has been observed.[230] In a study of the pyrolysis of γ-methylallyl chloride, Rodgers[229] observed fast starts, which can be interpreted as the rapid decomposition of a small amount of the *cis* compound in a mixture which is predominantly *trans*. Similarly Harding[87] has shown that γ,γ-dimethylallyl chloride pyrolyzes appreciably faster (with a lower activation energy, and a lower frequency factor) than does the α,α compound (Table V). These facts are consistent with a transition state XXVI, the low values of the Arrhenius parameters being

XXVI
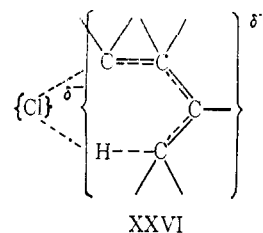
expected from such a formulation. Similarly Wong has observed elimination of hydrogen chloride from α-chloro-*o*-xylene.[231]
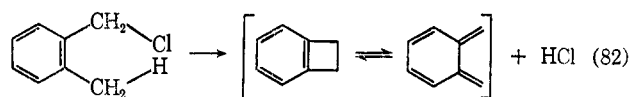
Grant and Swinbourne[232] have examined the isomerization of chloro- and bromocyclopropane. In the case of the chloro

(226) A. Maccoll and R. A. Ross, *J. Amer. Chem. Soc.*, 87, 4997 (1965).
(227) A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, 2836 (1960).

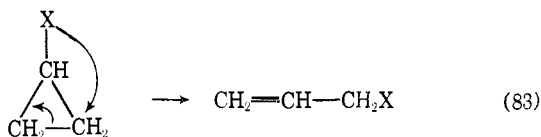(228) C. H. DePuy and R. W. King, *Chem. Rev.*, 60, 431 (1960).
(229) P. G. Rodgers, Ph.D. Thesis, University of London, 1966.
(230) C. J. Harding, A. G. Loudon, A. Maccoll, P. G. Rodgers, R. A. Ross, S. K. Wong, J. Shapiro, E. S. Swinbourne, and V. R. Stimson, *Chem. Commun.*, 1187 (1967).
(231) S. K. Wong, Ph.D. Thesis, University of London, 1968.
(232) R. C. S. Grant and E. S. Swinbourne, *Chem. Commun.*, 620 (1966).

compound, the chloropropene produced was uniquely the 3-substituted compound; in the case of bromocyclopropane, the 3-substituted compound was predominant in the early stages of the reaction but suffered isomerization to 1-bromopropene. It was suggested that isomerization occurred by halogen-atom transfer.

$$
\begin{array}{c}
\text{X} \\
\vert \\
\text{CH} \\
/ \ \ \backslash \\
\text{CH}_2\text{—CH}_2
\end{array}
\longrightarrow \quad \text{CH}_2\text{=CH—CH}_2\text{X} \qquad (83)
$$

This accounts for the unique product found initially. This behavior is in marked contrast with that observed for cyclopropane, methylcyclopropane, and fluorocyclopropane (Table XXXV) for which hydrogen transfer has been postulated.

Table XXXV
Some Isomerization Reactions of Substituted Cyclopropanes

Compound	Products	E, kcal mole^{-1}	Log A	k_X/k_H (336°)
Cyclopropane	Propene	65.1	15.3	1
Methylcyclopropane	Butene-1 (48)% Butene-2 (44%) Isobutylene (8%)	65.0	15.5	2
Fluorocyclopropane	1-Fluoropropene (44%) 2-Fluoropropane (48%) 3-Fluoropropene (8%)	61.0	14.6	6
Chlorocyclopropane	3-Chlorocyclopropene	56.2	14.8	500
Bromocyclopropane	1-Bromocyclopropene 3-Bromocyclopropene	47.3	13.5	40,000

The great enhancement of the rate on chloro or bromo substitution contrasts with the small effect on methyl or fluoro substitution. Subsequently Robinson, et al.,[233] have shown by studies of 1,1-dichlorocyclopropane that it is really the halogen that migrates. It is not impossible that further investigation of substituent effects in the cyclopropane system will require the postulation of polar character for the transition state.

In reviewing the field of molecular elimination reactions in the gas phase, the author and Thomas[234] have suggested that there exists a spectrum of polarities in the transition state, running from the highest in the case of the alkyl halides to the lowest in the case of cyclobutanes. The argument was based on the effect of α-methyl substitution on the rate of elimination (Table XXXVI). Included in the table are some results recently obtained by Barroeta[235] for the alkyl isothiocyanates and by Bamkole and Emovon for t-butyl vinyl ether.[236] It yet remains to put the concept of varying polarity on a quantitative basis.

Table XXXVI
The Effect of α-Methyl Substitution

System	Temp, °C	Parent	α-Methyl	α,α-Dimethyl
Chloride	360	1	150	25,000
Bromide	325	1	160	46,000
Iodide	285	1	102	35,000
Formate	400	1	20	720
Acetate	400	1	27	1,600
Isothiocyanate[235]	307	1	35	690
Vinyl ether[236]	350	1	13	126
Alcohol	525	1	10	38
Cyclobutane	450	1	1.5	3.4

Kraus[237] has pointed out that the Taft equation[238] can give satisfactory correlation of the pyrolyses of alkyl halides and of acetates. When the rate constants for a series of compounds were plotted against σ^*, straight lines were obtained with very large slopes. Points for the cyclopentyl, cyclohexyl, and α-phenylethyl compounds lay off the line. In the first two cases, steric effects play a role and, in the last, the mesomeric effect. The pyrolysis of the alkyl chlorides was used to define new σ^* values, namely -0.225, -0.215, and -0.235 for the three groups, respectively. The values adjusted in this way gave a good linear relationship. As with the correlation with σ^* values discussed earlier (section VI.B.6), the σ^* constants were determined at room temperature, while the olefin-forming eliminations occur in the range 300–500°.
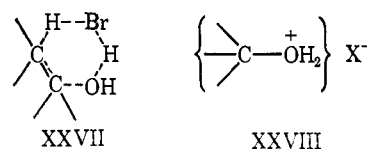
The last area to be discussed is the gas-phase decomposition of alcohols and ethers catalyzed by hydrogen halides, as investigated by Stimson and his school.[239] The reactions follow clear-cut bimolecular mechanisms in nearly all cases, the stoichiometry being

$$
\text{C}_n\text{H}_{2n+1}\text{OH} + \text{HX} \longrightarrow \text{C}_n\text{H}_{2n} + \text{H}_2\text{O} + \text{HX} \qquad (84)
$$

and the results fit the pseudo-first-order equation

$$
-\frac{d}{dt}[\text{ROH}] = k_2[\text{ROH}][\text{HX}]_0 \qquad (85)
$$

On the basis of variation of R and HX, the two transition states XXVII and XXVIII were discussed,[227] and it was

$$
\begin{array}{cc}
\begin{array}{c}
\text{H--Br} \\
/\diagdown \quad \backslash \\
\text{C} \quad \text{H} \\
\backslash \diagup / \\
\text{C--OH} \\
/ \ \backslash
\end{array}
&
\left\{ \ \diagdown \ \ \overset{+}{\text{C}}\text{—OH}_2 \ \right\} \ \text{X}^-
\\
\text{XXVII} & \text{XXVIII}
\end{array}
$$

shown that XXVIII could not be ruled out on purely energetic grounds. A very interesting extension of this work was the investigation of trimethylacetic acid[240] and its methyl ester.[241] The reaction scheme was summed up as in eq 86, the presence of esterification and transesterification being confirmed experimentally.

Reported experiments over a wide field of gas-phase eliminations would appear to suggest that polar mechanisms play an important role in many such processes. As the gas phase

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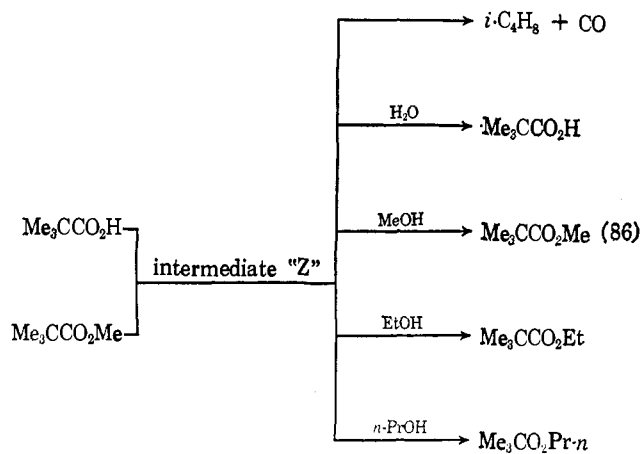(236) T. O. Bamkole and E. U. Emovon, *J. Chem. Soc., B*, 523 (1967).

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Me₃CCO₂H ⟍
　　　　　　│ intermediate "Z"
Me₃CCO₂Me ⟋

→ i-C₄H₈ + CO

—H₂O→ Me₃CCO₂H

—MeOH→ Me₃CCO₂Me (86)

—EtOH→ Me₃CCO₂Et

—n-PrOH→ Me₃CO₂Pr-n

provides a medium of low dielectric constant, the types of transition states involved must of necessity be intimate ion-pairs, with a degree of bond-extension and charge transfer still to be determined. The extent to which the β-hydrogen atoms involved in the elimination participates in the transition state has not yet fully been elucidated. The gas phase does, however, offer the advantage of studying the behavior of an isolated molecule unaffected by the cooperative effects of the solvent. On the other hand, the wealth of information that has been uncovered in studies of solvolysis has led to a body of theory which correlates excellently the observed effect of substitution on the rate of reaction. It is not unreasonable to expect that further studies in these two seemingly unrelated areas will lead eventually to an increased understanding of both.