Some Reactions of the Perbromate Ion in Aqueous Solution[1]

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Abstract: The reaction of the perbromate ion with a number of two-equivalent reductants have been studied in aqueous solution at an ionic strength of approximately one. Reaction rates increase in the order $N_3^- < ClO_2^- \sim SeO_3^{2-} \sim NO_2^- <$ P(III) $\ll$ S(IV) $\leq$ As(III) $<$ Sb(III). The perbromate–sulfur (IV) reaction obeys the rate law $-d[BrO_4^-]/dt = k_S[BrO_4^-]\,[SO_3^{2-}]$ in solutions more basic than pH 4.5. At 25 °C, $k_S = 5.8 \times 10^{-3}$ L/mol·s. The perbromate–arsenic(III) reaction obeys the rate law $-d[BrO_4^-]/dt = [(k_1[H^+] + k_2K_1 + k_3K_1/[H^+])/(K_1 + [H^+])][BrO_4^-][As(III)]$. At 39.7 °C, $k_1 = 5.6 \times 10^{-4}$ L/mol·s, $k_2 = 1.96 \times 10^{-2}$ L/mol·s: $k_3 = 1.16 \times 10^{-13}\ s^{-1}$, and $K_1 = 1.6 \times 10^{-9}$ M. This rate law can be interpreted in terms of increasing reactivity of the species H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$ toward perbromate. In strong base, the perbromate–antimony(III) reaction obeys the rate law $-d[BrO_4^-]/dt = k_{Sb}[BrO_4^-][Sb(III)]$, where $k_{Sb} = 0.47$ L/mol·s at 25 °C. Activation parameters were determined for the sulfur(IV), arsenic(III), and antimony(III) reactions, and the dependences of the S(IV) and As(III) reactions on total salt concentration were elucidated. The results of isotopic tracer studies show that in its reactions with S(IV) and As(III) the perbromate ion transfers one of its oxygen atoms to the reductant. Oxygen exchange between 0.14 M $KBrO_4$ and water proceeded to less than 7% of completion in the course of 19 days at 94 °C, in solutions ranging from 0.06 M acid to 0.02 M base. The implications of all of these results are discussed.

Introduction

Although the first preparation of a perbromate was reported in 1968,[4] there is still little known about the mechanisms by which these compounds react. The earliest studies indicated perbromate to be quite sluggish in its reactions, though not as inert as perchlorate.[5] This inertness of the perbromate ion stands in sharp contrast to its high thermodynamic oxidizing power,[6] which is greater than that of any other oxy halogen ion that persists in aqueous solution.

The perbromate ion is tetrahedral and shows no tendency to form octahedral species.[5] Hence we may expect perbromic acid to be an extremely strong acid, comparable in strength to perchloric acid. It seems likely, therefore, that perbromate will enter into reactions as a tetrahedral oxy anion, and will bring no protons into the activated complex. Thus any hydrogen ion dependence that is found in reactions of perbromate will almost certainly be attributable to characteristics of the reductant. An example of this behavior is the reaction between perbromate and iodide, which is essentially independent of pH,[7] whereas the reactions of other halogen oxy anions with I^- are usually second order in $[H^+]$. In this respect perbromate should resemble perchlorate, but not periodate. However, there are rather few redox reactions of the perchlorate ion that can be conveniently studied, and the enhanced reactivity of perbromate opens a promising area of investigation.

An intuitively simple mechanism for the reduction of probromate would consist of transfer of one of the perbromate oxygen atoms to the reductant. And, in fact, most common reductants (halide ions, sulfite, etc.) are at least in principle capable of accepting such an oxygen atom. It is therefore tempting to suggest that the the most energetically favored mode of oxidation by perbromate actually is a two-equivalent process involving transfer of an oxygen atom, and that the sluggishness of this process results from the inertness of the perbromate oxygens to substitution.

Periodate is thermodynamically a poorer oxidant than perbromate, but it is much more reactive, presumably because of the lability of its oxygens. It is interesting to note, however, that the hydrated electron reacts with both perbromate and periodate at rates that are close to the diffusion-controlled limit.[8] In this case oxygen transfer is almost certainly not involved, and oxygen lability is not a factor in determining the rates of reaction.

These considerations have led us to examine the reactivity of perbromate toward a number of potentially two-equivlanet reductants, and in two cases to study the oxygen transfer that accompanies reaction.

Experimental Section

Reagents. Potassium perbromate was prepared by a procedure that has been described elsewhere.[9] Commercial reagent grade sodium perchlorate was recrystallized before use. Laboratory distilled water was redistilled first from alkaline permanganate and then from a dichromate solution in sulfuric acid. Other chemicals were commercial products of reagent grade.

Analytical Procedures. Reactions were monitored by volumetric determination of one or more of the species present. Arsenite was determined by titration with I_3^- in a pH 7 buffer. Sulfite and antimonite were determined by the addition of an excess of I_3^-, followed by titration with a standard arsenite solution in a pH > buffer. Phosphite was determined similarly, but the final I^- concentration was kept below 0.1 M because of a literature report that higher I^- concentrations interfered with the reaction between phosphite and I_3^-.[10] Nitrite and azide were determined by potentiometric titration with Ce(IV) in sulfuric acid. Cyanide was determined by titration with I_3^- in a carbonate–bicarbonate buffer.

After the stoichiometry of the perbromate–arsenite reaction had been established, it was used as a method for determination of perbromate. The unknown perbromate solution was made basic with NaOH, an excess of standard arsenite was added, and the solution was allowed to stand for 1–2 h at 50 °C. The pH of the solution was then adjusted to ca. 7 and the unreacted arsenite was titrated with I_3^-

Bromate was determined by acidifying the solution, adding excess iodide and a trace of ammonium molybdate, and titrating the I_3^- formed with thiosulfate. This method was also used to monitor the reaction of chlorite with perbromate. Both chlorite and bromate, but not chlorate, reacted with the I^-, and a net increase in titer resulted from the oxidation of ClO_2^- with concomitant formation of BrO_3^-. The reaction between selenite and perbromate was monitored in similar fashion. In this case both bromate and selenate reacted with the iodide, as did the unreacted selenite, so that the titer increased substantially as reaction proceeded.

pH Control and Determination, and Determination of Ionization Constants. pH values were measured with a Beckman Research pH meter, using a "low sodium error" combination electrode standardized against buffers prepared in accordance with NBS specifications. pH values between 4 and 6 were controlled with acetate–acetic acid buffers, between 6.8 and 7.5 with Borax–boric acid buffers, between 8.9 and 10.1 with carbonate-bicarbonate buffers, and between 9.6 and 11.2 with PO_4^{3-}–HPO_4^{2-} buffers. Higher pH values were maintained with sodium hydroxide solutions. The pH values were substantially different from the "normal" values of the solutions used because of the high total salt content of our reaction mixtures (ionic strength ~1). We therefore measured the pH of each buffer solution

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Table I. Reaction of Perbromate with Various Reductants at Elevated Temperature[a]

reductant	extent of reaction in 3 days at 93 °C
azide	<10%
chlorite	50%
cyanide	substantial or complete[b] (<2% in 24 h at 40 °C)
nitrite	65%
phosphite	50% at pH 5 complete in 0.6 M NaOH 3-h half-time when $[NaOH]_0 = 0.12$ M[c]
selenite	19% in 0.6 M NaOH

[a] Except as otherwise noted $[BrO_4^-]_0 = 0.1$ M, $[\text{reductant}]_0 = 0.2$ M, and $[NaOH]_0 = 1$ M. [b] Extensive hydrolysis prevented quantitative interpretation. [c] $[P(III)]_0 = 0.04$ M, $[BrO_4^-]_0 = 0.08$ M, $[NaClO_4] = 0.76$ M. Reaction did not follow second-order kinetics but was complete within 36 h.

under conditions comparable to those prevailing at the beginning of the reaction, the only difference being that the $KBrO_4$ was replaced with $NaClO_4$. The pH values that were controlled with NaOH were determined from an empirical curve of pH vs. log $[OH^-]$ obtained by adding successive portions of 1 M NaOH to a solution 1 M in $NaClO_4$. This curve was found to be essentially linear below 0.25 M NaOH. In the arsenite–perbromate system the pH value assigned to a particular reaction mixture was corrected for changes that occurred as reaction proceeded. The corrected value was the one that would have prevailed at approximately the midpoint of the period over which the reaction was followed. This correction, which was almost always less than 0.1 pH unit, was calculated from mass action laws and the measured ionization constants of H_3AsO_3 and H_3AsO_4. The values of these constants in our media were determined by potentiometric titration of 0.1 M H_3AsO_3 and H_3AsO_4 solutions in 1 M $NaClO_4$ with 1 M NaOH. The first ionization constant of H_3AsO_3 was found in this way to be 4.4×10^{-9} M at 40 °C, while the ionization constants of H_3AsO_4 at 40 °C were found to be 0.013, 1.3×10^{-6}, and 4×10^{-12} M. No evidence was found for a second dissociation of arsenious acid. The second ionization constant of sulfurous acid at 25 °C was determined by titration of a 0.15 M Na_2SO_3 solution containing 0.55 M $NaClO_4$ with 1 M $HClO_4$. The value obtained was 7×10^{-7} M.

General Kinetic Procedures and Data Processing. Reactions were followed to 50–95% of completion. Reaction temperatures were controlled to ±0.1 °C, except for reactions at 93 °C, which were controlled to ±1 °C. Sulfite and antimonite reaction mixtures were flushed with nitrogen to prevent air oxidation. Dissolved oxygen was found to have no effect on the arsenite–perbromate system. Reactions at 50 °C or lower were carried out in stoppered vessels. Samples for analysis were quenched by dilution with a pH 7 buffer or by reaction of the reductant with I_3^-. Reactions at 93 °C were carried out in sealed ampules containing solutions that had been flushed with nitrogen. One set of "blank" ampules contained all reagents except perbromate, while another set contained all reagents except the reductant. Reactions were usually followed by monitoring the disappearance of reductant. In some cases, however, as noted in the section on analytical methods, the formation of an oxidizing product was also involved in the monitoring. Unreacted perbromate did not interfere with the analyses, nor did reaction products except as noted for the chlorite and selenite systems.

Kinetic results were fitted by a nonlinear least-squares computer program to the integrated second-order rate equation. Activation parameters and their uncertainties were obtained from a linear least-squares treatment of the variation of the second-order rate constants with temperature.

Oxygen Tracer Experiments and Oxygen Isotopic Analysis. The exchange of oxygen between perbromate and water was investigated by adding normal perbromate to acidic, neutral, or basic solutions in water that was ca. 1.5% in ^{18}O. The reaction mixtures were sealed in glass ampules and were kept at 94 °C for 19 days, after which the ampules were opened and the solutions were evaporated to dryness under vacuum. The $KBrO_4$ residue was sealed in an evacuated tube equipped with a break-seal, and the tube was heated at 400 °C to decompose the perbromate to KBr and O_2. The isotopic composition of the oxygen was determined with a Consolidated 21-620 mass spectrometer. Similar ignition of tubes containing tagged KIO_4 showed that exchange of O_2 with the glass tubes was not significant.

The transfer of oxygen from perbromate to sulfite was determined by allowing an excess of normal perbromate to react with sulfite that had been prepared by addition of base or buffers to a solution of SO_2 in water containing ca. 0.4% ^{18}O. Under such conditions the sulfite oxygens should have been in equilibrium with the solvent.[11] After reaction was complete, the solution was acidified with HBr to destroy bromate, and barium sulfate was precipitated. The sulfate oxygen was converted to CO_2 by ignition in a graphite crucible,[12] and the isotopic composition of the CO_2 was determined with a Consolidated 21-201 isotope ratio mass spectrometer. In reference experiments, the sulfite was oxidized with an excess of Br_2 instead of with perbromate.

The transfer of oxygen from perbromate to arsenite was determined in a similar fashion, except that the solutions were flushed with nitrogen and handled in serum-capped vessels to prevent absorption of carbon dioxide. Arsenite enriched in ^{18}O was prepared by adding normal As_2O_3 to a sodium hydroxide solution in enriched water and neutralizing with HCl. (Exchange of oxygen between arsenite and water is reported to be rapid.[13]) After reaction between arsenite and perbromate was complete, the reaction mixture was diluted threefold with enriched water, and 1.5 mol of $Ba(NO_3)_2$ was added per mol of arsenic. The barium arsenate precipitate was washed twice with 0.01 M $Ba(NO_3)_2$ in enriched water and then with methanol. It was dried for 1 h at 110 °C and then overnight in a vacuum desiccator. Portions (20 mg) were mixed with 50 mg of $Hg(CN)_2$ and were sealed in evacuated tubes equipped with break-seals. These tubes were heated to 500 °C to convert the arsenate oxygen to CO_2.[14] They were then cooled to ca. −126 °C (methylcyclohexane slush) and opened on a vacuum line. The CO_2 formed was transferred to a liquid nitrogen trap, while N_2 and CO were pumped away. The −126 °C bath held back most of the $(CN)_2$ that was formed.[14] The isotopic composition of the CO_2 was again determined with the isotope ratio mass spectrometer. As in the sulfite system, reference experiments were carried out in which the arsenite was oxidized with an excess of Br_2 instead of with perbromate.

To determine the extent of exchange between arsenate and solvent in the course of the reaction and separation, normal arsenate was added to an alkaline solution in enriched water and barium arsenate was precipitated as described above. A barium arsenate sample was also precipitated from a solution of normal arsenate in normal water and from a solution obtained by oxidizing normal arsenite in normal water with normal perbromate. The oxygen from $KBrO_4$ was converted to CO_2 by the $Hg(CN)_2$ method, and its isotopic composition served as a reference for both the sulfite and arsenite systems.

A bulk sample of barium arsenate was prepared by the method described above and was subjected to chemical analysis. Barium was determined by titration with EDTA, arsenic by atomic absorption, and oxygen by ignition with carbon.[15] The compound was found to be nonstoichiometric, with a Ba/As mole ratio of 1.27 and an O/As mole ratio of 4.16. The latter may reflect partial hydration or contamination with carbonate.

The abundance of oxygen-17 was neglected in calculations of isotopic composition.

Results

Reaction Stoichiometries. Stoichiometries were determined for the reactions of perbromate with phosphite and antimonite in 0.5–1 M NaOH, with arsenite between 1 M NaOH and pH 4.4, and with sulfite between 0.1 M NaOH and pH ~4.5. Except for the sulfite system at pH 4.5, the stoichiometry was always found to be 1:1 within experimental uncertainty (average deviation 1–2%). In the case of sulfite at pH 4.5, 4.6_3 mol of reductant was consumed per mol of perbromate. This is consistent with the rapid reaction of bromate with sulfite at this pH,[16] and with the formation of a small quantity of dithionate from the bromate reaction.[17] We may note that the low steady-state concentration of bromate present in these experiments may be expected to maximize the production of dithionate.

Survey of Slow Reactions. A number of relatively slow reactions of perbromate were surveyed at 93 °C. The results are summarized in Table I. Only in the case of phosphite in 1 M

Table II. Reaction of As(III) with Perbromate at Various Temperatures and Salt Concentrations

temp, °C	added reagents, M					$10^3 k_{As}$, L/mol·s
	$[H_3AsO_3]$	$[KBrO_4]$	[NaOH]	$[NaClO_4]$	[buffer]	
39.7	0.0970	0.0510		0.400	$NaC_2H_3O_2$, 0.500 HCl, 0.250[a]	0.55_6
49.3	0.0970	0.0510		0.400	$NaC_2H_3O_2$, 0.500 HCl, 0.250[a]	1.4_0
59.9	0.0970	0.0510		0.400	$NaC_2H_3O_2$, 0.500 HCl, 0.250[a]	3.1_0 3.0_1[b]
59.9	0.0970	0.0510			$NaC_2H_3O_2$, 0.500 HCl, 0.250[a]	3.00
30.4	0.0200	0.0100	0.100	0.690	$NaHCO_3$, 0.200[c]	5.9_5
39.7	0.0200	0.0100	0.100	0.690	$NaHCO_3$, 0.200[c]	$14._4$, $13._2$[b]
50.2	0.0200	0.0100	0.100	0.690	$NaHCO_3$, 0.200[c]	$32._7$
39.6	0.0200	0.0100	0.100		$NaHCO_3$, 0.200	$11._7$
25.0	0.009 00	0.005 00	0.100	0.900		$50._9$
25.0	0.008 00	0.0215	0.100	0.880		$47._8$
25.0	0.009 00	0.005 00	0.100	0.295		$27._7$
25.0	0.009 00	0.005 00	0.100			$14._5$
15.0	0.009 00	0.005 00	0.100	0.900		$25._0$
35.0	0.009 00	0.005 00	0.100	0.900		$94._8$
39.7	0.0100	0.005 00	0.100	0.890		121, 127,[b] 109[b]
25.0	0.009 00	0.005 00	0.310	0.690		124
15.0	0.009 00	0.005 00	0.985			$34._1$
20.0	0.009 00	0.005 00	0.985			119
25.0	0.009 00	0.005 00	0.994			240

[a] pH 4.48 at 39.6 °C. [b] Duplicate experiments. [c] pH 9.23_3 at 30 °C, 9.24_5 at 40 and 50 °C.

base was the stoichiometry of the reaction verified. In the other cases a 1:1 stoichiometry with production of bromate was assumed.

Perbromate–Arsenite Reaction. The rate law for this reaction was found to be first order each in BrO_4^- and As(III). Experiments were carried out with $[BrO_4^-]_0/[As(III)]_0$ ranging from 0.5 to 10, and a number of runs were followed to 90% of completion. Satisfactory fits to the bimolecular rate equation were obtained in all cases.

An extensive series of experiments was carried out at 39.7 °C to establish the dependence of the bimolecular rate constant, k_{As}, on pH. In these experiments $NaClO_4$ was added to maintain the total cation molarity at unity. The results of these experiments are shown in Figure 1. The smooth curve is a least-squares fit of the data to the four-parameter equation

$$k_{As} = \frac{k_1[H^+] + k_2K_1 + k_3K_1/[H^+]}{K_1 + [H^+]} \tag{1}$$

where $[H^+] = 10^{-pH}$ and K_1 is the first acid dissociation constant of arsenious acid. The fitted values of the parameters and their calculated standard deviations are $k_1 = (5.6 \pm 0.4) \times 10^{-4}$ L/mol·s, $k_2 = (1.96 \pm 0.09) \times 10^{-2}$ L/mol·s, $k_3 = (1.16 \pm 0.04) \times 10^{-13}\ s^{-1}$, and $K_1 = (1.59 \pm 0.16) \times 10^{-9}$ M. The fitted value of K_1 is considerably different from the value of 4.4×10^{-9} that we measured directly by potentiometric titration. Attempts to fix K_1 at the measured value and to fit the data to a three parameter equation led to a considerably poorer fit.

Table II gives the results of experiments carried out at several temperatures and salt concentrations. The activation parameters derived from the temperature dependences at several pH values are presented in Table V.

Perbromate–Sulfite Reaction. This reaction was also first order in perbromate and in reductant. Satisfactory kinetic plots were obtained to 90% of completion, regardless of whether perbromate or sulfite was in excess. The reaction was studied in the alkaline region, in which bromate is the final reaction product, and in acetate buffer, in which sulfite reacts much more rapidly with bromate than with perbromate.[16] We avoided the intermediate region, in which bromate and perbromate react at comparable rates. We also avoided the more acid region, in which the slowness of the reaction led to difficulties in retaining the volatile SO_2 in the solutions. The results are given in Table III, and the activation parameters derived from the temperature dependence are shown in Table V.

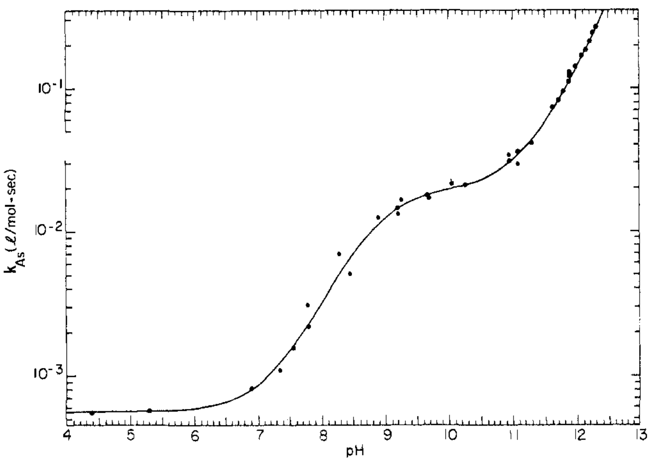

Figure 1. Dependence on pH of the reaction of As(III) with BrO_4^- at 39.7 °C. $[As(III)]_0 = 0.002–0.1$ M, $[BrO_4^-]_0 = 0.005–0.05$ M, $[As(III)]_0/[BrO_4^-]_0 = 0.1–2.0$, $[Na^+] = 1.0$ M.

Perbromate–Antimonite Reaction. This reaction was again first order each in perbromate and reductant. Satisfactory kinetic plots were obtained over 90% of reaction with perbromate in twofold excess. The rate appeared to be independent of base concentration over the rather narrow region studied. (The low solubility of Sb(III) salts makes it difficult to work at low alkalinity.) The results appear in Table IV, and the activation parameters are given in Table V.

Oxygen Exchange and Transfer Studies. The exchange of perbromate oxygens with water was sought in solutions 0.14 M in $KBrO_4$ that were either neutral, 0.06 M in HNO_3, or 0.02 M in NaOH. After 19 days at 94 °C less than 1% exchange was observed in the acidic and neutral solutions and less than 7% in the basic solution. (The 7% exchange observed in base

Table III. Reaction of Sulfite and Bisulfite with Perbromate

temp,	added reagents, M						$10^3 k_S$,
°C	$[Na_2SO_3]$	$[KBrO_4]$	[NaOH]	$[NaClO_4]$	[buffer]	stoichiometry[a]	L/mol·s
25.0	0.0345	0.0249	0.100	0.771		1.01	5.6_4
25.0	0.0300	0.0405	0.100	0.770		1.05	5.8_2
25.0	0.0300	0.0405	0.100			1.04	2.9_8
25.0	0.0359	0.0249	0.0100	0.857		1.05	6.0_2
25.0	0.0352	0.0248	0.0428	0.773	$NaHCO_3$, 0.101[b]	0.995	5.7_6
25.0	0.0347	0.0250		0.789	$Na_2B_4O_7$, 0.050 $HClO_4$, 0.0184[c]		5.6_2
25.0	0.149	0.0723			$NaC_2H_3O_2$, 0.521 $HClO_4$, 0.317[d]	0.216	0.13_1
15.0	0.0283	0.0405	0.100	0.775			2.3_6
35.0	0.0277	0.0410	0.100	0.775			$12._7$

[a] Stoichiometry ≡ $\Delta[BrO_4^-]/\Delta[S(IV)]$. [b] Initial pH ~9.3. [c] Initial pH ~8.4. [d] Initial pH 4.7; final pH 4.2.

Table IV. Reaction of Sb(III) with Perbromate[a]

temp, °C	NaOH, M	$NaClO_4$, M	k_{Sb}, L/mol·s
25.0	0.95		0.47_5, 0.50[b]
25.0	0.41	0.33	0.47
25.0	0.24	0.71	0.44
34.4	0.24	0.71	0.73
15.7	0.24	0.71	0.19_1

[a] $[Sb(III)]_0 = 0.0019\text{–}0.0025$ M, $[BrO_4^-]_0 = 0.0048\text{–}0.0083$ M. [b] Duplicate experiment.

Table V. Activation Parameters for Perbromate Reactions

reaction	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/mol·deg
BrO_4^- + As(III), pH ~4.4	16.8 ± 1.1	−20 ± 4
BrO_4^- + As(III), pH ~9.2	16.2 ± 0.2	−15 ± 0.3
BrO_4^- + As(III), 0.1 M NaOH	11.1 ± 0.1	−27 ± 0.4
BrO_4^- + As(III), 1 M NaOH	12.1 ± 0.3	−21 ± 0.5
BrO_4^- + SO_3^{2-}, 0.1 M NaOH	14.3 ± 0.1	−21 ± 1
BrO_4^- + Sb(III), 0.24 M NaOH	12.0 ± 1.5	−20 ± 5

was not time dependent and probably resulted from exchange between perbromate and sodium hydroxide upon ignition of the solid obtained by evaporating the solution.)

The results of the experiments on transfer of oxygen from perbromate to sulfite and arsenite appear in Tables VI and VII, respectively. The oxygen exchange that we observe between arsenate and solvent is comparable in magnitude to the "separation-induced exchange" reported in a recent paper on the arsenate–water exchange.[18] Uncertainties in the extent of this exchange and in the oxygen/arsenic ratio in the precipitated barium arsenate lead to the relatively large uncertainty in the extent of oxygen transfer to arsenic.

Discussion

The observed rate law for the reaction of arsenite with perbromate is consistent with three parallel reaction paths involving respectively H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$ as the reducing species. The disagreement between the measured K_1 and the kinetically fitted value is a little surprising. It may indicate specific effects of the buffers on the reaction kinetics.

The second ionization constant of arsenious acid has never been reliably measured, although the existence of $HAsO_3^{2-}$ in strong base has been claimed on the basis of potentiometric titrations and Raman spectra.[19,20] The lack of any leveling of the reaction rate in our experiments up to 0.25 M NaOH implies that the pK for the second ionization is considerably greater than 13 in our medium. The tendency of the rate of level a little near 1 M NaOH (Table II) may reflect the formation of substantial concentrations of $HAsO_3^{2-}$ or it may be due to medium effects.

We may rewrite eq 1 as

$$k_{As} = \frac{k_1(H_3AsO_3) + k_2(H_2AsO_3^-) + k_3'(HAsO_3^{2-})}{[As(III)]_{total}} \quad (2)$$

where k_3' is equal to k_3 divided by the second dissociation constant of arsenious acid, K_2. If we assume that K_2 has a value around 10^{-14} M, we find that k_1, k_2, and k_3' stand to one another in the ratio 1:35:20 000.

In acetate buffer H_3AsO_3 is the predominant As(III) species, and it is carrying the bulk of the reaction. Hence the activation parameters determined in acetate apply directly to k_1. A similar situation applies approximately with respect to $H_2AsO_3^-$ and k_2 in the carbonate buffer at pH 9.2. In alkaline solution, however, the situation is complicated by the need to involve both K_2 and the water dissociation constant, K_w, since the temperature dependence is measured at constant $[OH^-]$ rather than at constant pH. The appropriate relationships are

$$\begin{aligned} \Delta H^\ddagger{}_3' &= \Delta H^\ddagger{}_{obsd} + \Delta H_w - \Delta H_2 \\ &= 24.4 - \Delta H_2 \text{ in } 0.1 \text{ M NaOH} \\ &= 25.4 - \Delta H_2 \text{ in } 1 \text{ M NaOH} \\ \Delta S^\ddagger{}_3' &= \Delta S^\ddagger{}_{obsd} + \Delta S_w - \Delta S_2 - R \ln a_{OH^-} \\ &= -42 - \Delta S_2 \text{ in } 0.1 \text{ M NaOH} \\ &= -41 - \Delta S_2 \text{ in } 1 \text{ M NaOH} \end{aligned}$$

if we take a_{OH^-} equal to $[OH^-]$.

By analogy with similar systems, we may estimate ΔS_2 to be −30 cal/mol·deg.[21] Then if we take K_2 to be about 10^{-14} M, ΔH_2 becomes ca. 10 kcal/mol, and we conclude that $\Delta H^\ddagger{}_3' \simeq 15$ kcal/mol and $\Delta S^\ddagger{}_3' \simeq -11$ to −12 cal/mol·deg.

The reaction rate shows very little salt dependence in the regions in which the k_1 and k_2 paths predominate, and a marked positive salt dependence in the k_3 region. This is qualitatively consistent with the changes in charge involved in formation of the three activated complexes, though we must bear in mind that a complex mixture of effects is involved in alkaline solution, since k_3', K_2' and K_w are all dependent on salt concentration. The salt effects on K_2 and K_w, however, are in the same direction, and they may roughly cancel each other.

The reaction between sulfite and perbromate can be accounted for entirely by the rate-determining step

$$BrO_4^- + SO_3^{2-} \rightarrow BrO_3^- + SO_4^{2-}$$

At pH 9 and above, SO_3^{2-} is the predominant form of the re-

Table VI. Oxygen Transfer from Perbromate to Sulfite[a]

experiment	atom % ^{18}O in $BaSO_4$	n^b
$KBrO_4$ decomposition	(0.1948)[c]	
$H_2SO_3 + Br_2$, 0.14 M $HClO_4$	0.3933	
$SO_3^{2-} + Br_2$, 0.12 M NaOH	0.3927	
$HSO_3^- + BrO_4^-$, 0.14 M $HC_2H_3O_2$ + 0.06 M $NaC_2H_3O_2$	0.3563	0.75
$SO_3^{2-} + BrO_4^-$, 0.2 M $NaHCO_3$	0.3452	0.98
$SO_3^{2-} + BrO_4^-$, 0.12 M NaOH	0.3425	1.03

[a] All experiments at ca. 25 °C with sulfite in equilibrium with water enriched ca. twofold in ^{18}O. $[S(IV)] = 0.03$ M, $[BrO_4^-] = 0.016$ M in the acetate system and 0.045 M in the carbonate and NaOH systems. All concentrations are those prevailing prior to reaction. Atom % $^{18}O \equiv 100[^{18}O]/([^{16}O] + [^{18}O])$. [b] n = number of perbromate oxygens in each SO_4^{2-} formed, corrected for minor variations in isotopic composition of the solutions that resulted from the use of normal 50% NaOH and 70% $HClO_4$. The correction was less than 0.01 in n. A realistic uncertainty for n is probably ±0.03. [c] Atom % ^{18}O in $KBrO_4$.

Table VII. Oxygen Transfer from Perbromate to Arsenite[a]

experiment	species enriched[b]	atom % ^{18}O in barium arsenate
$KBrO_4$ decomposition	none	(0.1948)[c]
$AsO_4^{3-} + H_2O$	none	0.2072
$AsO_4^{3-} + H_2O$	H_2O	0.2483
$H_2AsO_3^- + H_2O + Br_2$	$H_2AsO_3^-$ H_2O	0.3907
		0.3918[d]
$H_2AsO_3^- + H_2O + BrO_4^-$	none	0.1979
$H_2AsO_3^- + H_2O + BrO_4^-$	$H_2AsO_3^-$, H_2O	0.3524
		0.3547[d]
calcd no. of perbromate oxygens in each arsenate ion: 0.99 ± 0.06[e]		

[a] At 40–50 °C, $[BrO_4^-]_0 = 0.065$ M, $[As(III)]_0$ or $[As(V)]_0 = 0.05$ M, $[NaOH]_0 = 0.1–0.2$ M. Atom % $^{18}O \equiv 100[^{18}O]/([^{16}O] + [^{18}O])$. [b] Approximately twofold enriched in ^{18}O. [c] Atom % ^{18}O in the $KBrO_4$. [d] Duplicate experiments. [e] Based on the analytical determination of 4.16 oxygens per arsenic in the barium arsenate precipitate.

ductant, and the reaction is independent of pH. In the acetate buffer SO_3^{2-} is ca. 2% of the total sulfur (IV), and the 44-fold decrease in rate constant gives no indication of a reaction path involving HSO_3^-. Such a path must have a rate constant at least 200-fold smaller than that for the SO_3^{2-} path. The activation parameters for the sulfite reaction are similar to those for the arsenite system, while the salt dependence is substantial and is comparable to that for the arsenic system in the alkaline region, where a similar change in charge is involved in the formation of the activated complex.

Over the limited range studied, the reduction of perbromate by antimony(III) would appear to involve reaction of BrO_4^- with a predominant singly charged antimonite anion.[22] The increase in rate compared to the arsenite and sulfite systems is largely reflected in a decrease in activation enthalpy.

The arsenite oxygen transfer studies and the sulfite studies at pH ≥9 indicate that reaction involves essentially quantitative transfer of a perbromate oxygen to the reductant. In acetate buffer, the reaction of perbromate with sulfite gives bromide rather than bromate as the reduction product. Halperin and Taube[11] have shown that under these conditions bromate only transfers about 2.1 of its three oxygens to sulfite. If we make allowance for this, we conclude that in acetate buffer, also, the first step of the reaction, which is presumably the reduction of perbromate to bromate, proceeds with complete transfer of a perbromate oxygen. On the basis of these observations, we suggest that the reaction of perbromate with two-equivalent reductants generally involves oxygen transfer, and that the slowness of these reactions is, indeed, a reflection of the inertness of the perbromate ion toward removal of its oxygens.

We may ask why it is that the reactions of perbromate involve an inverse hydrogen-ion dependence, whereas those of other oxy halogen ions generally involve first- or second-order positive hydrogen ion dependences. It has been suggested that in reactions of bromate and chlorate one role of the proton may be to labilize the halate oxygen.[23] The perbromate ion, however, is a very poor base, and it probably cannot utilize a proton in this way. Hence, the only role that protons play is to protonate the reductant, forming species that are less basic, and therefore less ready to accept a perbromate oxygen. When the reductant cannot be protonated, as in the case of I^-, the reaction tends to be independent of pH.[7] This difference in pH dependence leads to interesting "crossovers" in reaction rates. Thus in acid solution both I^- and sulfur(IV) react more rapidly with bromate than with perbromate, while in base both react more rapidly with perbromate. It is therefore possible in acid to reduce bromate preferentially in the presence of perbromate, while in base it is possible to reduce perbromate preferentially in the presence of bromate.

If we consider the relative rates of reaction of perbromate with the reductants studied in this paper, we find that they increase in the order $N_3^- < ClO_2^- \sim SeO_3^{2-} \sim NO_2^- < P(III) \ll S(IV) \leq As(III) < Sb(III)$. There is no consistent overall correlation of rate with electrode potential, though this may be a factor in the low reactivity of ClO_2^-, SeO_3^{2-}, and NO_2^-. The increasing rate as one goes to heavier elements in group 5 probably reflects increasing polarizability, which makes it easier for the reductant to accept a perbromate oxygen.[24] Phosphite is a particularly interesting case. Since the phosphite ion has one proton bonded directly to the phosphorus, it has no electron pair free to accept an oxygen atom from the perbromate. In order for reaction to take place, it may actually be necessary to dislodge this nonacidic, nonlabile proton, resulting in a very slow reaction despite the high thermodynamic driving force.

Although oxygen transfer may well be the most often encountered mechanism for oxidation by perbromate, it need not be the only one, as we have already indicated in our introductory remarks. It would therefore be of interest to undertake a series of studies of the reactions of perbromate with such one-equivalent reductants as $Fe(CN)_6^{4-}$, Ti^{3+} and Eu^{2+}, where oxygen transfer seems particularly unlikely.

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References and Notes

(1) Work performed under the auspices of the Division of Basic Energy Sciences of the Department of Energy.
(2) Kemisk Institut, University of Aarhus, Aarhus, Denmark.
(3) Department of Chemistry, University of Missouri, Columbia, Mo. 65201.
(4) E. H. Appelman, *J. Am. Chem. Soc.*, **90**, 1900 (1968).
(5) E. H. Appelman, *Inorg. Chem.*, **8**, 223 (1969).
(6) F. Schreiner, D. W. Osborne, A. V. Pocius, and E. H. Appelman, *Inorg. Chem.*, **9**, 2320 (1970).
(7) L. A. Lazarou, P. A. Siskos, M. A. Koupparis, T. P. Hadjiioannou, and E. H. Appelman, *Anal. Chim. Acta*, **94**, 475 (1977).
(8) K. J.Olsen, K. Sehested, and E. H. Appelman, *Chem. Phys. Lett.* **19**, 213 (1973).
(9) E. H. Appelman, *Inorg. Synth.*, **13**, 1 (1972).
(10) P. K. Norkus, A. M. Lunyatskas, and S. P. Tsarankute, *Zh. Anal. Khim.*, **20**, 753 (1965).
(11) J. Halperin and H. Taube, *J. Am. Chem. Soc.*, **74**, 375 (1952).

(12) B. D. Holt, *Anal. Chem.*, **49**, 1664 (1977).
(13) W. C. Copenhafer and P. H. Rieger, *J. Am. Chem. Soc.*, **100**, 3776 (1978).
(14) B. Z. Shakhashiri and G. Gordon, *Talanta*, **13**, 142 (1966).
(15) These analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.
(16) F. S. Williamson and E. L. King, *J. Am. Chem. Soc.*, **79**, 5397 (1957).
(17) W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957).
(18) A. Okumura and N. Okazaki, *Bull. Chem. Soc. Jpn.*, **46**, 2937 (1973).
(19) C. S. Bhatnagar and K. Govind, *Z. Naturforsch. B*, **21**, 190 (1966).
(20) T. M. Loehr and R. A. Plane, *Inorg. Chem.*, 7, 1708 (1968).
(21) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 270-3**, 96 (1968).
(22) W. M. Latimer, "Oxidation Potentials", Prentice-Hall, Englewood Cliffs, N.J., 1952, p 118.
(23) H. Taube, *Rec. Chem. Prog.*, 17, 25 (1956).
(24) J. O. Edwards, "Inorganic Reaction Mechanisms", W. A. Benjamin, New York, N.Y., 1964, Chapters 4 and 5.

A Directing Effect of Neighboring Aromatic Groups on the Regiochemistry of Formation and on the Stereochemistry of Alkylation and Bromination of Ketone Lithium Enolates. Evidence for Lithium–Arene π Coordination and for a Dramatic Effect of Even Small Amounts of Copper(I) in Controlling Stereochemistry and in Limiting Polyalkylation

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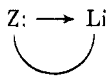
Abstract: A series of β-aryl- and β-aralkylcyclopentanones and cyclohexanones and 5-tolyl-3-hexanone was studied in the presence of lithium diisopropylamide in THF at room temperature. Enolization occurred preferentially toward the aryl group, and the magnitude of this regioselectivity paralleled the π-electron *donating* ability of the aryl group: *p*-methoxyphenyl > phenyl > *p*-nitrophenyl. A critical lithium-arene π coordination is postulated to account for these unusual results. Evidence for such π coordination came from ^{1}H and ^{13}C NMR data and from the effects of coordinating solvents. The enolate intermediates were isolated as their enol silyl ethers, or they were treated with methyl iodide, allyl bromide, methyl bromoacetate, or molecular bromine. The course of enolate reaction with these electrophiles was distinctly and reproducibly different in the absence or in the presence of copper(I). Even small amounts of copper(I) decreased the amount of polyalkylation and increased the amount of *cis*-2-alkyl-3-phenylcyclopentanone produced, even though this epimer is less stable thermodynamically then the corresponding *trans*-2-alkyl-3-phenylcyclopentanone. An explanation for this dramatic and catalytic effect of copper(I) is offered. Reaction of the more substituted enolate of 2-methyl-3-phenylcyclopentanone with methyl bromoacetate gave 2,2,3-trisubstituted cyclopentanone **25** stereospecifically; cyclopentanones like **25** should be useful precursors to AB-aromatic 19-norsteroids.

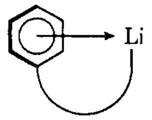
Introduction

Heteroatom-directed and -assisted lithiation reactions are well-known and useful, and they result from a strongly stabilizing Lewis base-Lewis acid coordinative interaction as represented in generalized structure 1.[1] In analogy, it can be expected that the basic π electrons of an aromatic group might also direct and assist some lithiation reactions at nonbenzylic positions (cf. 2). Indeed lithium complexation with the π electrons of aromatic groups has precedent. For example, an X-ray study of benzyllithium revealed lithium coordination to the π cloud of the benzyl group,[2] and this type of association has been suggested to account for the stereospecificity of the *n*-butyllithium-promoted polymerization of styrene.[3]



1

Z = OR, SR, NR$_2$, PR$_2$



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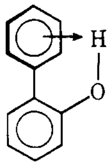
Strong spectroscopic evidence indicates the existence of hydrogen-arene π coordination in such systems as *o*-arylphenols (**3**)[4] and 2-phenylethanol (**4**).[5] Because the lithium atom in lithium enolates resembles to a significant degree the hydroxyl hydrogen atom in enols, it seemed reasonable to expect lithium-arene π coordination in lithium enolates derived from some aralkyl ketones (e.g., **5**). We reasoned that it might be possible to use the neighboring aromatic groups in some unsymmetrical aralkyl ketones to direct the lithiation of these compounds, thus providing a mild, useful, and yet unusual method for controlling the regiochemistry of ketone lithium enolate formation and possibly also for controlling the stereochemistry of alkylation and bromination of these enolates.



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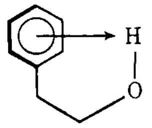

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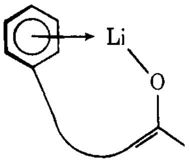

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In 1977 we reported preliminary results dealing with regioselective formation and stereoselective alkylation of some β-aryl- and β-aralkylcyclopentanone lithium enolates;[6] we now report the full details of that work as well as its extension to aryl-substituted cyclohexanones and to acyclic 5-tolyl-3-hexanone. The effects of solvent, temperature, and lithiating agents, as well as some ^{1}H and ^{13}C NMR data, all support our original proposal of an enolate intermediate having lithium-

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