25. *The Thermal Decomposition of* 1-*Chloroethyl Methyl Ether.*

By P. J. Thomas.

The decomposition of 1-chloroethyl methyl ether in the temperature range 180—250° is a homogeneous first-order reaction, the rate constant k_1 being

$$2{\cdot}90 \times 10^{11} \exp(-33{,}300/\boldsymbol{R}T) \text{ sec.}^{-1}$$

The reaction mechanism is the unimolecular elimination of hydrogen chloride. The methoxyl group exerts a large accelerating effect in this type of gas-phase reaction.

The mechanism of unimolecular dehydrohalogenation has been observed in thermal, gas-phase decomposition of a number of alkyl chlorides [1] and bromides.[2] The effect of molecular structure on this type of reaction has been discussed by Maccoll and Thomas [3] who suggest that the important rate-controlling stage is initial polarisation of the carbon–halogen bond, basing this on two general observations: (*a*) the rate of reaction is almost wholly determined by the substituents in the α-position to the carbon–halogen bond, (*b*) the α-substituent effects show a marked parallel with the structural effects exerted by the same substituents in S_N1 and E_1 reactions in polar solvents, suggesting that common electronic effects are involved in both types of reaction.

In the present investigation this hypothesis was tested by studying the effect of an α-methoxyl group on the rate of unimolecular elimination of hydrogen chloride in the particular case of 1-chloroethyl methyl ether. This compound and its analogues readily undergo solvolytic reactions involving nucleophilic displacement of the halogen, in which the mechanism is of the unimolecular S_N1 type.[4] The accelerating effect of the methoxyl group in these reactions can be attributed to mesomeric release of electrons to the developing carbonium-ion centre; [5] a comparable acceleration is now found for the gas-phase molecular elimination of hydrogen chloride.

Experimental

1-Chloroethyl methyl ether, b. p. 72—73°, was prepared as described by Henze and Murchison.[6] The reaction was followed by measuring the rate of change of pressure in a static system. The apparatus and technique have been described previously.[7] Owing to the instability of the chloro-ether, it was not practicable to use a heated vapour-reservoir for admitting the reactant to the reaction vessel. The following method was adopted. A small side-arm was connected to the capillary inlet of the reaction vessel. Before a run this side-arm was immersed in the liquid air, and the required amount of the ether was distilled into it from a reservoir at room temperature. The reaction vessel and side-arm were then isolated from the main system, and the run was started by rapidly " flaming " the material from the side-arm into the reaction vessel. This method avoided heating the bulb containing the ether.

In a clean glass reaction vessel, appreciable decomposition of 1-chloroethyl methyl ether was observed at temperatures as low as 110°. After the walls had been coated with a thin layer of carbon by decomposing allyl bromide in the vessel at 350°, a much slower reaction was observed which was conveniently measurable in the temperature range 180—250°. The homogeneity of the reaction in vessels coated in this manner was established by comparing the rates of decomposition in an unpacked (surface/volume ratio 0·95 cm.$^{-1}$) and a packed reaction vessel (surface/volume ratio 2·8 cm.$^{-1}$). The results are included in Table 4. Only

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[1] Barton *et al.*, *J.*, 1951, 2039, and earlier papers there cited; Howlett, *J.*, 1953, 945, and earlier papers there cited.

[2] Maccoll *et al.*, *J.*, 1960, 184 and earlier papers there cited.

[3] Maccoll and Thomas, *Nature*, 1955, **176**, 392.

[4] Ballinger, de la Mare, Kohnstam, and Prestt, *J.*, 1955, 3641.

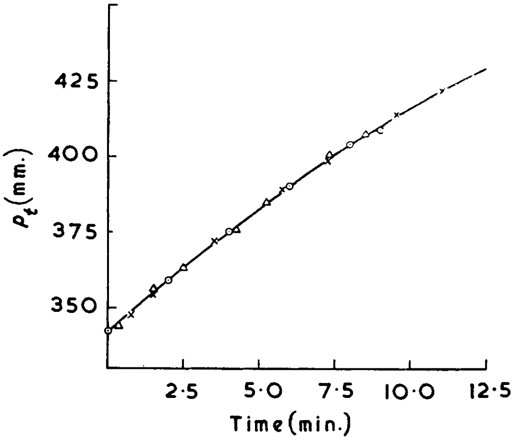
[5] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 333.

[6] Henze and Murchison, *J. Amer. Chem. Soc.*, 1931, **53**, 4077.

[7] Maccoll and Thomas, *J.*, 1955, 979.

a slight increase in rate was observed in the packed vessel. On condensation, the reaction products recombined quantitatively to yield the original ether. If, during a run, the contents of the reaction vessel were condensed in the side-arm, allowed to warm gradually, and then re-admitted to the reaction vessel, the pressure then observed was equal to the pressure of the ether originally introduced. The subsequent pressure–time curve was also identical with the original curve within the limits of experimental error. A series of pressure–time curves illustrating this behaviour is shown in the Figure. First-order rate constants calculated from the separate curves agree within 4%. Although the rapid recombination of the products prevented their determination by standard analytical methods, the observed behaviour indicates that the forward reaction is the elimination of hydrogen chloride. It also indicated that no appreciable side reaction or further decomposition was involved.

In runs which were followed until no further increase in pressure was detectable, the ratio of the final pressure to the initial pressure was ~1·75. That this ratio was less than 2·0 can be attributed partly to dead-space errors and partly to the establishment of an equilibrium between reactant and products (cf. butyl chloride [8]).



Pressure–time curves demonstrating quantitative recombination of reaction products on condensation.

○, *Original pressure–time curve.*
△, *After condensation and readmission to reaction vessel.*
×, *After condensation and readmission to reaction vessel a second time.*

In previous investigations of this type, the use of pressure measurements to follow the course of the reaction has been justified by showing that the observed pressure change Δp is a direct measure of the amount of hydrogen halide formed. This involved determination of the hydrogen halide in the condensed products by standard analytical methods, a procedure which could not be applied in the present case because of the tendency of the products to recombine. The alternative method of estimating the hydrogen chloride *in situ* by precipitating it as ammonium chloride was adopted. The pressure-change in the system after addition of gaseous ammonia could not be directly related to the amount of hydrogen chloride removed because the equilibrium in the system was disturbed. If, however, ammonia was admitted to the system in measured quantities at time intervals sufficient to allow the system to regain equilibrium, the total pressure in the system decreased until the ether had been completely decomposed and the chloride precipitated. Thereafter, the pressure increased as a direct measure of the excess of ammonia added. If the overall reactions involved are

$$CH_3\cdot CHCl\cdot OMe \longrightarrow CH_2{:}CH\cdot OMe + HCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$HCl + NH_3 \longrightarrow NH_4Cl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

then, at the minimum pressure observed, the pressure of added ammonia and the residual pressure of methyl vinyl ether should both be equivalent to the initial pressure of the chloroether, p_0. The results of four determinations are shown in Table 1. Agreement between the three quantities is reasonable. Appreciable deposits of ammonium chloride were formed in the reaction system which had to be cleaned and recoated between experiments. Mass-spectrometric analysis (kindly performed by Dr. C. J. Danby) of a sample of the gas remaining after the chloride had been precipitated gave a mass-spectral pattern consistent with that of methyl

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[8] Howlett, *J.*, 1951, 1409.

vinyl ether. These observations were added proof that the overall reaction is that represented by (1) above.

TABLE 1. *Temperature* 200°.

p_0 (chloro-ether) (mm.)	148	178	180	264
p (NH_3 added) (mm.)	156	170	166	248
p (min.*) (mm.)	146	176	175	259

* The results have been corrected to allow for the slight dissociation of ammonium chloride.

TABLE 2. *Reaction at* 218·5°.

p_0 (mm.)	420	382	299	242	216	196	189	187	135	92	33
10^4k_1 (sec.$^{-1}$)	4·39	4·22	4·44	4·22	4·54	4·44	4·50	4·46	4·31	4·59	4·82

TABLE 3. *Reaction at* 232°.

p_0 (ether) (mm.)	245	236	243	200	202
p (cyclohexene) (mm.)	—	—	35	40	115
10^4k_1 (sec.$^{-1}$)	11·8	12·2	11·8	12·8	12·6

TABLE 4.

Temp.	188°	201°	206° *	215·5°	218·5°	227° *	232°	245°
No. of runs	7	8	6	8	8	6	8	8
10^4k_1 (sec.$^{-1}$)	0·49	1·26	2·23 (1·84)	3·55	4·39	8·84 (7·94)	12·1	25·9

* Runs in a packed vessel (surface/volume ratio 2·80 cm.$^{-1}$). Values in parentheses are interpolated values for k_1 in the unpacked vessel.

The logarithmic plots were linear for the first 35—40% of the reaction only. Subsequent decrease in the first-order rate was attributed to appreciable reversal of the reaction. First-order rate constants were measured over a wide range of initial pressures (33—420 mm.), as shown in Table 2. No significant variation in the first-order rate constants was observed.

The rate of decomposition was not affected by added cyclohexene (see Table 3) which has been shown to be an effective inhibitor of the chain mechanism of decomposition of several alkyl bromides.

The rate of decomposition was measured at several different temperatures as summarized in Table 4. The variation of the first-order rate constant with temperature is given by the Arrhenius equation

$$k_1 = 2{\cdot}90 \times 10^{11} \exp(-33{,}300/\boldsymbol{R}T) \text{ sec.}^{-1}$$

DISCUSSION

The experimental results establish that the thermal decomposition of 1-chloroethyl methyl ether in the temperature range 180—250° is a homogeneous, first-order reaction. The overall reaction is the elimination of hydrogen chloride and the formation of methyl vinyl ether (reaction 1 above).

The low activation energy, the absence of side reactions, and the lack of inhibition by added cyclohexene indicate that reaction does not proceed by a free-radical mechanism either of a chain or of a non-chain character. It is concluded, therefore, that the mechanism is direct loss of molecular hydrogen chloride, a conclusion consistent with the observed kinetic behaviour. The decomposition is thus another example of the unimolecular dehydrohalogenation observed in the decomposition of numerous alkyl bromides and chlorides.

Decomposition in a manner analogous to that of alkyl ethers would have involved one or both of the following reactions:

$$CH_3{\cdot}CHCl{\cdot}OMe \longrightarrow CH_3{\cdot}COCl + CH_4$$

$$CH_3{\cdot}CHCl{\cdot}OMe \longrightarrow CH_3{\cdot}CH_2Cl + CH\ O$$

No evidence for the occurrence of either of these reactions was obtained. In this respect the chloro-ether behaves as a typical halide, and the methoxyl group is not directly involved in the rearrangement.

The effect of the methoxyl group on the rate of unimolecular dehydrochlorination may be assessed by comparing the Arrhenius parameters and the relative rate of decomposition of 1-chloroethyl methyl ether with those of other alkyl chlorides,[9] as in Table 5. The relative rates of decomposition at 330° have been calculated from the Arrhenius equations. An intermediate temperature was chosen in order to minimise errors of extrapolation.

TABLE 5.

Compound	log *A*	*E* (kcal. mole^{-1})	Rel. rate at 330°	Compound	log *A*	*E* (kcal. mole^{-1})	Rel. rate at 330°
$CH_3{\cdot}CH_2Cl$	14·6	60·8	1	$(CH_3)_3CCl$	12·41	41·2	$7{\cdot}1 \times 10^4$
$CH_3{\cdot}CH_2{\cdot}CH_2Cl$	13·45	55·5	6·0	Me·CHCl·OMe ...	11·46	33·3	$6{\cdot}9 \times 10^6$
$(CH_3)_2CHCl$ ...	13·40	50·5	$3{\cdot}7 \times 10^2$				

Substituent effects are most conveniently discussed in terms of α- and β-substitution in ethyl chloride, the simplest chloride which can undergo decomposition by the unimolecular mechanism. Introduction of an α-methoxyl group markedly lowers the activation energy and correspondingly increases the rate of decomposition greatly. The effect of the methoxyl group is much greater than that of an α-methyl group (isopropyl chloride) or the combined effect of two α-methyl groups (t-butyl chloride).

Although still within the range considered " normal " for unimolecular reactions, the value of log *A* for 1-chloroethyl methyl ether is lower than those reported for the other chlorides. This result agrees with the observation by Barton and his co-workers that a positive linear relation holds between log *A* and *E* for this series of reactions. No such relation was observed in the corresponding reactions of the alkyl bromides, although in other respects the two series of reactions are very similar. The possible significance of a relation of this type is outside the scope of the present discussion. The variation in log *A* is in any case small compared with the variation in *E*, and the substituents influence reactivity primarily by altering the latter.

Unimolecular solvolyses (S_N1 mechanism) of a series of chloro-ethers have been studied by de la Mare and his co-workers.[4] By combining their results with others these authors give the following approximate estimate of relative reactivities in the temperature range 0—100° C: $CH_3{\cdot}CH_2{\cdot}CH_2Cl$ 1, $(CH_3)_3CCl$ 10^7, $MeO{\cdot}CH_2Cl$ 10^{13}, $CH_3{\cdot}CHCl{\cdot}OMe$ $>10^{15}$. Comparison of these figures with the relative rates of the gas-phase reactions (Table 5) reveals a qualitative similarity of substituent effects in the two types of reaction. The magnitude of the rate difference for a given substituent is much smaller in the gas-phase reaction, but this is largely due to the much higher temperature at which the latter have been studied. If the relative rates of unimolecular elimination of n-propyl chloride and 1-chloroethyl methyl ether at 0° are compared the rate ratio is $1 : 10^{16}$, which is of the same order of magnitude as the difference observed in the corresponding solution reactions.[10] The quantitative similarity of the acceleration effected by the methoxyl group is a very strong indication that both reactions involve the same type of electron-displacements. The reactions in solution undoubtedly involve heterolysis of the carbon–chlorine bond. The corresponding change in the gas-phase mechanism would be a partial or complete polarisation of the bond during the rate-determining stage of the reaction. (Heterolytic dissociation into separate ions in the gas phase is not feasible at the experimental temperature on energetic grounds and it is not suggested that this occurs.)

The decomposition of 1-chloroethyl methyl ether thus affords a further striking example of the general parallel between unimolecular dehydrohalogenation in the gas phase and

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[9] Barton and Howlett, *J.*, 1949, 165; Barton, Head, and Williams, *J.*, 1951, 2039; Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.

[10] Ingold, *Proc. Chem. Soc.*, 1957, 279.

the S_N1 and $E1$ reactions of the same compounds in polar solvents, and supports the hypothesis that the rate-determining stage in the gas phase involves a polar transition state.

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