

Conductances of Some Quaternary Ammonium and Sulphonium Salts in Chloroform

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Conductances of diethylmethylsulphonium and tetra-n-butylammonium salts have been measured in chloroform solution, both for the pure salts and for equimolar mixtures. The dissociation constants and concentrations of the single ions, ion-pairs, and triple ions have been calculated. The concentrations of the single and triple ions were found to be markedly different in solutions of the pure sulphonium salts from those in the equimolar mixture of sulphonium and ammonium salts.

STUDIES of the decomposition of tetra-alkylammonium halides which contain a benzyl group, in chloroform solution, showed that these compounds undergo a clean nucleophilic substitution to yield the benzyl halide and tertiary amine by an unusual mechanism. The kinetics of the reaction are strictly first-order, not in the stoichiometric concentration of the substrate, but in the concentration of triple ions present in solution. These kinetics indicate a unimolecular decomposition of the triple ion.¹⁻⁵ The secondary deuterium isotope effect on the first-order rate constant resulting from the deuteration at the benzylic position atoms gave a k_H/k_D value of 1.25 at 30 °C, earlier thought to be diagnostic for a carbocationic transition state, but more recently found to be only indicative of a loose or uncrowded transition state.⁴ The further observation that the rate constant for the reaction was dependent on the identity of the anion led to the formulation of the mechanism as a unimolecular ionic internal nucleophilic substitution of a triple ion.¹

The study of this mechanism has now been extended to sulphonium salts, for which there is a considerably

larger literature of kinetic and mechanistic studies of nucleophilic substitutions. Since it seemed desirable to apply the further mechanistic test of the addition of common-ion and non-common-ion salts to the reaction mixture, it was decided to carry out an electrochemical study of pure sulphonium salts and of mixtures of sulphonium and tetra-alkylammonium salts in chloroform as solvent before proceeding to the kinetic study.

Although in the kinetic measurements benzyldimethylsulphonium salts were subsequently used, we selected diethylmethylsulphonium salts for the conductance studies, in order to avoid the difficulties arising from the decomposition of the benzyl-containing salt under the experimental conditions.

The calculation of the concentrations of the different species requires a knowledge of the equilibrium constants for the ion-pair and triple-ion dissociations. These constants can be obtained when the limiting equivalent conductance for the particular salts is available, and it is in the determination of the limiting equivalent conductance that the greatest uncertainties are encountered.

³ E. C. F. Ko and K. T. Leffek, *Canad. J. Chem.*, 1970, **48**, 1865.

⁴ E. C. F. Ko and K. T. Leffek, *Canad. J. Chem.*, 1971, **49**, 129.

⁵ E. C. F. Ko and K. T. Leffek, *Canad. J. Chem.*, 1972, **50**, 1297.

¹ K. T. Leffek and F. H. C. Tsao, *Canad. J. Chem.*, 1968, **46**, 1215.

² J. T. Burns and K. T. Leffek, *Canad. J. Chem.*, 1969, **47**, 3725.

RESULTS AND DISCUSSION

(a) *Equivalent Conductance at Infinite Dilution* (Λ^0).— Since the equivalent conductance at infinite dilution is known for many tetra-alkylammonium salts in acetone,^{6,7} this quantity was evaluated for tetra-n-butylammonium bromide, chloride, iodide, and perchlorate in chloroform solvent by means of Walden's Rule.^{8,9} This rule states that the product of the limiting equivalent conductance, Λ^0 , for a given electrolyte and viscosity of the solvent is a constant, independent of temperature. Departures from Walden's Rule have been noted, especially for small or unsymmetrical ions when compared in solvents of widely differing polarizability and molecular volume. The rule appears to be most closely obeyed by large spherical ions of the R_4N^+ type. By using the data of Kraus *et al.*^{6,7} and a viscosity of 5.24 mP for chloroform at 25 °C¹⁰ the Λ^0 values shown in Table I were calculated.

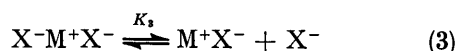
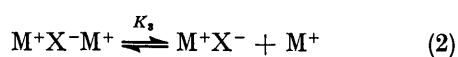
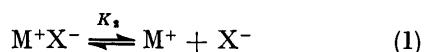
For sulphonium salts no Λ^0 values were available; therefore, the trial and error method of Fuoss and Kraus¹¹ was used, yielding the Λ^0 values in Table I.

TABLE I

Limiting equivalent conductances of ammonium and sulphonium salts in chloroform at 25 °C

(a) Tetra-n-butylammonium salts	Br ⁻	Cl ⁻	I ⁻	ClO ₄ ⁻
Anion	110	104	108	110
10 ⁴ Λ^0 /ohm ⁻¹ m ² mol ⁻¹				
(b) Diethylmethylsulphonium salts				
10 ⁴ Λ^0 /ohm ⁻¹ m ² mol ⁻¹	65	65	65	65
(c) Benzyldimethylsulphonium salts				
10 ⁴ Λ^0 /ohm ⁻¹ m ² mol ⁻¹				66

(b) *Dissociation Constants for Single Salts.*—The dissociation of salts in solvents of low dielectric constant, such as chloroform, involves equilibria amongst single ions, ion-pairs, and triple ions as shown in equations (1)–(3). The limiting conductance of the



triple ions was assumed to be one-third of that of the simple ions,¹² and the technique of Fuoss and Kraus¹³ was applied to plots of the logarithm of the equivalent conductance, Λ , versus the logarithm of the concentration to calculate the dissociation constants K_2 and K_3 , it being assumed that K is identical for equations (2) and (3). The method has been applied previously to tetra-n-butylammonium salts in benzene.¹⁴

The plots of $\log_{10}\Lambda$ vs. $\log_{10}c$ for the ammonium and

⁶ M. B. Reynolds and C. A. Fraus, *J. Amer. Chem. Soc.*, 1948, **70**, 1709.

⁷ M. J. McDowell and C. A. Kraus, *J. Amer. Chem. Soc.*, 1951, **73**, 3293.

⁸ P. Walden, H. Ulich, and G. Busch, *Z. phys. Chem.*, 1926, **123**, 429.

⁹ P. Walden and E. J. Birr, *Z. phys. Chem.*, 1931, **153A**, 1.

¹⁰ 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, Ohio, 49th edn., 1969.

sulphonium salts (Figures 1 and 2) pass through a minimum, c_{min} , in the concentration range $2-4 \times 10^{-3}M$. At these minima, single and triple ions each carry half of the current. When the single ions carry almost all

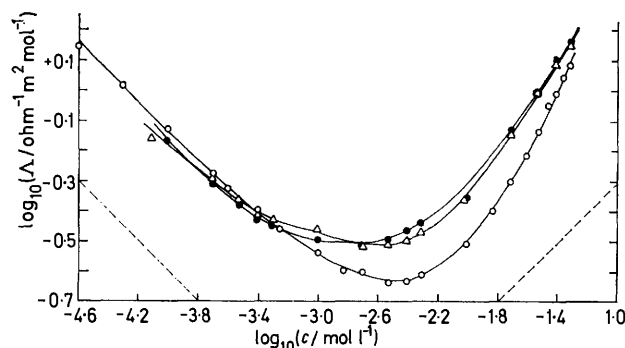


FIGURE 1 Plots of $\log_{10}\Lambda$ vs. $\log_{10}c$ for tetra-n-butylammonium salts: (●) $Bu_4N^+ClO_4^-$; (△) $Bu_4N^+I^-$; (○) $Bu_4N^+Br^-$

the current, Ostwald's law should be obeyed. The dashed line in the lower left portions of Figures 1 and 2 has the Ostwald-law slope $-1/2$, when simple ions carry the current; the one in the lower right portion with a slope of $1/2$ is obtained if triple ions carry all the current.

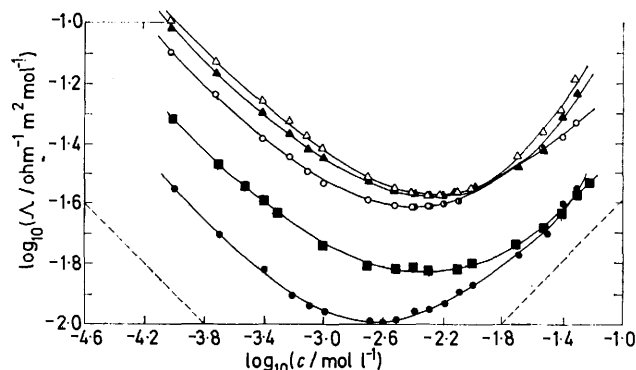


FIGURE 2 Plot of $\log_{10}\Lambda$ vs. $\log_{10}c$ for sulphonium salts: (△) $PhCH_2S^+ClO_4^-$; (△) $Et_2S^+MeClO_4^-$; (○) $Et_2S^+MeI^-$; (●) $(C_2H_5)_2S^+(CH_3)Br^-$

Immediately on the high concentration side of the minimum of the $\log_{10}\Lambda$ – $\log_{10}c$ plots, the main carriers of the current are the triple ions. At higher concentrations, quadrupoles and other charged complexes are formed. The equation for the equivalent conductance, in a solution in which the degree of dissociation of ion-pairs is very small is equation (4), where $\Lambda = \sqrt{K_2\Lambda^0}$, and

$$\Lambda = Ac^{-1/2} + Bc^{1/2} \quad (4)$$

$B = \sqrt{K_2\Lambda^0/K_3}$; Λ^0_1 and Λ^0_3 being the limiting conductances of the single and triple ions respectively.

¹¹ R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476.

¹² R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1955, p. 392.

¹³ R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 2387.

¹⁴ E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1957, 1206.

By differentiating equation (4) one obtains the condition for a minimum in Λ as a function of concentration,

$$(-1/2)Ac^{-3/2} + (1/2)Bc^{-1/2} = 0 \quad (5)$$

$$\therefore c_{\min.} = A/B \quad (6)$$

c [equations (5) and (6)]. Substituting this value of $c_{\min.}$ in equation (4) gives equation (7). From equations

$$\Lambda_{\min.} = A(B/A)^{1/2} + B(A/B)^{1/2} = 2(AB)^{1/2} \quad (7)$$

(6) and (7) the equilibrium constants K_2 and K_3 can be obtained [equations (8)–(11)]. For solutions which

$$c_{\min.} = \frac{A}{B} = \frac{\sqrt{K_2\Lambda_1^0}}{\sqrt{K_2\Lambda_3^0/K_2}} = K_3 \frac{\Lambda_1^0}{\Lambda_3^0} \quad (8)$$

$$K_3 = c_{\min.}(\Lambda_3^0/\Lambda_1^0) \quad (9)$$

$$\Lambda_{\min.} = 2\sqrt{AB} = 2(K_2\Lambda_1^0\Lambda_3^0/K_3)^{1/2} \quad (10)$$

$$\therefore K_2 = \frac{(\Lambda_{\min.})^2 K_3}{4\Lambda_1^0\Lambda_3^0} = \frac{(\Lambda_{\min.})^2 c_{\min.} \Lambda_3^0}{4\Lambda_1^0 \Lambda_3^0} = c_{\min.} \left(\frac{\Lambda_{\min.}}{2\Lambda_1^0} \right)^2 \quad (11)$$

obey equation (4), a plot of $\Lambda c^{1/2}$ against c will give a straight line with an intercept equal to A and a slope equal to B . These plots are shown in Figure 3, from which the values of A and B were determined and used

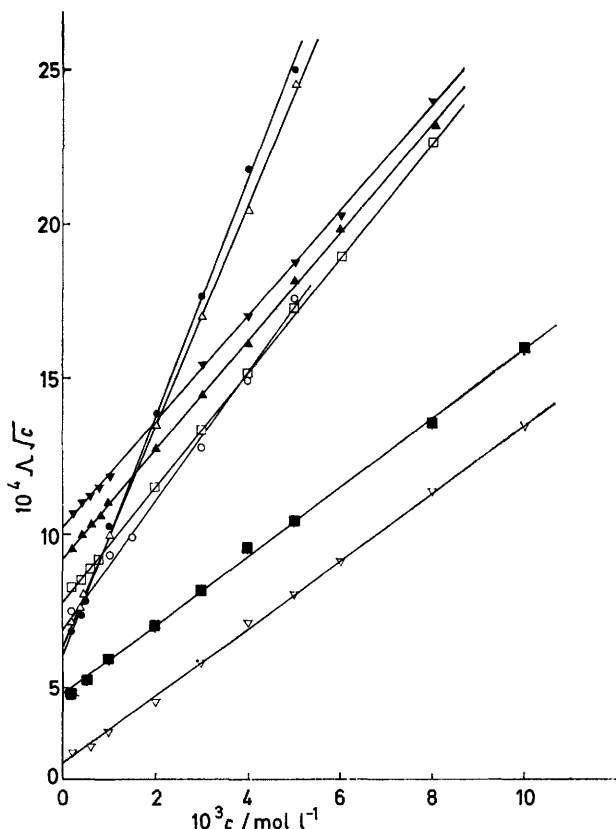


FIGURE 3 Plots of $\Lambda\sqrt{c}$ vs. c for ammonium and sulphonium salts: (●) $\text{Bu}_4\text{N}^+\text{ClO}_4^-$; (△) $\text{Bu}_4\text{N}^+\text{I}^-$; (○) $\text{Bu}_4\text{N}^+\text{Br}^-$; (▽) $\text{PhCH}_2\text{S}^+\text{ClO}_4^-$; (▲) $\text{Et}_2\text{S}^+\text{MeClO}_4^-$; (□) $\text{Et}_2\text{S}^+\text{MeI}^-$; (■) $\text{Et}_2\text{S}^+\text{MeBr}^-$; (∇) $\text{Et}_2\text{S}^+\text{MeCl}^-$

to calculate K_2 and K_3 for each salt. The results are summarized in Table 2 and the ionic concentrations derived from them are given in Table 3.

(c) *Dissociation Constants for Mixed Salts.*—The equilibrium constants involved in the ion-pair and

TABLE 2

Electrolytic constants of single ammonium and sulphonium salts and of equimolar binary mixtures in chloroform at 25 °C

Tetra-n-butylammonium salts					
	Br ⁻	I ⁻	ClO ₄ ⁻		
$10^{10}K_2/\text{mol l}^{-1}$	45.66	35.20	34.00		
$10^3 K_3/\text{mol l}^{-1}$	1.21	1.21	0.54		
Diethylmethylsulphonium salts					
	Br ⁻	Cl ⁻	I ⁻	ClO ₄ ⁻	PhCH ₂ SMe ₂ ClO ₄
$10^{10}K_2/\text{mol l}^{-1}$	0.510	0.14	1.45	1.98	2.38
$10^3 K_3/\text{mol l}^{-1}$	1.39	0.72	1.40	1.77	2.00
Diethylmethylsulphonium salts					
	Br ⁻	Br ⁻	Br ⁻		
Tetra-n-butylammonium salts					
	Br ⁻	I ⁻	ClO ₄ ⁻		
Calculated from data on pure salts					
$10^{10}K_{2m}/\text{mol l}^{-1}$	23.09	20.45	20.54		
$10^3 K_{3m}/\text{mol l}^{-1}$	1.29	1.30	1.01		
Calculated from data on mixed salts					
$10^3 K_{3xy}/\text{mol l}^{-1}$	3.22	0.09	0.61		
$10^3 K'_{3yz}/\text{mol l}^{-1}$	0.04	0.01	0.01		
$10^3 K''_{3xy}/\text{mol l}^{-1}$		1.17	0.81		
$10^3 K'_{3yz}/\text{mol l}^{-1}$		0.04	0.03		

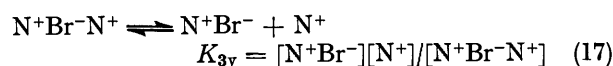
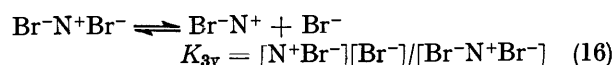
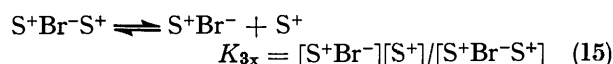
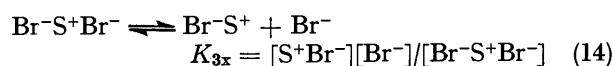
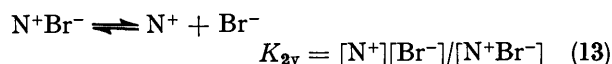
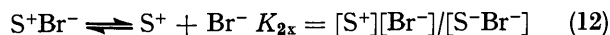
TABLE 3

Concentrations of simple and triple ions ($10^6 c/\text{mol l}^{-1}$) in solutions of sulphonium and ammonium salts in chloroform at 25.0 °C^a

Sulphonium salts (0.05M)					
	S ⁺ Br ⁻	S ⁺ Cl ⁻	S ⁺ I ⁻	S ⁺ ClO ₄ ⁻	PhCH ₂ SMe ₂ ClO ₄
[X ⁻]	0.160	0.082	0.269	0.314	0.345
[S ⁺]	0.160	0.082	0.269	0.314	0.345
[X ⁻ S ⁺ X ⁻]	5.770	5.690	9.600	8.870	8.620
[S ⁺ X ⁻ S ⁺]	5.770	5.690	9.600	8.870	8.620
Ammonium salts (0.05M)					
	N ⁺ Br ⁻	N ⁺ I ⁻	N ⁺ ClO ₄ ⁻		
[X ⁻]	1.511	1.327	1.304		
[N ⁺]	1.511	1.327	1.304		
[X ⁻ N ⁺ X ⁻]	62.30	54.80	122.3		
[N ⁺ X ⁻ N ⁺]	62.30	54.80	122.3		

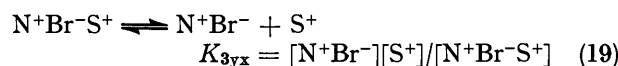
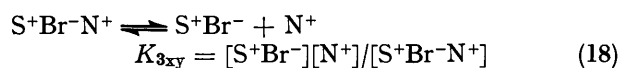
^a X⁻ = anion of the salt; S = Et₂SMe; N = Bu₄N.

triple-ion dissociations in equimolar mixtures of ammonium and sulphonium salts with a common anion are given by the equations (12)–(19). The method used



to evaluate the dissociation constants was that of Ingold and his co-workers.¹⁴

Since the relationship (20) holds, there are actually



five independent equilibrium constants, four of which have been evaluated from the conductances of the pure salts. The two additional relationships (21) and (22)

$$K_{3yx}/K_{2x} = K_{3xy}/K_{2y} \quad (20)$$

$$[\text{Br}^-] + [\text{Br}^-\text{S}^+\text{Br}^-] + [\text{Br}^-\text{N}^+\text{Br}^-] = [\text{S}^+] + [\text{N}^+] + [\text{S}^+\text{Br}^-\text{S}^+] + [\text{N}^+\text{Br}^-\text{N}^+] + [\text{S}^+\text{Br}^-\text{N}^+] \quad (21)$$

$$[\text{S}^+\text{Br}^-] = [\text{N}^+\text{Br}^-] = c/2 \quad (22)$$

arising out of charge balance and mass balance allow the determination of the fifth constant. However, for the purposes of elucidating the mechanism of the nucleophilic substitution reactions of these salts, it is more convenient to carry out the calculations in such a way as to yield readily the actual concentration of each

$$K_{2m} = 1/2(K_{2x} + K_{2y}) \quad (23)$$

$$K^{-1}_{3M} = 1/2(K_{3x}^{-1} + K_{3y}^{-1}) \quad (24)$$

$$\rho_x = K_{2x}/K_{3x} \quad (25)$$

$$\rho_y = K_{2y}/K_{3y} \quad (26)$$

$$\rho_{xy} = K_{2x}/K_{3yx} = K_{2y}/K_{3xy} \quad (27)$$

$$S = \rho_x + \rho_y + \rho_{xy} \quad (28)$$

$$F = \left(1 + \frac{cS}{K_{2m}}\right)^{1/2} \left(1 + \frac{c}{K_{3M}}\right)^{-1/2} \quad (29)$$

$$R = (cK_{2m})^{1/2}F \quad (30)$$

$$[\text{Br}^-] = R \quad (31)$$

$$[\text{S}^+] = cK_{2x}/2R \quad (32)$$

$$[\text{N}^+] = cK_{2y}/2R \quad (33)$$

$$[\text{Br}^-\text{S}^+\text{Br}^-] = cR/2K_{3x} \quad (34)$$

$$[\text{Br}^-\text{N}^+\text{Br}^-] = cR/2K_{3y} \quad (35)$$

$$[\text{S}^+\text{Br}^-\text{S}^+] = c^2K_{2x}/4RK_{3x} \quad (36)$$

$$[\text{N}^+\text{Br}^-\text{N}^+] = c^2K_{2y}/4RK_{3y} \quad (37)$$

$$[\text{S}^+\text{Br}^-\text{N}^+] = c^2K_{2x}/4K_{3yx} = c^2K_{2y}/4K_{3xy} \quad (38)$$

$$\bar{\Lambda} = \Lambda^0_1\phi_1 + 1/3\Lambda^0_3\phi_3 \quad (39)$$

ionic species as well as the dissociation constants. The technique used by Ingold *et al.*¹⁴ was, therefore, followed.

Eight derived parameters are defined by equations (23)—(30). The simple and triple ion concentrations are then given by equations (31)—(38). The equation for the equivalent conductance of the mixed salts is (39), where ϕ_1 and ϕ_2 are the fractions of the total salts present

as single and triple ion respectively, and are given by equations (40) and (41). Expansion of equation (39)

$$\phi_1 = \left(\frac{K_{2m}}{c}\right)^{1/2} \left(\frac{F^2 + 1}{2F}\right) \quad (40)$$

$$1/3\phi_3 = \left(\frac{cK_{2m}}{K_3}\right)^{1/2} F + \left(\frac{K_{2m}}{c}\right)^{1/2} \left(\frac{F^2 - 1}{2F}\right) \quad (41)$$

as a power series of c leads to equation (42), if all powers of $c \geq 3/2$ are neglected. Thus the $\log_{10}\bar{\Lambda}$ vs. $\log_{10}c$ plots

$$\bar{\Lambda} = \bar{A}c^{-1/2} + \bar{B}c^{1/2} + \dots \quad (42)$$

where

$$\bar{A} = \Lambda^0_1\sqrt{K_{2m}} \text{ and } \bar{B} = \Lambda^0_3 \frac{\sqrt{K_{2m}}}{2K_{3M}} + \frac{S}{8\sqrt{K_{2m}}}$$

for mixed salts, shown in Figure 4, are very similar to those of the pure salt solutions. Plots of $\Lambda c^{1/2}$ vs. c for the mixed salts (Figure 5) give straight lines at small

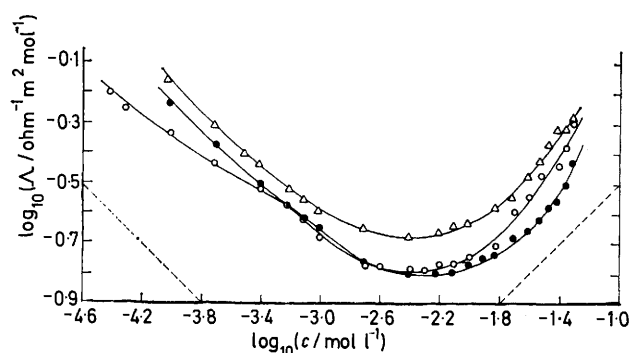


FIGURE 4 Plots of $\log_{10}\bar{\Lambda}$ vs. $\log_{10}c$ for equimolar mixtures of ammonium and sulphonium salts: (○) $\text{Bu}_4\text{N}^+\text{Br}^- + \text{Et}_2\text{S}^+\text{Br}^-$; (Δ) $\text{Bu}_4\text{N}^+\text{ClO}_4^- + \text{Et}_2\text{S}^+\text{MeBr}^-$; (●) $\text{Bu}_4\text{N}^+\text{I}^- + \text{Et}_2\text{S}^+\text{MeBr}^-$

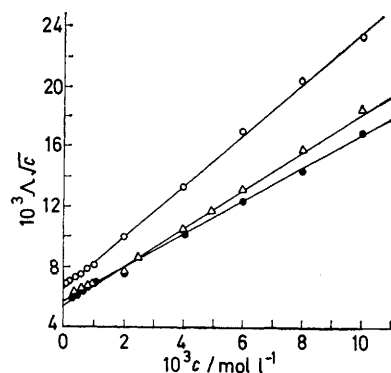
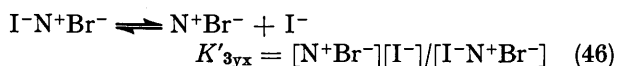
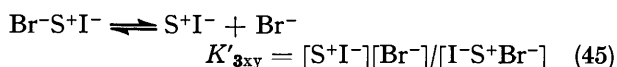
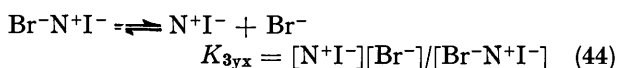
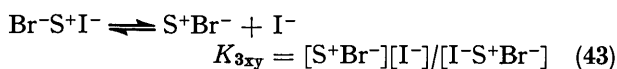


FIGURE 5 Plots of $\Lambda\sqrt{c}$ vs. c for equimolar mixtures of ammonium and sulphonium salts: (○) $\text{Bu}_4\text{N}^+\text{ClO}_4^- + \text{Et}_2\text{S}^+\text{MeBr}^-$; (Δ) $\text{Bu}_4\text{N}^+\text{Br}^- + \text{Et}_2\text{S}^+\text{MeBr}^-$; (●) $\text{Bu}_4\text{N}^+\text{I}^- + \text{Et}_2\text{S}^+\text{MeBr}^-$

concentrations and the intercepts and slopes give \bar{A} and \bar{B} , respectively. Values of K_{2m} and K_{3M} are known from the study of the single salts; hence S can be calculated from \bar{B} , from which F may be obtained, from which R may be obtained. The equilibrium constants K_{3xy} and K_{3yx} and the concentrations of all the ionic species listed

in equations (31)—(38) may then be calculated. The results for an equimolar mixture of sulphonium and ammonium bromides are given in Tables 2 and 4.

For a binary salt mixture containing four different ions, the situation becomes complex because of the large number of equilibrium constants. For a sulphonium salt represented by S^+Br^- and an ammonium salt represented by N^+I^- , the equilibria involved are the eight listed as equations (12)—(19), a second corresponding set of eight with Br^- replaced by I^- in equations (12)—(19), and the four given in equations (43)—(46).



In addition, from charge and material balance, the relations (47) and (48) are obtained. For this salt

the present case, the individual concentrations cannot be assumed to be $1/4c$. It was, therefore, necessary to apply a successive approximation technique. This was applied to the calculation of the concentrations of the four single ions and continued until these concentrations remained constant to three significant figures. An

$$K_{2m} = 1/4(K_{2x} + K_{2y} + K'_{2x} + K'_{2y}) \quad (49)$$

$$K_{3M}^{-1} = 1/4(K_{3x}^{-1} + K_{3y}^{-1} + K'_{3x}^{-1} + K'_{3y}^{-1}) \quad (50)$$

$$\rho_x = K_{2x}/K_{3x}; \quad \rho_y = K_{2y}/K_{3y}; \quad \rho'_x = K'_{2x}/K'_{3x};$$

$$\rho'_y = K'_{2y}/K'_{3y} \quad (51)$$

$$\rho_{xy} = K_{2x}/K_{3yx} = K_{2y}/K_{3xy} = K'_{2x}/K'_{3yx}$$

$$= K'_{2y}/K'_{3xy} \quad (52)$$

$$S = \rho_x + \rho'_x + \rho_y + \rho'_y + \rho_{xy} \quad (53)$$

internal check was then made by using these concentrations to calculate each of the four ion-pair concentrations. The sum of these ion-pair concentrations was found to exceed the stoichiometric concentration of the salt solution by 11—14%. This discrepancy is not considered to be outside of accumulated experi-

TABLE 4

Concentrations (10^5 c/mol l⁻¹) of ionic species in 0.05M-solutions of diethylmethylsulphonium bromide and of its equimolar solutions with ammonium salts in chloroform at 25.0 °C^a

	S ⁺ Br ⁻	1/2(S ⁺ Br ⁻ + N ⁺ Br ⁻)	1/2(S ⁺ Br ⁻ + N ⁺ I ⁻)	1/2(S ⁺ Br ⁻ + N ⁺ ClO ₄ ⁻)
[Br ⁻]	0.16	0.94	0.21 ₅	0.21
[S ⁺]	0.16	0.01 ₄	0.04 ₃	0.05
[N ⁺]		1.21	2.01	1.95
[I ⁻] or [ClO ₄ ⁻]			0.32	0.36
[S ⁺ Br ⁻]	ca. 5 000	ca. 2 500	1 830	2 000
[S ⁺ I ⁻] or [S ⁺ ClO ₄ ⁻]			950	800
[N ⁺ Br ⁻]		ca. 2 500	950	900
[N ⁺ I ⁻] or [N ⁺ ClO ₄ ⁻]			1 820	2 000
[Br ⁻ S ⁺ Br ⁻]	5.77	16.9	2.84	3.00
[S ⁺ Br ⁻ S ⁺]	5.77	0.25	0.56	0.72
[S ⁺ Br ⁻ N ⁺]		9.0	25 ± 15	39 ± 24
[Br ⁻ N ⁺ Br ⁻]		19.2	1.7	1.56
[N ⁺ Br ⁻ N ⁺]		25.00	15.8	14.50
[Br ⁻ S ⁺ I ⁻] or [Br ⁻ S ⁺ ClO ₄ ⁻]			12 ± 5	7 ± 5
[N ⁺ I ⁻ S ⁺] or [N ⁺ ClO ₄ ⁻ S ⁺]			38 ± 20	60 ± 40
[I ⁻ N ⁺ I ⁻] or [ClO ₄ ⁻ N ⁺ ClO ₄ ⁻]			4.8	13.33
[N ⁺ I ⁻ N ⁺] or [N ⁺ ClO ₄ ⁻ N ⁺]			30.2	72.22
[Br ⁻ N ⁺ I ⁻] or [ClO ₄ ⁻ N ⁺ Br ⁻]			190 ± 100	264 ± 156
[I ⁻ S ⁺ I ⁻] or [ClO ₄ ⁻ S ⁺ ClO ₄ ⁻]			2.17	1.63
[S ⁺ I ⁻ S ⁺] or [S ⁺ ClO ₄ ⁻ S ⁺]			0.29	0.23

^a S = Et₂SMe; N = Bu⁴N.

mixture, parameters analogous to the common anion case may be defined [equations (49)—(53)]. For equimolar salt mixtures with a common anion, the two ion-

$$[S^+] + [N^+] + [S^+Br^-S^+] + [N^+I^-N^+] +$$

$$[S^+Br^-N^+] + [N^+I^-S^+] + [S^+I^-S^+] + [N^+Br^-N^+]$$

$$= [Br^-] + [I^-] + [Br^-S^+Br^-] + [I^-N^+I^-] + [I^-S^+Br^-]$$

$$[Br^-N^+I^-] + [I^-S^+I^-] + [Br^-N^+Br^-] \quad (47)$$

$$[S^+Br^-] + [N^+Br^-] = [S^+I^-] + [N^+I^-] = c/2$$

and

$$[S^+Br^-] + [S^+I^-] = [N^+Br^-] + [N^+I^-] = c/2 \quad (48)$$

pairs may each be assumed to have a concentration equal to $1/2c$; however, with four different ion-pairs in

mental error. Eight equilibrium constants are used in the calculation and each is obtained from values read from a graph to two significant figures. An error in each equilibrium constant of 1.5% would account for a 12% discrepancy; in fact, the equilibrium constants probably have an error significantly greater than this.

All the electrolytic constants obtained for the mixed salts are shown in Table 2. From these equilibrium constants the concentrations of the different ionic species for mixed salts were calculated (Table 4). Because of the approximations in the calculations, it was not possible to obtain the concentrations of the unsymmetrical triple ions, except in a semi-quantitative manner. The error ranges shown represent estimates

of the limits within which the concentrations of the particular ions lie.

Tables 2 and 3 show that the two sulphonium perchlorates studied give very similar values for the electrochemical constants, equilibrium constants, and ionic concentrations. The diethylmethylsulphonium ion, therefore, is a good model for use in the interpretation of kinetic measurements on benzyldimethylsulphonium salts.

The results of Table 3 show that the single- and triple-ion concentrations in pure ammonium salts are several times greater than the concentrations of the corresponding ions in the pure sulphonium salt solutions. In the sulphonium salts, formation of the triple ion starts at concentrations of *ca.* $4 \times 10^{-3}M$, except for the chloride for which this concentration is a little lower, whereas for the ammonium salts the corresponding concentration is *ca.* $2 \times 10^{-3}M$. Since only a small fraction of the ammonium or the sulphonium salt exists as single and triple ions, these solutions consist almost entirely of ion-pairs.

In the mixed salt solutions, our major interest is in the concentrations of the triple ions, since it is *via* these species that the benzyl-containing ammonium salts in chloroform solution are believed to decompose.¹ In Table 4 $[Br^{-}S^{+}Br^{-}]$ and $[S^{+}Br^{-}S^{+}]$ are seen to change on addition of an equimolar amount of ammonium bromide in a dramatic fashion. The $[Br^{-}S^{+}Br^{-}]$ value increases by a factor of 3, whereas $[S^{+}Br^{-}S^{+}]$ decreases by a factor of 20. When ammonium iodide is added to sulphonium bromide, a slightly different situation occurs with both the sulphonium triple-ion concentrations decreasing, although the decrease in $[S^{+}Br^{-}S^{+}]$ is 10-fold whereas $[Br^{-}S^{+}Br^{-}]$ drops by only a factor of 2. In addition, other triple ions, such as $I^{-}S^{+}I^{-}$ and $S^{+}I^{-}S^{+}$, are formed, through which the reaction may also proceed.

In general, it is concluded that the sensitivity of the triple-ion concentrations to the presence of second salts in the solution should make the study of salt effects on kinetic measurements an effective way of obtaining

knowledge of the mechanism of the decomposition of sulphonium salts in chloroform solution.

EXPERIMENTAL

Materials.—The tetra-*n*-butylammonium salts were prepared from commercial tetra-*n*-butylammonium iodide by treating this salt (5 g, 0.0135 mol) dissolved in methanol (25 ml) with freshly prepared silver oxide (0.015 mol). The mixture was stirred until the supernatant liquid gave a negative test for iodide with acidified silver nitrate. The solution was then filtered and neutralized with the appropriate acid in methanol. The solvent was removed at reduced pressure and the salt was recrystallized. The salts prepared by this method had m.p.s in agreement with literature values and all were >99.9% pure (by analysis for the anion).

The sulphonium perchlorate salts were prepared from the corresponding sulphonium bromides by a method similar to that given above.

The diethylmethylsulphonium halides were prepared from the methyl halides and diethyl sulphide (in excess). After stirring the mixture in a closed flask for about 12 h, the crystalline sulphonium salt was filtered off under nitrogen and recrystallized.

The chloroform solvent was 'Matheson, Coleman, Bell chromatography reagent grade 99+ mol per cent' and was used without further purification. The gas chromatogram supplied with the solvent showed the presence of traces of hydrocarbon stabilizer.

Conductance Measurements.—The conductance cells had a capacity of *ca.* 30 cm³ and disc-shaped shiny platinum electrodes, about 12 mm in diameter and about 5 mm apart. The cell constants were *ca.* 0.25 cm⁻¹. A Wayne-Kerr Universal B221 conductance bridge and an oil-filled Tamson TV40 constant temperature bath, with maximum temperature variation $\leq \pm 0.01^{\circ}$, were used.

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