

significant shifts in the ratio of O:C protonation. Reliable quantitative data will only come from measurements at low solute concentration, well below the concentrations necessary for continuous wave nmr work, using carefully purified acids of precisely deter-

mined composition. Ambident bases have not yet been the subject of such a study in superacid media.

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Nucleophilic Reactivities of Halide Ions in Molten Triethyl-*n*-hexylammonium Triethyl-*n*-hexylboride

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Abstract: Reactions of tetraethylammonium halides with methyl *p*-toluenesulfonate in molten triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) at 35° proceed with relative rate constants Cl^- 2.1, Br^- 1.2, and I^- 1.0. The halide ions in $N_{2226}B_{2226}$ follow the same reactivity order as dissociated halide ions in polar aprotic solvents, but the range of relative rate constants in $N_{2226}B_{2226}$ is much narrower, probably because the smaller the halide ion, the more its activity is reduced by neighboring tetraalkylammonium ions.

Molten tetraalkylammonium tetraalkylborides¹ are a unique class of solvents. They can interact with themselves or with solutes only by electrostatic, ion-dipole, ion-induced dipole, and dispersion forces; their structures permit no Lewis acid-base interactions. One goal of our investigation of this new class of solvents is to determine how they affect rates of several important types of chemical reactions.²

The rates of bimolecular nucleophilic substitution reactions of anions with neutral substrates are markedly affected by ion association. Before 1960 the accepted relative nucleophilicities of the halide ions were $I^- > Br^- > Cl^-$, based only on data in protic solvents.³ Winstein and coworkers⁴ found the reactivity order $Cl^- > Br^- > I^-$ for reactions of dissociated halide ions with *n*-butyl *p*-bromobenzenesulfonate in acetone, and the same order has been found for S_N2 reactions in other dipolar aprotic solvents.⁵⁻⁸ We report here rates of reaction of tetraethylammonium halides with methyl *p*-toluenesulfonate in molten triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$), which provide information on the effect of neighboring tetraalkylammonium ions on halide ion reactivities.

Results

Rates of disappearance of halide ions were followed

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(2) W. T. Ford and R. J. Hauri, *J. Amer. Chem. Soc.*, **95**, 7381 (1973).

(3) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 9-11; (b) C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).

(4) S. Winstein, L. G. Svedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, No. **9**, 24 (1960).

(5) W. M. Weaver and J. D. Hutchison, *J. Amer. Chem. Soc.*, **86**, 261 (1964).

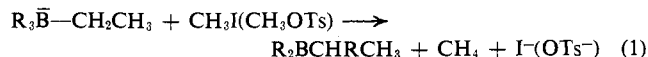
(6) (a) R. F. Rodewald, K. Mahendran, J. L. Bear, and R. Fuchs, *J. Amer. Chem. Soc.*, **90**, 6698 (1968); (b) R. Fuchs and K. Mahendran, *J. Org. Chem.*, **36**, 730 (1971).

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titrimetrically. However, the calculated second-order rate constant⁹ decreased throughout each kinetic run. The deviation of the data from a second-order rate law was greater for reactions of iodide salts than for reactions of bromide and chloride salts.

To determine the cause of the decreases in observed rate constants, the stabilities of methyl tosylate and methyl iodide in $N_{2226}B_{2226}$ were investigated. The pmr spectrum of a 0.44 *M* solution of methyl tosylate in $N_{2226}B_{2226}$ remained unchanged after 24 hr at 35°, but at 60° the methyl tosylate methyl signals disappeared with a first-order rate constant of $1.0 \times 10^{-6} \text{ sec}^{-1}$. Similar pmr experiments with initially 0.15-0.28 *M* methyl iodide in $N_{2226}B_{2226}$ showed that methyl iodide disappeared with a half-life of less than 24 hr at 35°. In the pmr spectra of both the methyl tosylate and the methyl iodide solutions, a new singlet appeared at δ 0.16, which we attribute to methane, the area of the B-CH₂ multiplet decreased, and the area of the broad methyl and methylene signals increased. Because these results are explained by eq 1 and are consistent with



earlier results of Haag and Hesse,¹⁰ who found that tetraalkylboride ions acted as hydride donors toward alkylating agents, no further investigation was made of the products of reactions of methyl iodide with $N_{2226}B_{2226}$.

In the reactions between iodide salts and methyl tosylate, the product, methyl iodide, reacts with the solvent to generate iodide ion, which results in a downward drift of the second-order rate constants calculated from titrimetric data. Presumably the lesser drifts in calculated rate constants of the reactions of chloride and bromide salts with methyl tosylate are due to reactions of methyl chloride and methyl bromide with $N_{2226}B_{2226}$.

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 17.

(10) A. Haag and G. Hesse, *Justus Liebig's Ann. Chem.*, **751**, 95 (1971).

To determine the reactivity of methyl iodide with $N_{2226}B_{2226}$ under conditions comparable to those used for reactions of iodide salts with methyl tosylate, the formation of iodide ion from initially 0.0259 *M* methyl iodide was followed titrimetrically at 35.08°. The rate was not simply first order. In the first 20 min *ca.* 0.012 *M* iodide ion was formed, and then iodide ion formation slowed to a first-order rate constant of $3.9 \times 10^{-5} \text{ sec}^{-1}$ for data taken from 0.5 to 8.5 hr reaction time. A rate constant for the rapid early reaction was not determined because of difficulty in transferring and weighing aliquots of the viscous molten salt solution. Analysis of a plot of iodide ion concentration *vs.* time suggests that the fast initial disappearance of methyl iodide is due to reaction with an impurity in the $N_{2226}B_{2226}$, whose initial concentration is in the 0.010–0.013 *M* range, and that the slow first-order reaction is due to reaction with $N_{2226}B_{2226}$.

Because of this complex kinetic behavior, rate constants for reactions of halide salts with methyl tosylate in $N_{2226}B_{2226}$ were determined by two methods. First, rate constants were calculated from the first data point, generally taken after disappearance of 39–43% of the initial halide ion. These approximate initial rate constants, shown in column 2 of Table I, are valid only if

Table I. Rate Constants k_3 ($10^2 M^{-1} \text{ sec}^{-1}$) for Reaction of Methyl Tosylate with Halide Ions in Molten $N_{2226}B_{2226}$ at $35.07 \pm 0.01^\circ$

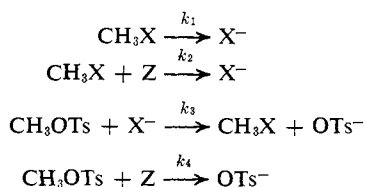
Halide	Assumed conditions			$k_4 = 3.82 \times 10^{-2} M^{-1} \text{ sec}^{-1}$
	One point ^b	$k_4 = 0^c$	$k_4 \gg k_3^c$	
Cl	2.27	2.11	3.03	2.50
Cl	1.89	1.99	3.00	2.39
Br	1.18	1.19	1.60	1.38
Br	1.11	1.15	1.54	1.35
Br	1.10	1.15	1.63	1.38
I	0.944	1.01	1.32	1.16
I	0.911	0.966	1.26	1.13

^a Initial concentrations were tetraethylammonium halides, 0.0233–0.0275 *M*, and methyl tosylate, 0.0470–0.0541 *M*. ^b Based on one point taken after *ca.* 40% disappearance of halide assuming k_1 , k_2 , and k_4 are negligible. ^c $Z = 0.012 M$; k_3 was determined from analog computer fit to experimental data as described in text.

production of halide ion from methyl halide is negligible during the first 40% of reaction of halide ion.

Second, the titrimetric data were fitted to the mechanism of Scheme I with the aid of an analog computer.

Scheme I



In this mechanism X^- is halide and Z is the component of the $N_{2226}B_{2226}$ to which we attribute the rapid initial liberation of iodide ion from methyl iodide. With $Z = 0.013 M$ rate constants k_3 for reactions of halide ions with methyl tosylate were determined for five different assumed values of k_4 ranging from $k_4 = 0$ to $k_4 \gg k_3$. Rate constants based on these extreme assumptions and on an intermediate value of k_4 , which assumes that

Z reacted with methyl tosylate about three times as fast as with methyl bromide, are in columns 3–5 of Table I. The analog computer fits of the mechanism to the experimental data were independent of k_2 as long as k_1 was adjusted. Consequently, k_2 was arbitrarily set equal to zero, and k_1 and k_3 were adjusted to fit the data. This procedure gave k_3 with the reasonable precision shown in Table I but gave poor precision in values of the much smaller k_1 .

Comparison of the initial rate constants in column 2 of Table I with the analog computer solutions for $k_4 = 0$ in column 3 shows reasonable agreement between the two methods. When $k_4 \gg k_3$ is assumed (column 4), the calculated values of k_3 are larger, and the assumption $k_4 = 3.82 \times 10^{-2} M^{-1} \text{ sec}^{-1}$ leads to intermediate values of k_3 . Regardless of which set of assumptions is made, the *relative* reactivities of halide salts toward methyl tosylate are $\text{Cl}^- 2.2 \pm 0.1$, $\text{Br}^- 1.2 \pm 0.1$, $\text{I}^- 1.0$, and the true rate constants k_3 must lie somewhere between the extremes of columns 3 and 4.

Most of the kinetic runs were carried out with a freshly prepared sample of molten $N_{2226}B_{2226}$. To test the stability of the molten salt and the reproducibility of rate constants, the third bromide run in Table I was performed with a sample of $N_{2226}B_{2226}$ nearly a year old. The results with the old $N_{2226}B_{2226}$ are indistinguishable from those obtained with fresh $N_{2226}B_{2226}$.

Discussion

Long after the original proposal by Acree¹¹ that both dissociated ions and ion pairs can participate in bimolecular reactions, numerous attempts have been made to determine rate constants for both species. For $\text{S}_\text{N}2$ reactions of halide ions these attempts generally fall into two classes. (1) Analyses of conductometrically determined ion pair dissociation constants of halide salts and observed second-order rate constants as a function of concentration most often lead to the conclusion that within experimental error only dissociated halide ions are kinetically active.¹² (2) In a few cases accurate data taken over a concentration range, where both ion pairs and dissociated ions are kinetically significant, have allowed calculation of rate constants for both species. For reactions of Cl^- and Br^- with *p*-nitrobenzyl bromide in liquid sulfur dioxide,¹³ Cl^- with *p*-nitrobenzyl chloride in acetone,¹⁴ Br^- with *n*-butyl bromide in acetone,¹⁴ and Br^- with dimethyl 2-bromosuccinate in acetone,¹⁵ halide ion pairs react with significant but much smaller rate constants than dissociated halide ions. The reactivities of ion pairs with *p*-nitrobenzyl bromide in sulfur dioxide depend on the counterion, decreasing in the order $\text{Et}_4\text{N}^+\text{Br}^- > \text{Me}_4\text{N}^+\text{Br}^- > \text{K}^+\text{Br}^- > \text{Li}^+\text{Br}^-$.¹³

(11) S. F. Acree, *Amer. Chem. J.*, **48**, 352 (1912).

(12) (a) C. C. Evans and S. Sugden, *J. Chem. Soc.*, 270 (1949); (b) L. J. le Roux and E. R. Swart, *ibid.*, 1475 (1955); (c) E. R. Swart and L. J. le Roux, *ibid.*, 2110 (1956); (d) Farhat-Aziz and E. A. Moelwyn-Hughes, *ibid.*, 2635 (1959); (e) P. Casapieri and E. R. Swart, *ibid.*, 4342 (1961); (f) P. Beronius and L. Pataki, *J. Amer. Chem. Soc.*, **92**, 4518 (1970); (g) P. Beronius, V. Isacson, and A.-M. Nilsson, *Acta Chem. Scand.*, **24**, 189 (1970); (h) P. Müller and B. Siegfried, *Helv. Chim. Acta*, **54**, 2675 (1971); **55**, 2400 (1972).

(13) (a) N. N. Lichtin and K. N. Rao, *J. Amer. Chem. Soc.*, **83**, 2417 (1961); (b) N. N. Lichtin, M. S. Puar, and B. Wasserman, *ibid.*, **89**, 6677 (1967).

(14) P. Beronius, A.-M. Nilsson, and G. Wikander, *Acta Chem. Scand.*, **24**, 2826 (1970).

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Another way to determine ion pair and dissociated ion reactivities is to apply spectrophotometrically determined concentrations of ion pairs and dissociated ions to rate data.¹⁶ In the only reported application of this method to halide ion pair reactivities, Mackay and Poziomek found that the 4-cyano-1-ethylpyridinium iodide ion pair reacted with methyl tosylate 0.4 and 0.6 times as fast as dissociated I⁻ in acetone and in acetonitrile, respectively.¹⁷

The relative reactivities of halide ions toward methyl tosylate in N₂₂₂₆B₂₂₂₆ are compared with their relative reactivities in other solvents in Table II. The data in

Table II. Dependence of Relative Reactivities of Halide Ions on Solvent and Substrate

Substrate	Solvent	Temp, °C	k_{rel}			Ref
			Cl ⁻	Br ⁻	I ⁻	
MeOTs	Methanol	25	0.019	0.13	1.0	a
<i>n</i> -BuOBs	Acetone	25	18	4.3	1.0	4
MeOTs	DMF	0	9.1	3.4	1.0	5
MeOTs	N ₂₂₂₆ B ₂₂₂₆	35	2.1	1.2	1.0	b
(<i>n</i> -C ₅ H ₁₁) ₄ N ⁺	(<i>n</i> -C ₅ H ₁₁) ₃ N ⁺ X ⁻	180	620	7.7	1.0	20

^a R. G. Pearson and J. Songstad, *J. Org. Chem.*, **32**, 2899 (1967).

^b Table I, column 5.

methanol, acetone, and dimethylformamide (DMF) are for reactions of dissociated halide ions. Although no directly comparable data at 35° in other solvents are available, extrapolation to 35° of data from two different sources^{5,8b} at 0 and 25° indicates that the reactions of Br⁻ and I⁻ with methyl tosylate in DMF proceed roughly eight and three times faster, respectively, than the corresponding reactions of tetraalkylammonium halides in N₂₂₂₆B₂₂₂₆. Lesser nucleophilic reactivity in N₂₂₂₆B₂₂₂₆ than in DMF has also been observed for reaction of thiophenoxide ion with cyclohexyl bromide.²

The opposite reactivity orders of dissociated halide ions in protic and dipolar aprotic solvents have been explained as follows.⁴⁻⁶ In the absence of solvation, the smaller its size and the more localized its charge, the greater the inherent reactivity of a halide ion. In protic solvents, the smaller the ion, the more strongly it is solvated, and the much higher solvation energies of small ions than of large ions invert the inherent halide reactivity order. Dipolar aprotic solvents solvate small anions only weakly compared to protic solvents, and the inherent reactivity order is observed. Our rate data now provide relative reactivities of halide ions which

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(17) R. A. Mackay and E. J. Poziomek, *J. Amer. Chem. Soc.*, **92**, 2432 (1970).

have tetraethylammonium and triethyl-*n*-hexylammonium ions as nearest neighbors.

Although the exact nature of association between halide ions and tetraalkylammonium ions in molten N₂₂₂₆B₂₂₂₆ is not known,¹⁸ N₂₂₂₆B₂₂₂₆ compresses the range of halide reactivities with methyl tosylate to little more than a factor of 2, compared to the wider reactivity ranges of dissociated halide ions in dipolar aprotic solvents. The compressed reactivity range is probably due to increase of interaction energy of halide ions with neighboring tetraalkylammonium ions with decreasing ionic radius. This interaction should reduce the nucleophilicity of chloride the most and of iodide the least relative to the nucleophilicities of the dissociated ions in dilute solutions. In other solvents reactivities of associated halide ions are often masked by the faster reactions of dissociated halide ions. Our data provide a model for relative reactivities of associated tetraalkylammonium halides in other solvents.

Our results differ substantially from those in Table II for production of *n*-pentyl halides in molten tetra-*n*-pentylammonium halides at 180°. Steric hindrance to substitution at the neopentyl-like carbon atom of tetra-*n*-pentylammonium ion may be responsible for Gordon's²⁰ expanded range of relative nucleophilicities. Our data are a better model for the nucleophilic reactivities of associated halide ions toward conventional substrates in conventional solvents.

Experimental Section

Materials. Triethyl-*n*-hexylammonium triethyl-*n*-hexylboride was prepared as described earlier.¹ Tetraethylammonium halides (Eastman Kodak) were recrystallized and dried at ≤0.015 Torr and 50–100°. Each had an equivalent weight of halide ion (determined by mercuric nitrate titration)² within ±1% of the calculated value. Methyl *p*-toluenesulfonate was distilled under vacuum. Methyl iodide was distilled and stored over copper wire in the dark.

Kinetics. The tetraethylammonium halide and N₂₂₂₆B₂₂₂₆ (7.0–8.5 g) were weighed into a flask and capped under argon with a silicon rubber septum. After equilibration at 35.07° with magnetic stirring, methyl *p*-toluenesulfonate was added by syringe (volume accurate to ±0.5%). Aliquots were withdrawn by syringe, weighed, and extracted with benzene and water. The aqueous phase was washed three times each with benzene and with chloroform and titrated for halide with aqueous mercuric nitrate.² Control experiments demonstrated that this extraction procedure removed 100.0 ± 0.6% of the halide ion from solutions of each of the tetraethylammonium halides in N₂₂₂₆B₂₂₂₆.

Acknowledgment. We thank the National Science Foundation for support of this research with Grant GP 38493.

(18) By conductivity and viscosity criteria molten tetraalkylammonium salts are dissociated,¹⁹ but in contrast to dilute solutions, ions in molten salts must be strongly affected by the electrostatic fields of one another.

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