13637-63-3; FNO, 7789-25-5; ClF_3O, 30708-80-6; IrF_6, 7783-75-7; $ClO_2^+PtF_6^-$, 38123-66-9; $ClO_2F_2^+PtF_6^-$, 36609-92-4; $ClF_6^+PtF_6^-$, 36609-91-3; $ClF_2^+PtF_6^-$, 38123-68-1; $ClF_4^+PtF_6^-$, 38123-69-2; $NO^+PtF_6^-$, 17250-51-0; $ClF_2O^+PtF_6^-$, 36544-28-2; $ClO_2^+IrF_6^-$, 38194-37-5; ClF_6^+, 38217-33-3; PtF_6^-, 38123-72-7; IrF_6^-, 22587-75-3.

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Halide-Ion Catalysis of the Bromate-Iodide Reaction in Dimethyl Sulfoxide-Water Solvents. Solvent Enhancement of Nucleophilicity

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The kinetics of the reaction $BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O$ have been measured spectrophotometrically in dimethyl sulfoxide (DMSO)-water solvents. The reaction is catalyzed by added chloride, bromide, and thiocyanate ions, leading to the observed rate law $d[I_3^-]/dt = [BrO_3^-][H^+]^2(k_I[I^-] + k_{Nu}[Nu])$. The mechanism proposed involves prior protonation of BrO_3^- followed by rate-determining attack by the nucleophilic anion on the $H_2BrO_3^+$ species. In 0.700-1.00 mole fraction of DMSO, the order of nucleophilic reactivity is $Cl^- > Br^- > I^-$ which represents an inversion in the order reported in water $I^- > Br^- > Cl^-$. The solvent influence is interpreted to suggest that nucleophilic substitution on $H_2BrO_3^+$ occurs at the harder bromine atom center, rather than at the softer, protonated-oxygen center.

The kinetics of the bromate-iodide reaction

$$BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O \quad (1)$$

and the accompanying ionic strength effects, have been studied thoroughly in aqueous solution.[1-4] Although several bromine intermediates must arise in the course of this reaction, they are apparently much more reactive than is bromate, thus permitting attention to be focused on the rate-determining step. Edwards[1] has made a significant contribution to the understanding of this reaction that has resulted in the mechanistic sketch shown in eq 2-5. Intermediates similar

$$BrO_3^- + 2H^+ \rightleftarrows H_2BrO_3^+ \quad (2)$$

$$I^- + H_2BrO_3^+ \rightarrow I\text{-}BrO_2 + H_2O \quad \text{(rate determining)} \quad (3)$$

$$I^- + H_2BrO_3^+ \rightarrow HOI + HBrO_2 \quad \text{(rate determining)} \quad (4)$$

$$I\text{-}BrO_2 + I^- \rightarrow I_2 + Br^{III} \quad \text{(fast)} \quad (5)$$

to $I\text{-}BrO_2$, with a halogen-halogen bond or a pseudo halogen-halogen bond, have been postulated by others.[5] However, other structures for the intermediate formed in the rate-determining step are possible. In their paper concerning carboxylate catalysis of the bromate-iodide reaction, Barton and Wright[3] have presented a thorough discussion of alternate structures for the transition state and intermediate involved in the rate-determining step.

The site of attack by iodide on the $H_2BrO_3^+$ species is an unresolved question. Attack on either the bromine atom or on a protonated oxygen is consistent with the rate law. Of these two acid centers, bromine would be regarded as the harder center and partially positive oxygen as the softer acid center.[6a] According to the HSAB principle,[6b] hard-base nucleophiles would prefer to react at the bromine center and soft-base nucleophiles at the oxygen center. Chloride and bromide are also oxidized by bromate and the relative rates of reaction for the three halide bases, *in water*, are $I^- > Br^- > Cl^-$. It has been suggested that this order of nucleophilicity may indicate attack on the softer oxygen center since iodide is the preferred nucleophile.[7]

The goal of the present study was to examine the rate of the bromate-iodide reaction in dimethyl sulfoxide (DMSO)-water solvents. In particular, since we had observed that this reaction is catalyzed by bromide and chloride ions,[8] our objective was to determine the order of halide ion nucleophilicity in DMSO-water and, thereby, to obtain information that bears on the question of attack at bromine *vs.* oxygen.

Experimental Section

Solvent and Reagents. All solutions were prepared from commercial grade DMSO (Van Waters and Rogers) and redistilled water as described earlier.[9] To minimize air oxidation of iodide, the pure solvents and the resulting mixtures were swept with prepurified nitrogen before use. B & A reagent grade potassium bromate, recrystallized from water and dried for 3 hr at 180°, was found to be 99.9% pure by iodometric analysis. B & A 60% reagent grade perchloric acid, diluted to 1 *M*, was used as the source of acid. Reagent grade potassium salts were used as received. Potassium perchlorate was used to maintain ionic strength at 0.121 *M*.

Stoichiometry. The stoichiometry of reaction 1 was verified in 0.500 mole fraction of DMSO. Spectrophotometric analysis indicated that 2.9 ± 0.1 mol of triiodide ion was produced per mole of bromate reacting. The amount of hydrogen ion consumed was deter-

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(8) Indelli, *et. al.*,[2] have also reported that the reaction in water proceeds somewhat more rapidly in the presence of chloride ion.

(9) J. H. Krueger and W. A. Johnson, *Inorg. Chem.*, **7**, 679 (1968).

mined by NaOH titration, following removal of iodine with sodium thiosulfate. It was found that 5.9 ± 0.1 mol of hydrogen was consumed per mole of bromate reacting.

Kinetic Measurements. The procedures were similar to those described previously.[10] Reactions were followed to completion, utilizing triiodide ion absorbance (ϵ_{365} 25,800 M^{-1} cm^{-1} in DMSO-H_2O). In all solvents, A_∞ values in good agreement with theoretical values were obtained. Pseudo-first-order rate constants were obtained throughout with hydrogen ion and iodide ion concentrations usually in 40-1000-fold stoichiometric excess over bromate. Rate constants for runs with smaller excess concentrations of hydrogen ion were corrected.

Results

Uncatalyzed Reaction. The rate law shown in eq 6 has

$$d[I_3^-]/dt = k_I[BrO_3^-][H^+]^2[I^-] \qquad (6)$$

been reported for the bromate-iodide reaction in aqueous solution.[2,3] This rate law has been confirmed for DMSO-water solutions in the present study. The appearance of triiodide ion was found to be strictly first order in bromate ion, based on plots of ln $(A_\infty - A)$ *vs.* time that were linear for the extent of reaction examined, generally 2-4 half-lives.

Pseudo-first-order rate constants were measured for a variety of initial hydrogen and iodide ion concentrations in five different solvent mixtures. Values of the fourth-order rate constant k_I, computed from the equation $k_I = k_1(\text{obsd})/[H^+]_0{}^2[I^-]_0$, are reported in Table I. Compared with the rate in water, the reaction in DMSO-water is relatively rapid ($t_{1/2} \approx 10^2$-10^3 sec), making it possible to work easily with low initial concentrations to minimize the problems of air oxidation and other side reactions.

No trend in k_I values was found for either increasing initial iodide ion or increasing initial hydrogen ion concentrations, the latter observation eliminating the possibility of extensive association of bromate ion to form $HBrO_3$.[11]

The temperature dependence of k_I was determined in 0.700 mole fraction of DMSO. At 10.4°, $k_I = 3.17\ (\pm 0.02) \times 10^4$ M^{-3} sec^{-1}, and at 29.7°, $k_I = 12.6\ (\pm 0.4) \times 10^4$ M^{-3} sec^{-1}, for which values of $\Delta H^\ddagger = 11.8 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = +4 \pm 3$ eu were calculated from transition-state theory.

The ionic strength effect was evaluated in 0.500 mole fraction of DMSO, and, as expected from eq 6, k_I decreases with increasing concentration of potassium perchlorate added. At 25.2°, values of $10^4 k_I, M^{-3}$ sec^{-1} (ionic strength in parentheses), were 1.95 (0.022), 1.54 (0.065), 1.24 (0.082), 1.04 (0.121), 0.93 (0.162), and 0.85 (0.202).

Catalyzed Reaction. As we had anticipated, the bromate-iodide reaction was found to be catalyzed significantly by bromide and chloride ions, especially in 0.700-1.00 mole fraction of DMSO. The rate law observed is shown in eq 7

$$d[I_3^-]/dt = [BrO_3^-][H^+]^2(k_I[I^-] + k_{Nu}[Nu]) \qquad (7)$$

in which Nu represents a generalized nucleophile, bromide or chloride. In all cases the rate of the catalyzed reaction was found to be first order in added bromide or chloride, and, at constant concentrations of I^- and Nu, the observed pseudo-first-order rate constant was proportional to $[H^+]^2$, even when the k_{Nu} term accounted for more than 50% of the total reaction. As shown in Table II, values of k_{Nu} were obtained in the several solvents. Each k_{Nu} value was computed from the equation $k_{Nu} = ([k_1(\text{obsd})/[H^+]_0{}^2] - k_I[I^-]_0)/[Nu]_0$, using the k_I value obtained in a control run in which no catalytic ion had been added. Fourth-order rate constants are shown as a function of solvent composition in Figure 1.

Table I. Kinetic Data for the Bromate-Iodide Reaction in 0.500-1.00 Mole Fraction of DMSO at 25.17° and 0.121 *M* Ionic Strength

Mole fraction of DMSO	Range of $10^3[H^+]$, *M*	Range of $10^2[I^-]$, *M*	Range of $10^5[BrO_3^-]$, *M*	No. of runs	Av value of $10^{-4} k_I, M^{-3}$ sec^{-1}
0.500	0.56-3.92	0.50-6.00	0.57-0.84	26	1.09 ± 0.06[a]
0.700	0.63-3.06	0.33-2.99	0.80-0.90	24	10.1 ± 0.3
0.800	0.73-1.09	0.30-0.50	0.81-0.92	14	$26._4$ ± 0.8
0.900	0.76-0.97	0.15-0.50	0.72-1.05	6	$62._5$ ± 1.3
1.00	0.82-0.84	0.30	0.54-0.60	3	112 ± 1

[a] One standard deviation.

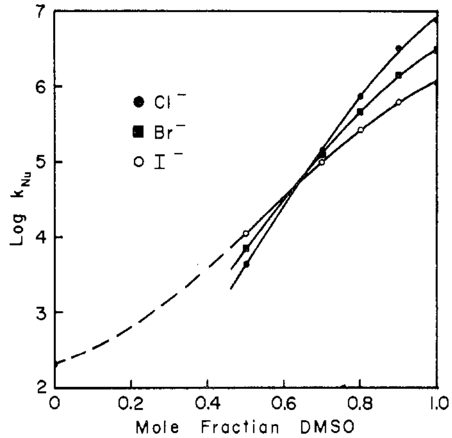

Figure 1. Log k_{Nu} for I^-, Br^-, and Cl^- plotted as a function of mole fraction of DMSO in the solvent. The value of k_{Nu} for I^- in water has been estimated at 0.121 *M* ionic strength and 25° from ref 2.

Thiocyanate ion catalyzed the reaction to a small extent in 0.700 mole fraction of DMSO. Although the catalyzed reaction appears to be first order in added SCN^-, the small contribution made in this case by the k_{Nu} term in eq 7 did not permit an accurate evaluation of thiocyanate behavior.

Discussion

The mechanistic scheme shown in eq 2-4 is consistent with the observed rate law for the uncatalyzed reaction. Prior protonation of bromate occurs to a slight extent,[12] followed by rate-determining attack of iodide on $H_2BrO_3^+$. Although DMSO affects the rate of reaction, there is no evidence that DMSO enters into the reaction by diverting any of the reactive intermediates formed. The rate law observed in the presence of an added nucleophile suggests a generalization of steps 3 and 5 in the mechanism to provide for attack of both iodide and the added nucleophile along parallel paths[13] (see eq 8-10). Regardless of the site of attack, the

$$Nu^- + H_2BrO_3^+ \rightarrow Nu\text{-}BrO_2 + H_2O \quad \text{(rate determining)} \qquad (8)$$

$$I^- + NuBrO_2 \rightarrow INu + Br^{III} \quad \text{(fast)} \qquad (9)$$

$$I^- + INu \rightarrow I_2 + Nu^- \qquad (10)$$

$$Nu^- = I^-, Br^-, Cl^-, SCN^-$$

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[10] J. H. Krueger, *J. Amer. Chem. Soc.*, 91, 4974 (1969).

[11] Similar oxy acids are reported to be strong acids in 100% DMSO: I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, 1, 89 (1962).

[12] Protonation prior to the rate-determining step is strongly indicated by the observation that $k_{D_2O}/k_{H_2O} = 2.4$ for rate measurements in D_2O relative to those in H_2O: E. Abel and F. Fabian, *Monatsh.*, 71, 153 (1938).

[13] Carboxylate anion catalysis has been described by Barton and Wright,[3] who reported a term in the rate law of the type $[H^+]^2 \cdot [BrO_3^-][I^-][B]$ in which B represents the carboxylate base. However, since both B and I^- are required in forming the corresponding activated complex, the nature of the catalysis by B must differ from that of the halide ion catalysis in the present study.

Table II. Kinetic Data for the Nucleophile-Catalyzed Bromate-Iodide Reaction in 0.500-1.00 Mole Fraction of DMSO at 25.17° and 0.121 *M* Ionic Strength

Mole fraction of DMSO	$10^3[H^+]$, *M*	$10^2[I^-]$, *M*	$10^3[Nu]$, *M*	No. of runs	Av value of $10^{-4}k_{Nu}$, M^{-3} sec^{-1}
0.500	1.36–2.29	1.49–2.50	7.0–40.5	6	Br^- 0.72 ± 0.04[a]
			10.0–29.9	4	Cl^- 0.45 ± 0.03
0.700	0.85–1.42	0.40–1.00	2.5–15.3	7	Br^- 12.7 ± 0.8
			2.5–20.5	12	Cl^- 14.7 ± 1.3
			1.5–4.70	3	SCN^- 0.7 ± 0.15
0.800	0.76–0.98	0.30–0.50	1.0–4.60	7	Br^- 46 ± 3
			2.5–3.06	3	Cl^- 76 ± 2
0.900	0.87–0.97	0.500	3.00	3	Br^- 146 ± 1
			0.77–0.82	3	Cl^- 320 ± 10
1.00	0.830	0.300	1.19	3	Br^- 310 ± 10
			0.420	3	Cl^- 780 ± 30

[a] One standard deviation.

catalyzing nucleophile generates an intermediate (*e.g.*, IBr or HOBr when $Nu^- = Br^-$) that reacts rapidly and completely with iodide ion, the strongest reducing agent present. Presumably, the rate constant for attack by Br^- (or Cl^-) is the same as that which would be observed under the same conditions for the reaction of Br^- (or Cl^-) with bromate in the absence of iodide ion, since reaction 8 is rate determining. We were unable to verify this because DMSO reacts with the bromine (or chlorine) species produced, in the absence of iodide. It should be noted that the concentration of bromide produced by reaction 1 makes less than a 1% contribution to the rate in the uncatalyzed runs.

In water, bromide and chloride react with bromate much more slowly than does iodide.[14] However, increasing DMSO content accelerates the reaction of each nucleophile with the effect being greatest for chloride. Although the change in dielectric constant of the solvent (from 78 in water to 46 in DMSO) accounts for part of this acceleration, changes in solvation of the nucleophile and of the activated complex increase the rate of reaction 3 as well. The solvent effect on rate must arise primarily from reaction 3, since a minor decrease in the equilibrium constant of reaction 2 is expected on going to the more basic DMSO-water solvents.[10] Rate enhancement of substitution reactions in DMSO has been elegantly characterized by Parker.[15] The essential picture is that solvation by means of hydrogen bonding diminishes greatly on going to solvent mixtures of increasing DMSO content, the effect being much greater for anionic nucleophiles than for the large, polarizable transition states formed.

The most significant feature of the present results is the inversion in the order of nucleophilicity. Similar inversions on going from protic to dipolar aprotic solvents have been reported for attack at carbon[16] and at sulfur.[17] Reported enthalpies of solution indicate that there are much smaller differences in solvation among anions in DMSO than in water[16d,18] but that Cl^- probably is still somewhat more solvated than I^- in DMSO.[16d] Thus, anion solvation can give rise to a reversed order of nucleophilicity if it is assumed that the order of nucleophilic reactivity of the unsolvated ions toward $H_2BrO_3^+$ is $Cl^- > Br^- > I^-$ (*i.e.*, there exists a preference for the hard base, Cl^-).[16d,19]

Despite its limitations, the HSAB principle[6] appears to provide the best framework available for discussion of the results. Application of the HSAB scheme leads to the identification of the bromine(V) atom, rather than a protonated oxygen atom, as the harder of the two acid centers in $H_2BrO_3^+$.[6] The conclusion that the harder base is preferred in the transition state suggests, but does not require, that nucleophilic attack occurs at the harder bromine center, in support of eq 3 and 8. Because of differences among solvents, conclusions based on results in DMSO-water may not apply to other solvent systems.

Registry No. Bromate, 15541-45-4; iodide, 20461-54-5.

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