Kinetics and Mechanism of Decomposition of Benzyldimethylsulphonium Salts in Chloroform

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The decomposition of benzyldimethylsulphonium halides has been studied with chloroform as solvent, in which the reaction goes to completion, yielding the benzyl halide and dimethyl sulphide as the only products. The kinetics show an exact first-order relation with respect to the conductivity of the solution rather than the molar concentration of the salt. The first-order rate constant is controlled by the nucleophilicity of the anion. Addition of small amounts of ammonium salt causes a sharp decrease in rate constant which becomes more gradual and linear at higher concentrations of added salt. This salt effect is completely insensitive to the nature of the anion of the added ammonium salt. Activation parameters and the α-deuterium isotope effect are reported. A mechanism is proposed involving a unimolecular decomposition of a triple ion consisting of two sulphonium cations and one halide ion.

SULPHONIUM salts frequently undergo nucleophilic substitution reactions at a saturated carbon atom to yield an alkyl compound and dialkyl sulphide. The kinetics of this type of reaction have been investigated on numerous occasions.[1-12] Early observations of first-order kinetics were misinterpreted as indicating a unimolecular mechanism, but Pocker and Parker [13] pointed out that the first-order kinetics arose, even though the reaction was S_N2, because the sulphonium halides were not completely dissociated in the solvents used. Some authors have proposed ion-pair mechanisms, in aqueous ethanol [14,15] and in ethanol, acetic acid, and 50% acetic acid–acetic anhydride,[16] and Sneen *et al.*[17] have put forward a mechanism involving an 'ion–dipole assemblage' intermediate for the reaction of benzyldimethylsulphonium salts in water.

Our earlier studies on tetra-alkylammonium halides undergoing S_N reactions in chloroform to yield alkyl halides and tertiary amines provided evidence for a unimolecular decomposition of a triple ion.[18-22] This paper presents kinetic evidence for the operation of this mechanism in the decomposition of benzyldimethylsulphonium salts in chloroform.

RESULTS AND DISCUSSION

Products.—The products of the decomposition of benzyldimethylsulphonium bromide were analysed by g.l.c. and n.m.r. spectroscopy. The g.l.c. analysis showed only three peaks, which were identified as due to dimethyl sulphide, chloroform, and benzyl bromide, by comparing retention times with those of authentic samples under the same conditions. The n.m.r. spectrum showed four peaks, identified as due to Me_2S (δ 2.1), $PhCH_2Br$ (δ 4.42), $CHCl_3$ (δ 7.3), and $PhCH_2Br$ (δ 7.4). Thus, the reaction goes to completion and benzyl bromide and dimethyl sulphide are the only products.

Kinetic Order of Reaction.—Since benzyl bromide is hydrolysed very readily under any conditions which can be used to titrate the remaining bromide ion of the salt, the reaction rate was determined by following the change in conductance with time. A few experiments were carried out by using the Me_2S^+ n.m.r. signal to monitor the rate of the reaction. This method is less precise than the conductimetric method but served to verify that the conductimetric measurements were providing the correct rate constants.

At the initial concentrations (0.05M) which were generally used, the conductance of the solution is due to the triple ions, although most of the salt is present as ion-pairs.[23] Therefore, a calibration curve relating conductance to concentration was obtained by measuring the conductances of reaction solutions containing various concentrations of benzyldimethylsulphonium bromide and its decomposition products, such that the total concentration was 0.05M. The calibration curve is shown in Figure 1.

However, when the conductance data were converted

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into molar concentrations, the Guggenheim plots for the first-order reaction were slightly curved. In contrast, the conductance data used directly gave straight lines. An example is shown in Figure 2. The concentration line has a correlation coefficient of 0.996 42, whereas that of the conductance line is 0.999 96. In all cases correlation coefficients greater than 0.9999 were obtained from the conductance data. Thus, although a coefficient of 0.996 would generally be considered to represent a satisfactory straight line, it is concluded that this reaction is not exactly first-order in molar concentration, but is exactly first-order in conductance.

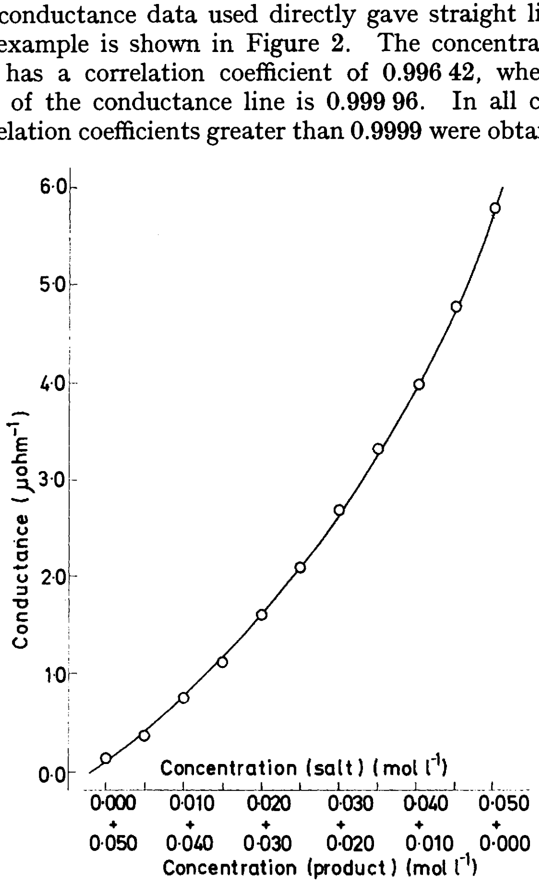

FIGURE 1 Plot of concentration *vs.* conductance for benzyldimethylsulphonium bromide in chloroform at 25 °C

This allows the elimination of several possible mechanisms. A unimolecular decomposition of the ion-pair would follow the rate equation (1), which requires first-

$$-d[R_3S^+X^-]/dt = k[R_3S^+X^-] \qquad (1)$$

order dependence on the stoicheiometric concentration of the salt. Thus ion-pair mechanisms, either (2) or (3), do not fit the experimental observation.

$$R_3S^+X^- \xrightarrow{\text{slow}} R_2S + R^+X^- \xrightarrow{\text{fast}} RX \qquad (2)$$

$$R_3S^+X^- \xrightarrow{\text{slow}} R_2S + RX \qquad (3)$$

An S_N2 mechanism, such as that found for the decomposition of trimethylsulphonium cation in ethanol,[13] also leads to first-order kinetics in stoicheiometric concentration [equations (4) and (5)].

$$X^- + R_3S^+ \longrightarrow RX + R_2S \qquad (4)$$

$$-d[R_3S^+]/dt = k[R_3S^+][X^-] \qquad (5)$$

The dissociation constant, *K*, for the ion-pair is given by equation (6), where α is the degree of ionization, if

$$K = [R_3S^+][X^-]/[R_3S^+X^-] = \alpha^2c/(1 - \alpha) \qquad (6)$$

activity coefficients are ignored. Since α is very small, $(1 - \alpha) \simeq 1$ and equations (7) and (8) apply. The same

$$[R_3S^+][X^-] = \alpha^2c^2 = Kc \qquad (7)$$

$$-d[R_3S^+]/dt = Kkc \qquad (8)$$

result would be obtained for an S_N2 reaction involving two triple ions.

For a unimolecular decomposition of a single or triple ion the rate equation (9) is first-order in the concentration of the ion.

$$-d[R_3S^+]/dt = [R_3S^+] = k\alpha c \qquad (9)$$

Since at 0.05M concentration of sulphonium salt in chloroform the current is carried almost exclusively by triple ions, the conductance of the solution is directly proportional to the triple-ion concentration to a very good approximation.

Dependence of Rate Constant on Initial Concentration of Salt.—Before the effect of added salts can be studied it is necessary to determine the dependence of the first-order rate constant on the initial concentration of the salt, since ionic strength effects may have to be taken into account. The rate constants for the decomposition of benzyldimethylsulphonium chloride, bromide, and iodide were determined at various initial concentrations.

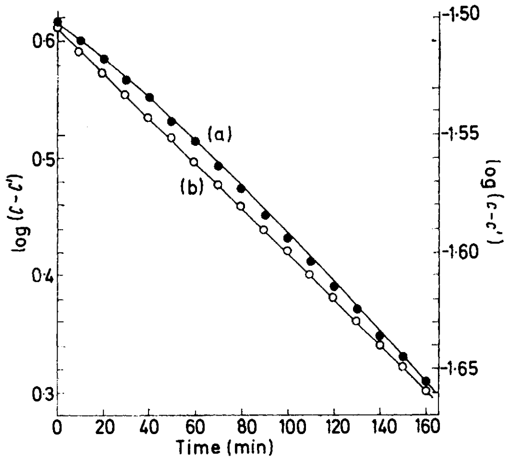

FIGURE 2 Guggenheim plots for the decomposition of benzyldimethylsulphonium bromide in chloroform at 25 °C: (a) concentration data (right-hand scale); (b) conductance data (left-hand scale)

At higher concentrations the rate constants are independent of initial concentration, but at lower concentrations slightly greater rates are observed. At 0.05M initial concentration and above for the chloride and bromide the first-order rate constants at 40 °C were 20.6×10^{-5} and 60.0×10^{-5} s^{-1} respectively. At 0.025M initial concentration the rate constants were 10—20% greater. The iodide gave a first-order rate constant of

53.9×10^{-5} s^{-1} at 20 °C for an initial concentration of 0.08M, which rose to 60.3×10^{-5} s^{-1} when the initial concentration was reduced to 0.04M. At 0.05M initial concentration and above, the kinetic measurements, taken over 90% reaction, are all under the conditions in which triple ions carry the current, whereas at lower concentrations during the latter part of the run current is being carried by single ions. The slight increase in rate at lower concentrations may be an artefact of the use of conductance to measure the rate or it may be due to the intervention of a mechanism involving the unimolecular decomposition of the single ion. In any event, the decompositions can be studied at 0.05M, in which region there appears to be no ionic strength effect.

Dependence of Rate Constant on Nucleophilicity of Anion.—The above figures show that the rate constant is dependent on the nucleophilicity of the anion, and the values of log k_1 for the three halides at 25 °C correlate very well with the Swain–Scott nucleophilicity [24,25] as shown in Figure 3.

A similar correlation has been observed for the S_N2 reactions of trimethylsulphonium cation in ethanol,[13] although in that case the slope of the line was 0.81; *cf.* 0.6 for Figure 3. This means that the benzyldimethylsulphonium decomposition is a little less sensitive to change in nucleophilicity of the anion than the above reaction.

Figure 3 verifies that the halide ion is present in the transition state, consistent with the triple-ion mechanism for the decomposition.

Effect of Added Nucleophiles.—Since the anion of the salt is undoubtedly present in the transition state of the reaction as the nucleophile, the effect of added nucleophiles on the rate of the reaction should give unequivocal information about the mechanism. The effect will be quite different if the mechanism is a simple S_N2 than if the mechanism is a unimolecular decomposition of a triple ion.

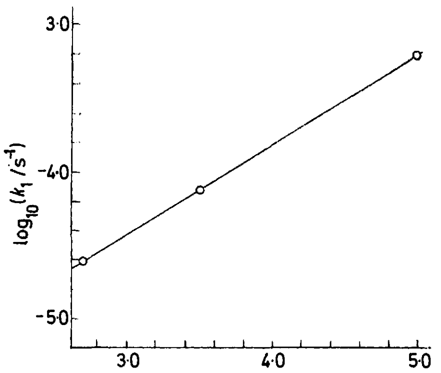

FIGURE 3 Dependence of the first-order rate constant on the nucleophilicity of the anion for the reactions of benzyldimethylsulphonium halides in chloroform

Benzyldimethylsulphonium bromide was allowed to decompose in the presence of tetra-n-butylammonium bromide, perchlorate, phenolate and benzenethiolate. The rate constants are plotted in Figure 4, which shows that the effect of the added nucleophiles is almost independent of the nucleophilic power of the addend. Thus, it appears that none of the bromide added in the tetra-n-butylammonium bromide acts as a nucleophile; it exerts only a salt effect very similar to the perchlorate and phenolate. This result rules out the S_N2 mechanism, involving either single or triple ions.

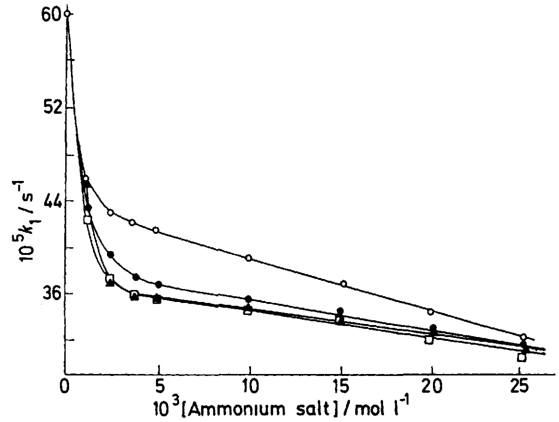

FIGURE 4 Decomposition of benzyldimethylsulphonium bromide in the presence of tetra-n-butylammonium salts in chloroform at 40 °C: (○) $Bu^n_4\overset{+}{N}ClO_4^-$; (●) $Bu^n_4\overset{+}{N}Br^-$; (▲) $Bu^n_4\overset{+}{N}O^-Ph$; (□) $Bu^n_4\overset{+}{N}S^-Ph$

Further experiments were carried out to test the effect of added tetra-n-butylammonium bromide on benzyldimethylsulphonium perchlorate, which does not decompose in chloroform on its own. Also, the effect of added ammonium iodide on sulphonium bromide was compared with the effect of added ammonium bromide on sulphonium iodide. These results are presented in Figure 5.

All these results can be reasonably interpreted in terms of the triple-ion mechanism. The electrochemical studies of the mixed sulphonium and ammonium salts showed [23] that the addition of an ammonium salt to the sulphonium bromide either increases or slightly decreases $[Br^-S^+Br^-]$ and at the same time dramatically decreases $[S^+Br^-S^+]$. The results in Figure 4 are, therefore, interpreted as a reflection of $[S^+Br^-S^+]$ decrease by the added ammonium salt. The products of these reactions are only benzyl bromide and dimethyl sulphide. In an analysis of the products by n.m.r., no benzyl phenyl ether or sulphide was detected. If the reaction is proceeding entirely, or almost entirely, through the triple ion $S^+Br^-S^+$, the sulphonium perchlorate alone would not decompose, but does when ammonium bromide is added, allowing the formation of some $S^+Br^-S^+$. The products of this reaction are benzyl bromide and dimethyl sulphide.

The decomposition of sulphonium iodide in the

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presence of ammonium bromide (Figure 5) exhibits the same characteristics as the decompositions shown in Figure 4, except that in this case $S^+I^-S^+$ is the active species and its concentration is depressed by the added ammonium bromide. When ammonium iodide is added to sulphonium bromide, the reaction, in the presence of small amounts of iodide, proceeds *via* $S^+Br^-S^+$, the concentration of which is depressed by the ammonium iodide. However, at higher concentrations of added iodide, some $S^+I^-S^+$ is thereby formed which decomposes more rapidly than $S^+Br^-S^+$; hence the rate of the reaction passes through a minimum and rises again as the ammonium iodide concentration is increased. In these reactions both benzyl bromide and benzyl iodide are formed as products, together with dimethyl sulphide.

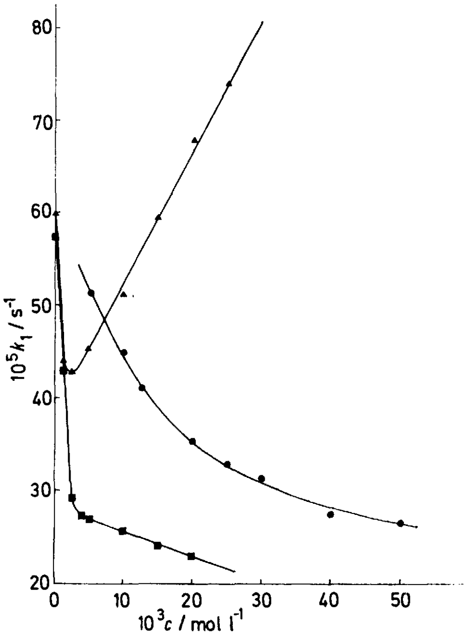

FIGURE 5 Decomposition of (●) benzyldimethylsulphonium perchlorate in the presence of added tetra-n-butylammonium bromide at 40 °C; (■) benzyldimethylsulphonium iodide in the presence of added tetra-n-butylammonium bromide at 25 °C; (▲) benzyldimethylsulphonium bromide in the presence of added tetra-n-butylammonium iodide at 40 °C

Activation Parameters.—The first-order rate constants for the decomposition of benzyldimethylsulphonium bromide at various temperatures are shown in the Table. The results were fitted to the transition state theory equation by a least-squares calculation and yielded:

$$\Delta H^\ddagger = 106.7 \pm 0.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = 33.5 \pm 2.5 \text{ J mol}^{-1} \text{ K}^{-1};$$

the errors quoted are standard deviations. These values are very similar to the corresponding parameters for benzyl-containing ammonium salts decomposing in chloroform.[22] The good fit to the transition state theory equation provides further evidence that the reaction proceeds by a single mechanism.

Secondary Deuterium Isotope Effect.—Deuteriation at the benzylic carbon atom provides a measure of the environment of these hydrogen atoms in the transition state. The value of k_H/k_D was determined at six temperatures as shown in the Table. The isotope effect is approximately independent of temperature: $k_H/k_D = 1.08 \pm 0.01$. The value greater than unity indicates a less crowded transition state than initial state, although it is much less than the value (1.25) found for [α-$^2H_2$]-benzylphenyldimethylammonium bromide in chloroform.[21] Although in solvolytic reactions the α-deuterium isotope effect seems to be a reasonably reliable indicator of mechanism, this is not necessarily so for non-solvolytic reactions. For instance a k_H/k_D value of 1.05 was observed for the radio-chloride exchange of [α-$^2H_2$]-benzyl chloride in *NN*-dimethylformamide.[26] Thus, the value 1.08 is not particularly diagnostic, but is not inconsistent with the triple-ion mechanism.

Thus, a combination of conductance and kinetic studies leaves no doubt that the mechanism is neither the standard S_N1 nor S_N2. All the evidence is consistant with the decomposition of the triple ion containing two sulphonium ions and one halide ion.

Rate constants for the decomposition of normal and [α-$^2H_2$]benzyldimethylsulphonium bromide[a] in chloroform

t/°C	$10^5k_H/s^{-1}$	$10^5k_D/s^{-1}$	k_H/k_D
25	7.49 ± 0.01	7.02 ± 0.01	1.07
30	15.24 ± 0.01	14.15 ± 0.03	1.08
35	30.20 ± 0.07	28.26 ± 0.06	1.07
40	60.0 ± 0.15	55.0 ± 0.1	1.09
45	116.0 ± 0.2	108.4 ± 0.4	1.07
50	228.2 ± 0.9	210.3 ± 0.8	1.08

[a] Initial concentration 0.05M.

EXPERIMENTAL

Materials.—The tetra-n-butylammonium salts were prepared as described in the preceding paper.[23] The phenolate had m.p. 132—135 °C (Found: 27.7% anion. Calc.: 27.7%) and the thiophenolate had m.p. 69—70 °C (Found: 31.0% anion. Calc.: 31.0%).

The benzyldimethylsulphonium halides were prepared by treating benzyl halides with an excess of dimethyl sulphide for several hours with continuous stirring. Crystals of the salt were filtered off under nitrogen, washed with dry ether, and recrystallized from alcohol–ether. The chloride had m.p. 109—110 °C (lit.,[27] 105—110 °C) (Found: Cl^-, 17.95. Calc.: 17.95%). The bromide had m.p. 100—100.5 °C (lit.,[27] 99—100 °C) (Found: Br^-, 34.3. Calc.: 34.3%). The iodide had m.p. 103—105 °C (lit.,[27] 102—104 °C) (Found: I^-, 45.35. Calc.: 45.35%). The perchlorate was prepared by the method used for tetra-n-butylammonium perchlorate; m.p. 105—107 °C (lit.,[28] 106—107 °C).

[α-$^2H_2$]Benzyl bromide was prepared from [α-$^2H_3$]toluene (Merck, Sharp, & Dohme, Canada, Ltd.) by refluxing for 20 min with an equimolar amount of *N*-bromosuccinimide and a small amount of benzoyl peroxide. The [α-$^2H_2$]-

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benzyl bromide was recovered in 95% yield and was distilled at 22 mmHg; b.p. 137—139 °C (lit.,[21] 135—138 °C at 22 mmHg).

The chloroform solvent was ' chromatoquality reagent grade ' (Matheson, Coleman, and Bell) and was used without further purification. The g.l.c. trace supplied by the manufactures showed only a small amount of hydrocarbon stabilizer.

Product Analysis.—The products of decomposition of the sulphonium salts, with and without added ammonium salts, were analysed by g.l.c. and n.m.r. spectroscopy. The g.l.c. analysis was carried out with an Autoprep A-700 chromatograph (SE 30 on HMDS Chromosorb column). The reaction mixture was maintained at the reaction temperature for 25 half-lives and then concentrated by removing most of the solvent at reduced pressure. The products were identified by matching the retention time of each peak with that of an authentic sample under identical conditions. The n.m.r. spectra were run on a Varian T-60 instrument.

Conductance–Concentration Calibration Curve.—Solutions of benzyldimethylsulphonium bromide and its decomposition products were made up such that the total concentration was 0.05M. The concentration of the salt was decreased while that of the products was increased at 0.005M intervals. For each solution about 10 readings were made at intervals, from which the conductance at time ' zero ' was obtained by extrapolation.

Kinetic Measurements.—The kinetic runs were carried out in the cells (30 cm^3 capacity) described in the previous paper,[23] except for the runs made to determine the deuterium isotope effect. For the latter runs, cells of 5 cm^3 capacity with concentric cylindrical shiny platinum electrodes were used. No difference in rate constant was found between measurements with the two types of cell. For the isotope effects the normal and deuteriated compounds were measured simultaneously in the same thermostatted oil-bath (Tamson TV40 with temperature control $\leqslant \pm 0.01$ °C). With the normal rate constant determinations duplicate runs were always made, except at temperatures 45 and 50 °C when the half-life of the reaction was inconveniently short.

The first-order rate constants were calculated by the Guggenheim method [29] using a least-squares analysis to obtain the slope of the graph. Figure 2 shows a typical run

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