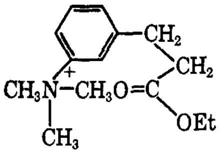
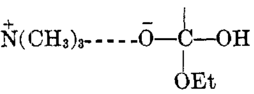
iodide analyses. Similar treatment of the *meta* compound gave a carbon analysis nearly 0.9% low, but satisfactory nitrogen and ionic iodide analyses. Both compounds decompose at the melting points [p-$(CH_3)_3N^+$, 176.4–176.8°; m-$(CH_3)_3N^+$, 76–78°] with evolution of methyl iodide. It appears that at the lower temperature, one-fourth to one-third fails to be oxidized to carbon dioxide during combustion analysis. Nitrogen and ionic iodide analyses are unaffected by this loss. A further indication of satisfactory purity was the consistency of the rate data for *m*- and *p*-ethyl and -methyl esters, corresponding with the reaction of at least 90% of the original ester in the kinetic solutions. Other physical constants are found in Table II.

The rate of alkaline hydrolysis of the m-$(CH_3)_3N^+$ ester is considerably greater than can reasonably be attributed (by comparison with the *para* isomer) to a slightly shorter inductive path through the carbon skeleton. Molecular models indicate that, in an extreme conformation, the carbonyl group is essentially in contact with the m-$(CH_3)_3N^+$ substituent



and a strong ion–dipole interaction (or, more probably, the ion–ion interaction



$$-\overset{+}{N}(CH_3)_3\text{- - - -}\overset{-}{O}-\underset{OEt}{\overset{|}{C}}-OH$$

following addition of hydroxide ion to the carbonyl[11]) should be possible. If an appreciable population of the extreme conformation existed in solutions of the *meta*-substituted ester, significant differences in the carbonyl region of the infrared might be anticipated. No such differences were found. The observed rate enhancement by the m-$(CH_3)_3N^+$ group would, however, be consistent with a very high reactivity of the relatively few molecules in the extreme conformation at a given time, due to the stabilization of the transition state for hydroxide ion attack.

Experimental Section

If the appropriately substituted cinnamic acid was not commercially available, it was synthesized by refluxing the corresponding benzaldehyde overnight with a 20% excess of malonic acid and a small amount of a 50:50 piperidine–pyridine mixture in 1,2-dimethoxyethane as the solvent. The resulting mixture was acidified while still hot with dilute HCl; the product was allowed to crystallize and was then recrystallized. The cinnamic acid was hydrogenated in 95% ethanol solution using a palladium on barium sulfate catalyst, and an initial hydrogen pressure of about 2 atm. The resulting β-phenylpropionic acid was isolated and recrystallized, and then esterified in a mixture of absolute ethanol, benzene, and HCl or H_2SO_4, with continuous removal of water as the ethanol–benzene–water azeotrope.

***m*-(β-Carbethoxyethyl)phenyltrimethylammonium Iodide.**—Ethyl β-(*m*-dimethylaminophenyl)propionate was dissolved in an excess of iodomethane. After several hours at room temperature the oily top layer was separated and taken up in absolute ethanol from which the product crystallized upon cooling. The crude crystals were recrystallized from acetone–heptane mixture. The somewhat hygroscopic ethyl ester appears to be converted by several recrystallizations from methanol to the methyl ester.

***p*-(β-Carbethoxyethyl)phenyltrimethylammonium Iodide.**—Ethyl β-(*p*-dimethylaminophenyl)propionate was dissolved in absolute ethanol, and an excess of iodomethane was added. The precipitated product was removed by filtration and was recrystallized from absolute ethanol. Repeated recrystallizations from methanol gave the corresponding methyl ester.

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(11) The authors are indebted to Professor E. S. Lewis for this suggestion.

Kinetics and Mechanism of Decomposition of the Trimethylsulfonium Cation

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The reactions (1) of the trimethylsulfonium cation with anions X^- (X = OEt, CN, I, SCN, N_3, Cl, F) to form dimethyl sulfide and CH_3X in ethanol and methanol at 100° are shown to be S_N2. Hydrolysis and methanolysis of $(CH_3)_3S^+$ also proceed by the S_N2 mechanism and methanol and ethanol are more nucleophilic toward $(CH_3)_3S^+$ than water. Ion association greatly influences the kinetics of (1) in ethanol. The equation $k_2^{\mu} = k_2^0\alpha^2$ (where α is the fraction of dissociated ions) fits the observed rates for (1) (X = Br), in ethanol at 100°, over a much larger range of ionic strength, μ, than does the Brønsted–Bjerrum equation. Nevertheless, the inclusion of formal activity coefficients leads to the conclusion that mechanisms involving separated ions $(CH_3)_3S^+$ and X^- are indistinguishable in terms of kinetic rate law from the ones involving $(CH_3)_3S^+X^-$ pairs.

In bimolecular decompositions (1) of trimethylsulfonium salts charges are being partially destroyed in the transition state and reaction rates increase with decreasing capacity of the medium to solvate charges. Such decompositions are particularly suitable for an investigation of salt effects, influence of solvent, and the

$$CH_3-\overset{+}{S}(CH_3)_2 + X^- \rightleftharpoons CH_3-X + (CH_3)_2S \qquad (1)$$

effect of X^-, on the kinetics of anion–cation reactions. The present paper describes such an investigation.

There has been some controversy[3–5] as to the mechanism of (1), but the reactions have been accepted as S_N2, by both Swain and Kaiser[4] and by Hughes Ingold, and Pocker.[6] The present work provides additional[6] evidence that in ethanol, the solvent used by

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(3) Y. Pocker, *Progr. Reaction Kinetics*, **1**, 224 (1961); *cf.* A. Strietweiser, Jr., *Chem. Rev.*, **56**, 610 (1956).

(4) C. G. Swain and L. E. Kaiser, *J. Am. Chem. Soc.*, **80**, 4089 (1958).

(5) J. L. Gleave, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 236 (1935).

(6) E. D. Hughes, C. K. Ingold, and Y. Pocker, *Chem. Ind.* (London), 1282 (1959).

Gleave, Hughes, and Ingold,[5] reaction 1 is S_N2 even with fairly weak nucleophiles and that both hydrolysis and methanolysis of $(CH_3)_3S^+$ are also S_N2 processes. The confusion as to mechanism arose because trimethylsulfonium halides are not completely dissociated in solvents like ethanol. Thus Jacobsen and Hyne[7] record an association constant of 150 for $(CH_3)_3SI$ in ethanol at 25°, and our measurements of conductance give association constants of 320 and 450 for $(CH_3)_3SBr$ in ethanol at 25 and 72°, respectively. Extrapolation gives an association constant K of 550 for $(CH_3)_3SBr$ in ethanol at 100°. Kinetic measurements on reaction 1 are usually made at ionic strengths 0.01–0.1 M, where $(CH_3)_3SI$ and $(CH_3)_3SBr$ are less than 50% dissociated in ethanol at 100°. Incomplete dissociation greatly influences the rate expressions used to interpret the observed rates for (1), as shown in eq 2–6. Neglecting activity coefficients, the rate of consumption of X^- in the S_N2 process 1 is given by

$$-\frac{d[X^-]}{dt} = k_i[(CH_3)_3S^+][X^-] + k_p[(CH_3)_3S^+X^-] \quad (2)$$

$$= (k_i + k_pK)[(CH_3)_3S^+][X^-] \quad (3)$$

$$= k[(CH_3)_3S^+][X^-] \quad (4)$$

$$= k\alpha^2C^2 \quad (5)$$

where k_i is the second-order rate constant for reaction between solvent separated ions, k_p is the first-order rate constant for reaction of ion pairs $[(CH_3)_3S^+X^-]$, K is the association constant for $(CH_3)_3S^+X^-$, and α is the fraction of the trimethylsulfonium salt at concentration C, which is dissociated. Neglecting activity coefficients, K is given by $(1 - \alpha)/\alpha^2C$, or if α is appreciably less than 1 by $1/\alpha^2C$, eq 5 tends toward (6) if

$$-\frac{d[X^-]}{dt} = \frac{kC}{K} = k'C \quad (6)$$

ion association is appreciable. Thus, the bimolecular reaction (1) will follow first-order kinetics if $(CH_3)_3SX$ is a weak electrolyte and second-order kinetics if $(CH_3)_3SX$ is a strong electrolyte, provided that $(CH_3)_3SX$ is the only electrolyte present.

Results and Discussion

Trimethylsulfonium bromide was chosen as a representative compound for a study of salt effects on reaction 1. We were interested in the question of whether collisions between solvent-separated ions lead more readily to the transition state than do the "sticky collisions"[8] resulting in the formation of an ion pair. However, it is not possible to determine k_i and k_pK separately from the rate of (1) (*cf.* eq 3) and the kinetic rate law cannot tell us if (1) proceeds as in (7) or (8). A reaction between X^- and the ion pair would be slower than (7) or (8) and in any case does not fit the observed kinetics (*vide infra*).

$$(CH_3)_3S^+ + X^- \rightleftharpoons \underset{\text{ion pair}}{(CH_3)_3S^+X^-} \text{—[transition state]} \rightarrow (CH_3)_2S + CH_3X \quad (7)$$

$$\underset{\text{ion pair}}{(CH_3)_3S^+X^-} \rightleftharpoons (CH_3)_3S^+ + X^- \text{—[transition state]} \rightarrow (CH_3)_2S + CH_3X \quad (8)$$

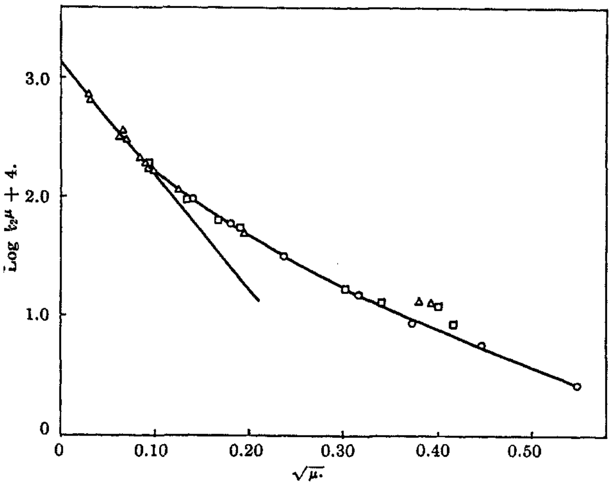

Figure 1.—Application of the Brønsted–Bjerrum equation to rate data (Table II) for reaction 1 (X = Br) in ethanol at 100° at ionic strength μ. Electrolytes present were △, $(CH_3)_3SBr$; ○, $(CH_3)_3SBr + LiClO_4$; □, $(CH_3)_3SBr$ + others (*cf.* Table II).

Trimethylsulfonium bromide decomposes 10^4 times more rapidly as the anion-solvating power of the solvent decreases from methanol to dimethylformamide.[9] The decomposition is also faster in solvents of lower dielectric constant[10a] (*cf.* methanol *vs.* ethanol, Table I). This would suggest that decomposition of $(CH_3)_3SBr$ would be fast at room temperature in a situation where anion and cation were only weakly solvated, and the dielectric constant was low. The back-reaction of (1), between two uncharged species, would be slow under these circumstances. Such a situation exists in dry solid trimethylsulfonium bromide; this compound is stable up to 194°. It then melts and is rapidly converted to gaseous products which have the odor of dimethyl sulfide. Apparently the lattice requirements of the crystal, the unfavorable orientation, and low kinetic

Table I

Decomposition of Trimethylsulfonium Salts[a]

X	n^b	log $k_2^{0.04}$ Ethanol (calcd[c])	Ethanol (obsd)	Methanol (obsd)
OEt[d]	5.86[e]	...	−0.745	...
CN[d]	5.1	−1.37	−1.4[f]	−2.15
I	5.04	−1.42	−1.41	...
SCN[d]	4.77	−1.63	−2.12	−2.80
N_3[d]	4.00	−2.26	−2.12	−2.84
Br	3.89	−2.35	−2.31	...
Cl	3.04	−3.04	−3.05	−3.83
F[g]	2.0	−3.88	−4.0[f]	−4.70[g]
ClO_4	0.0	−5.50	−5.37	−5.22

[a] Rate constants (log $k_2^{0.04}$) for reaction 1 in ethanol and methanol at 100°. Correlation with the equation log $k_2^{0.04} = -5.50 + 0.81n$ (where n is the nucleophilic constant of X^- in water[12]). Initially, $[(CH_3)_3SX] = 0.0200$ M, and $[LiClO_4]$ or $[NaClO_4] = 0.0200$ M. [b] See ref 12. [c] See eq 13. [d] These reactions had $NaClO_4$ as buffer, others had $LiClO_4$. [e] New nucleophilic constant calculated from eq 13. [f] Value calculated from the empirical relation log k_2(EtOH) − log k_2(MeOH) = 0.73 ± 0.05. [g] Reaction at 0.040 M $(CH_3)_3SF$ (no buffer).

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(7) A. L. Jacobsen and J. B. Hyne, *J. Am. Chem. Soc.*, **82**, 2418 (1960).

(8) F. M. Beringer and E. M. Gindler, *ibid.*, **77**, 3203 (1955).

(9) A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

(10) (a) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp 123–130; (b) "International Critical Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p 85. Listed values for the dielectric constant of ethanol from −80 to 60° give on extrapolation to 100° a value of 16.

TABLE II

SALT EFFECTS IN THE DECOMPOSITION OF TRIMETHYLSULFONIUM BROMIDE[a]

$[(CH_3)_3S^+]$	$[Br^-]$	$[Li^+]$	$[ClO_4^-]$	$[NO_3^-]$	μ	$10^3k_2^{\mu}$, M^{-1} sec^{-1}	% reaction
20.0	20.0	280.0	280.0	...	300.0	0.340	*b*
20.0	20.0	180.0	180.0	...	200.0	0.575	*b*
13.8	153.8	160.0	20.0	...	174.7	0.843	11
11.4	151.4	160.0	20.0	...	172.6	0.875	18
20.0	20.0	140.0	...	140.0	160.0	1.23	*b*
149.0	149.0	...	...	...	154.0	1.26	6
141.0	141.0	...	...	...	145.0	1.35	5
20.0	20.0	120.0	120.0	...	140.0	0.892	*b*
97.6	17.6	20.0	...	100.0	118.6	1.70	9
96.8	16.8	20.0	...	100.0	117.2	1.52	5
14.8	94.8	100.0	20.0	...	115.7	1.26	11
12.4	92.4	100.0	20.0	...	113.6	1.09	16
20.0	20.0	80.0	80.0	...	100.0	1.55	*b*
14.4	74.4	80.0	20.0	...	95.7	1.71	15
12.4	72.4	80.0	20.0	...	93.4	1.63	14
15.6	15.6	40.0	40.0	...	57.3	3.00	18
34.8	14.8	20.0	...	40.0	56.9	3.32	11
14.8	34.8	40.0	20.0	...	56.6	3.17	19
14.3	14.3	40.0	40.0	...	54.9	2.72	8
32.4	12.4	20.0	...	40.0	53.6	3.30	7
12.4	32.4	40.0	20.0	...	53.6	2.88	16
15.6	15.6	20.0	...	20.0	37.4	5.87	18
35.2	35.2	...	...	...	37.1	4.77	10
16.0	16.0	20.0	20.0	...	37.1	4.88	13
14.0	14.0	20.0	...	...	35.0	4.95	12
13.4	13.4	20.0	...	20.0	34.5	5.25	14
31.2	31.2	...	...	...	33.2	6.15	11
7.2	17.2	20.0	...	10.0	28.2	6.53	22
5.6	15.6	20.0	...	10.0	26.4	6.30	22
8.4	8.4	10.0	10.0	...	19.1	9.54	14
8.1	8.1	10.0	...	10.0	18.8	9.81	18
7.3	7.3	10.0	10.0	...	17.8	9.61	13
6.9	6.9	10.0	...	10.0	17.5	9.80	15
15.0	15.0	...	...	...	16.3	11.4	15
12.4	12.4	...	...	...	13.7	11.4	16
10.95	0.95	...	10.0	...	11.0	16.1	10
0.94	10.45	9.51	...	...	11.0	18.0	11
8.97	8.97	...	...	...	9.50	16.2	10
8.23	8.23	...	...	...	8.60	18.6	8
7.50	7.50	...	...	...	8.20	17.3	17
7.61	7.61	...	...	...	7.92	18.4	7
6.00	6.00	...	...	...	6.80	20.9	20
4.37	4.37	...	...	...	4.64	29.7	11
3.99	3.99	...	...	...	4.18	36.0	9
3.71	3.71	...	...	...	3.85	30.7	7
0.86	0.86	...	...	...	0.90	63.7	7
0.76	0.76	...	...	...	0.80	69.5	12

[a] Rate data at 100° from reaction 1 (X = Br) in ethanol, in the presence of other ions at ionic strength μ. Concentrations of ions, in millimoles per liter, are the stoichiometric values at time *t*, μ is the mean ionic strength over the percentage reaction recorded, and k_2^{μ} is the stoichiometric second-order rate constant calculated over the percentage of reaction in time *t*. [b] k_2^{μ} was constant over the first 20% reaction, so initial rates, at the initial ionic strength, are recorded.

energy of $(CH_3)_3S^+$ and Br^- ions help to prevent decomposition of solid trimethylsulfonium bromide at lower temperatures. Insofar as ion pairs and higher aggregates in solution resemble trimethylsulfonium bromide in the crystal lattice, the stability of solid trimethylsulfonium bromide warns that the possibility should not be dismissed that the partners of an ion pair like $(CH_3)_3S^+X^-$ possess less kinetic energy than the separated ions and are also held in an unfavorable orientation of X^- and the carbon atom at which substitution eventually takes place.

The observed rates of reaction 1 (X = Br) at 100°, expressed as initial stoichiometric second-order "constants," k_2^{μ}, in ethanol, at ionic strength μ are in Table II. If trimethylsulfonium bromide is the only electrolyte, k_2^{μ} decreases by a factor of 60 for a 200-fold increase in μ and this can be analyzed in two ways (Table III).

A. Brønsted–Bjerrum Treatment.[11]—The Brønsted–Bjerrum equation for a reaction like (1), *i.e.*, between two oppositely charged univalent ions, is

$$\log k_2^{\mu} = \log k_2^{\circ} - 9.2\sqrt{\mu} \tag{9}$$

where μ is the ionic strength, k_2° is the rate constant at infinite dilution, and the coefficient 9.2 is evaluated using a dielectric constant of 16, for ethanol at 100° (*cf.* ref 10b). A plot of log k_2^{μ} *vs.* $\sqrt{\mu}$ is shown in Figure 1. The data were obtained using a variety of support-

Table III

Brønsted–Bjerrum *vs.* Ion-Pair Treatment[a]

$[(CH_3)_3SBr]$, mole$^{\mu}$/l.	α	$10^3k_2^{\alpha}$, M^{-1} sec^{-1} Obsd	Calcd (eq 9)	Calcd (eq 10)
0.154	0.0987	1.26	0.027	1.26
0.145	0.102	1.35	0.036	1.35
0.0900	0.128	1.88	0.256	2.13
0.0371	0.191	4.77	2.02	4.75
0.0332	0.209	6.15	2.59	5.68
0.0163	0.272	11.4	8.33	9.62
0.00950	0.340	16.2	15.9	15.0
0.00820	0.360	17.3	18.5	16.8
0.00464	0.445	29.7	30.0	25.8
0.00385	0.476	30.7	34.2	29.5
0.00900	0.720	68.6	68.3	67.4
0.000802	0.737	69.5	70.7	70.6

[a] Rates of reaction 1 (X = Br) at ionic strength μ (*cf.* Table II) in ethanol at 100°, in the absence of other electrolytes, expressed in terms of the rate eq 9 and 10 (where α is the degree of dissociation of $(CH_3)_3SBr$, and $k_2°$ is 1.30×10^{-1} M^{-1} sec^{-1}).

ing electrolytes to obtain the "stoichiometric" ionic strength μ taken from Table II. The slope d log $k_2^{\mu}/d\sqrt{\mu}$ is 9.35 at $\mu < 0.01$ M, and the deviations from linearity at higher ionic strengths are to be expected in terms of the Brønsted–Bjerrum treatment.[10a] Extrapolation to zero ionic strength gives $k_2° = 1.3 \times 10^{-1}$ M^{-1} sec^{-1} (Figure 1 and Table II and III).

Despite the limited success of the Brønsted–Bjerrum equation (9) in the interpretation of rate data for reaction 1 (X = Br) in ethanol at 100°, we prefer a simpler treatment, based on the incomplete dissociation of trimethylsulfonium bromide, for the interpretation of the rate data in Table III, which were obtained when trimethylsulfonium bromide was the only electrolyte present.

B. Ion-Pair Treatment.—Equation 5 can be expressed as in (10). This fits the rate data of Table III

$$k_2^{\mu} = k_2°\alpha^2 \qquad (10)$$

at *all* ionic strengths studied, *i.e.*, 0.0008 to 0.30 M. Values of α were calculated from $K_{100} = 550$ for trimethylsulfonium bromide in ethanol. The rate constant at infinite dilution, $k_2°$, is 1.30×10^{-1} M^{-1} sec^{-1} which is identical with the value obtained by the Brønsted–Bjerrum treatment.

Beringer and Gindler[11] derived an equation (11) for anion–cation reactions, by assuming that ion pairs are the only reactive species (*i.e.*, reaction path 7). Their equation, in our notation, would be

$$k_2^{\mu} = \frac{k_pK}{1 + KW} \qquad (11)$$

where $W = [(CH_3)_3S^+] + [Br^-] + [(CH_3)_3S^+Br^-]$. Since $k_pK = k_2°$ (*cf.* eq 3 where $k_pK >> k_i$) and W is $(1 + \alpha)c$, eq 11 is identical with (10). It is not necessary to assume greater reactivity for either ion pairs or separated ions in order to derive the simpler equation (10).

The rate data for reaction 1 (X = Br) in the presence of $(CH_3)_3SClO_4$, $(CH_3)_3SNO_3$, LiBr, $LiNO_3$, and $LiClO_4$, respectively (Table II), can in principle be treated by eq 12, which is a modified form of (10),

$$k_2^{\mu} = k_2°\alpha\alpha^1 \qquad (12)$$

where α and α^1 are the fractions of the stoichiometric concentration of $(CH_3)_3S^+$ and Br^-, respectively, which exist as separated, reactive ions. There is little variation in k_2^{μ} at the same stoichiometric ionic strength μ up to 0.10 M, no matter which of the above salts is the accompanying electrolyte. This is only possible in terms of (12) if these salts have association constants within the range 200–800 in ethanol at 100°. This is not unlikely, but appropriate measurements have not been made. In the presence of a relatively high concentration of lithium perchlorate, the reaction is slightly slower at the same ionic strength than if $(CH_3)_3SBr$ is the only electrolyte present. This could be because lithium perchlorate is slightly more dissociated than $(CH_3)_3SBr$, LiBr, or $(CH_3)_3SClO_4$ in ethanol.

Mechanism of Displacement by Anions.—The following observations suggest that, in the solvents studied, reaction 1 is an SN2 process.

A. Kinetics.—Tables II and IV show that reaction 1 (X = Br, Cl) is first order in $[(CH_3)_3S^+]$ and $[X^-]$ at a variety of concentrations of $(CH_3)_3S^+$ and X^-, provided that the ionic strength is effectively constant, indicating that the stoichiometric composition of the activated complex is $(CH_3)_3S^+$, X^-. The dependence of rate on the first power of $[X^-]$ confirms that the reaction between X^- and the ion pair $(CH_3)_3S^+X^-$ is not kinetically significant.

B. Salt Effects.—The large salt effects observed for (1) (X = Br) were similar when X was Cl or I (Table IV). The salt effects can be rationalized in terms of both the Brønsted–Bjerrum equation and the ion-pair equation (10). These equations would only hold if (1) were a bimolecular reaction between ions of opposite unit charge.

Table IV

Decomposition of Trimethyl Sulfonium Chloride and Iodide[a]

$[(CH_3)_3S^+]$	$[Cl^-]$	$[I^-]$	$[Li^+]$	$[ClO_4^-]$	μ	$10^3k_2^{\mu}$, M^{-1} sec^{-1}
10.4	...	10.4	20.0	20.0	31.2	52
30.4	...	10.4	...	20.0	31.0	53
10.0	...	10.0	...	...	10.6	89
7.2	...	7.2	...	...	7.9	140
20.0	50.0	...	50.0	20.0	70.0	0.62
20.0	20.0	...	50.0	50.0	70.0	0.62
20.0	20.0	...	20.0	20.0	40.0	0.89
18.6	18.6	...	...	...	18.9	1.46
14.0	14.0	...	...	...	14.8	2.66

[a] Rates at 100° for reaction 1 (X = Cl and I) in ethanol at ionic strength μ. Concentrations are in millimoles per liter, μ and k_2^{μ} are as described in Table II.

C. Solvent Effects.—Reaction 1 (X = CN, SCN, N_3, Cl) is five times faster in ethanol than in methanol at the same ionic strength (Table I) as would be expected for a bimolecular reaction between ions of opposite charge in media of decreasing solvating capacity and dielectric constant.[10a]

D. Nucleophilicity of X⁻.—The rates of (1) at ionic strength 0.04 M in ethanol at 100° fit eq 13 (where n is the Swain and Scott[12] nucleophilic constant of X^- in water) as shown in Table I. Only the reaction with

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(11) F. M. Beringer and E. M. Gindler, *J. Am. Chem. Soc.*, **77**, 3200 (1955).

(12) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953); J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 161.

$$\log k_2^{0.04} = -5.50 + 0.81n \qquad (13)$$

SCN^- does not fit (13). The observed rate required $n = 4.17$ rather than 4.77.[12] We also find $n = 5.86$ for ethoxide ion in ethanol, which is much greater than the value 4.20[12] for hydroxide ion in water. Hydroxide ion in water has a much greater nucleophilic constant for its reaction with the mustard cation than for its reaction with methyl bromide.[12] That this is not a general feature of reactions of *lyate* ions with cations, brought about by ease of penetration of the cation solvation shell, is shown by the behavior of ethoxide ion in ethanol, which reacts three times more rapidly than the nonylate iodide ion in ethanol with $(CH_3)_3S^+$ and with methyl bromide[12,13] at 100°. It is of interest to note that the reaction constant 0.81 found for the decomposition of $(CH_3)_3SBr$ in EtOH is similar to the value 1.0 recorded for the generally accepted SN2 reactions of CH_3Br in water at 25.0°.

E. Reaction Products.—Acid is not formed during the first 30% of (1) (X = Cl, Br, N_3, SCN, CN) in ethanol at 100°. The ambident nucleophile,[14] CN^-, gives exclusively CH_3CN, not CH_3NC. These observations accord with our suggestion that the SN2 mechanism is operative here, for if CH_3^+ were produced it would be expected to be an extremely reactive and indiscriminating intermediate.

Free *vs.* Paired Ions.—All the above might be taken as a strong indication that the reaction must go by way of a bimolecular collision process involving dissociated sulfonium ions and X^-. Actually, because of the equilibrium between free and paired ions, it is no more proof for an SN2 mechanism involving two free ions than for one involving pairs. If activity coefficients are included, the rate equations will become for (7)

$$v = k[(CH_3)_3S^+][X^-]\frac{f^+f^-}{f^*}$$

and for (8)

$$v = k'[(CH_3)_3S^+X^-]\frac{f^\pm}{f^*} = k'K[(CH_3)_3S^+][X^-]\frac{f^+f^-}{f^*}$$

Clearly the free-ion mechanism and the ion-pair mechanisms are indistinguishable as far as the effect of ionic strength, pressure,[15] etc., on activity coefficients is concerned. According to transition-state theory the rate constant k includes an equilibrium constant for the formation of a neutral dipolar activated complex from two oppositely charged ions, and the apparent rate constant $k'K$ includes an equilibrium constant for the formation of an ion pair (*i.e.*, a formally neutral species) from two oppositely charged ions. Therefore, the theoretical effect of changing dielectric constant and ionic strength on the rate constant will be the same for both mechanisms.

The Solvolytic Mechanism.—The second-order rate constant for solvolysis was calculated by means of (14).

$$\frac{d[H^+]}{dt} = k_2[(CH_3)_3S^+][ROH] \qquad (14)$$

Trimethylsulfonium perchlorate in water, methanol, or ethanol at 100° decomposes to give dimethyl sulfide and acid (eq 15), and the formation of acid follows first-order kinetics. Three possible reaction schemes (16, 17, and 18) fit these observations. In these solvolytic

$$(CH_3)_3SClO_4 + ROH \longrightarrow (CH_3)_2S + HClO_4 + CH_3OR \qquad (15)$$

$$CH_3{-}\overset{+}{S}(CH_3)_2 + ClO_4^- \xrightleftharpoons{S_N2} CH_3ClO_4 + (CH_3)_2S \xrightarrow[\text{fast}]{ROH} CH_3OR + HClO_4 + (CH_3)_2S \qquad (16)$$

$$CH_3{-}\overset{+}{S}(CH_3)_2 \xrightleftharpoons{S_N1} \overset{+}{C}H_3 + (CH_3)_2S \xrightarrow[\text{fast}]{ROH} CH_3OR + H^+ + (CH_3)_2S \qquad (17)$$

$$CH_3{-}\overset{+}{S}(CH_3)_2 + ROH \xrightleftharpoons{S_N2} CH_3\overset{+}{O}RH + (CH_3)_2S \rightleftharpoons CH_3OR + H^+ + (CH_3)_2S \qquad (18)$$

reactions, SN2 attack by RO^- is not kinetically significant because k_1 does not decrease as $[H^+]$ increases with progress of the reaction. Trimethylsulfonium perchlorate at 100° decomposes more rapidly in methanol ($k_1 = 2.4 \times 10^{-7}$ sec^{-1}) than in ethanol ($k_1 = 1.64 \times 10^{-7}$ sec^{-1}) than in water ($k_1 = 1.3 \times 10^{-9}$ sec^{-1}). This eliminates (16) and (17) as a possible mechanism because SN2 attack by ClO_4^- as suggested in (16) would be faster in ethanol than in the more ionizing solvent methanol (Table I).

The solvolytic rate of *t*-butyldimethylsulfonium perchlorate is faster (in terms of k_1) in the less ionizing solvent, ethanol, than in methanol and than in water,[16] as expected, because in SN1 reactions of sulfonium salts charge is dispersed on going from ground state to the transition state.[17] However, reaction 15 has a greater k_1 in methanol than in ethanol, indicating that the solvolysis of $(CH_3)_3S^+ClO_4^-$ cannot be SN1 in methanol. Since (15) is not SN1 in methanol, it is unlikely to be SN1 in the more ionizing solvent, water.[17] Methyl halides rarely if ever ionize by an SN1 mechanism in hydroxylic media despite the assistance given to ionization by solvation of the forming halide ion. There is even less reason for $CH_3{-}S^+(CH_3)_2$ to react as in (17) in solution because solvation retards rather than assists formation of the activated complex. The second-order rate constants at 100°, calculated from (14) and k_1 for solvolysis are $k_2^{MeOH} \cong 1.0 \times 10^{-8}$ l. mole^{-1} sec^{-1}; $k_2^{EtOH} \cong 1.0 \times 10^{-8}$ l. mole^{-1} sec^{-1}; $k_2^{H_2O} \cong 2.3 \times 10^{-11}$ l. mole^{-1} sec^{-1}. The order of nucleophilicity MeOH = EtOH > H_2O is not unexpected, and since (16) and (17) are not applicable, the SN2 solvolytic mechanism (18) is suggested for reaction 15.

In conclusion we would like to point out that no matter how weakly nucleophilic the accompanying anion, the solvolysis of $(CH_3)_3S^+$ in methanol and water is not an SN1 process (17), nor is there any indication that the reaction becomes SN1 in ethanol.

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Experimental Section

Solvents.—Ethanol was distilled from ethyl phthalate-sodium ethoxide, methanol was distilled from magnesium amalgam.

Salts.—Trimethylsulfonium iodide was precipitated from a mixture of methyl iodide and excess dimethyl sulfide left for over 24 hr in nitromethane at room temperature. It was converted to the hydroxide with moist silver oxide, and then to the appropriate $(CH_3)_3SX$ compound by neutralization with HX ($X = Cl, Br, ClO_4, NO_3$). These salts and all lithium or sodium salts were recrystallized from acetone–ether mixtures and dried *in vacuo* at 50° for at least 48 hr. They were neutral in aqueous solution. In the cases where AgX is only sparingly soluble, the purity of $(CH_3)_3SX$, NaX, and LiX was confirmed by a potentiometric titration against standard silver nitrate. For reactions in the presence of a buffer salt (*cf.* Table I), trimethylsulfonium perchlorate and the sodium or lithium salts of X were mixed in the solvent without isolation of Me_3SX. This was an advantage for X = OEt, because the salt is difficult to isolate without decomposition. Trimethylsulfonium fluoride was prepared from $(CH_3)_3SClO_4$ and potassium fluoride by precipitation of $KClO_4$.

Technique of Runs.—Reactions were carried out in sealed tubes at 100.0° in an oil-bath thermostat. Triplicate tubes were removed at each time interval, the contents poured into ice–water, and X^- was estimated potentiometrically with silver nitrate, for X = Br, Cl, I, SCN, N_3, and CN. With X = F, reaction was in sealed silver reaction tubes at 100°. The contents of duplicate tubes were washed into cold methanol and nitrogen was bubbled through each to remove methyl fluoride and dimethyl sulfide. An equal volume of excess sodium methoxide was added to each sample and one sample was analyzed immediately for methoxide by titration with hydrochloric acid to pH 4. The other sample was heated at 100° for 2 hr to decompose $(CH_3)_3S^+$ (reaction 1, X = OMe) and was then analyzed for methoxide as above. The differences between the two titrations gave the concentration of $(CH_3)_3S^+$ which had not reacted with fluoride ion in the original sample. Methanolysis accompanied attack by fluoride ion, as shown by formation of acid during reaction. This was allowed for[18] in the calculation of k_2 for reaction 1 (X = F).

Solvolysis of trimethylsulfonium perchlorate was followed by measuring $d[H^+]/dt$ by titration with sodium hydroxide. Reaction 1 (X = OEt) was killed with excess hydrochloric acid and back-titrated with sodium hydroxide.

Reactions were rarely followed to >30% completion because solvolysis of CH_3X and the reverse reaction (1) interfered with the kinetics in some cases (X = I). The pH of each sample was measured (X = Br, Cl, I, SCN, N_3, SCN). Acid was often detected after 20% reaction (X = halogen) at high ionic strength; such samples were affected by solvolysis and were not used in the calculation of rate constants.

Calculation of Rate Constants.—Equation 19 was used to calculate rate constants.

$$k_2^{\mu} = \frac{x}{at_x(a - x)} \qquad (19)$$

where x is the decrease of $[X^-]$ in time t_x between two successive samples, a and $a - x$ are the stoichiometric concentrations of X^- at the first and the second of two successive samples, respectively, and μ is the mean ionic strength between the two successive samples.

Reaction Products.—Dimethyl sulfide was identified as the mercuric chloride complex,[19] and consumption of X^- was followed with silver nitrate. Acid was not produced in samples used for estimation of rate constants except for solvolysis reactions and attack by fluoride ion. Methyl cyanide from (1) (X = CN) was hydrolyzed and the ammonia was estimated.[20] The yield was quantitative, showing that CH_3NC was not formed.

Conductance of Trimethylsulfonium Bromide.—The conductance of this salt in dry ethanol was measured[7] at 25 and 72° in a tightly stoppered cell. Measurements were made between 10^{-2} and 10^{-4} M. Association constants were calculated by the Fuoss method.[21] A linear extrapolation of $K_{25} = 320$ and $K_{72} = 450$ gave $K_{100} = 550$.

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The Boron–Nitrogen Bond from the Boron–Sulfur Bond

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Boron sulfide and alkyl orthothioborates react with primary and secondary amines and with hydrazines to give aminoboron derivatives.

The boron–nitrogen bond can be formed by means of several types of reactions between organic bases and inorganic sources of boron. Boron halides,[1,2] boron hydrides,[3,4] and organometallic derivatives with boron halides[5,6] have been used as sources of compounds containing boron and nitrogen. In the course of a systematic investigation of the reactivity of boron sulfide toward organic molecules, the reaction of B_2S_3 with bases (amines and hydrazines) as a source of nitrogen derivatives of boron has been examined.

Mikhailov and his co-workers have reported the formation of the B–N bond starting from the B–S bond.[4,7] In one instance the new nitrogen derivative of boron was obtained by the action of 1,6-hexanediamine on 2,4,6-triisobutylthio-1,3,5-trimethylborazine to give polymeric material. But neither boron sulfide (B_2S_3) nor orthothioboric esters [$(RS)_3B$] have been used as starting material for the preparation of aminoboron compounds. In fact, dialkyl alkylthioborate esters have been prepared by the reaction of alkanethiols with trimethylamine alkylboranes.[8]

We have already shown that boron sulfide behaves as a dehydrogenating agent with organic molecules containing labile hydrogens, such as alcohols, mercaptans, and active methylene groups,[9–11] and it was expected that the hydrogen carried by amino groups would be reactive enough to interact with B_2S_3.

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