+20 °C the B_2H_6 signal was growing in slowly.

C. Equilibrium Studies. 1. $(CH_3)_3P{\cdot}BH_3 + THF{\cdot}B_3H_7 \rightleftharpoons THF{\cdot}BH_3 + (CH_3)_3P{\cdot}B_3H_7$. The reaction solution in section B.3.a was allowed to stand at room temperature (about 25 °C), and its ^{11}B NMR spectra were recorded from time to time. Another tube containing 0.485 mmol of $(CH_3)_3P{\cdot}B_3H_7$ and 0.261 mmol of B_2H_6 in 1.8 mL of tetrahydrofuran was prepared, and the spectra of its contents were recorded likewise. The intensities of the four species in the title reaction were measured on each spectrum and were used to find the value of $[THF{\cdot}BH_3][(CH_3)_3P{\cdot}B_3H_7]/[(CH_3)_3P{\cdot}BH_3][THF{\cdot}B_3H_7]$ at the time of the spectrum recording. The values for the two samples slowly converged to a value of 4 ± 1 in a period of 8 months. The signals of B_2H_6 and B_5H_9 and a signal of an unidentified species at +26 ppm were present in the final spectra. The solutions were clear and colorless.

2. $H_3P{\cdot}BH_3 + THF{\cdot}B_3H_7 \rightleftharpoons THF{\cdot}BH_3 + H_3P{\cdot}B_3H_7$. The solutions, which were used for the studies of reactions of $H_2B(THF)_2{}^+B_3H_8{}^-$, "$THF{\cdot}BH_3 + THF{\cdot}B_3H_7$", and B_4H_{10} with PH_3, were stored at 0 °C for 67 h. The equilibrium appeared to have been reached within 24 h. The values of $[THF{\cdot}BH_3][H_3P{\cdot}B_3H_7]/[H_3P{\cdot}BH_3][THF{\cdot}B_3H_7]$ for the three samples were 0.43, 0.42, and 0.38; average 0.41 ± 0.02. Prolonged standing (ca. 1 month) of the sample solutions at room temperature resulted in the formation of a white precipitate. Various identified ($THF{\cdot}B_3H_7$, B_2H_6, and B_5H_9) and unidentified signals were seen in the ^{11}B spectra of these deteriorated samples, and no signals of $H_3P{\cdot}BH_3$ and $H_3P{\cdot}B_3H_7$ were found.

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Registry No. $H_2B(THF)_2{}^+B_3H_8{}^-$, 55669-45-9; $THF{\cdot}BH_3$, 14044-65-6; $THF{\cdot}B_3H_7$, 52842-96-3; B_4H_{10}, 18283-93-7; $(CH_3)_3P{\cdot}BH_3$, 35527-73-2; $(CH_3)_3P{\cdot}B_3H_7$, 12543-29-2; $(CH_3)_2O{\cdot}B_3H_7$, 12347-17-0; $(CH_3)_2O{\cdot}BH_3$, 13292-86-9; $(C_2H_5)_2O{\cdot}B_3H_7$, 52842-97-4; $P(CH_3)_3$, 594-09-2; CH_2Cl_2, 75-09-2; $(CH_3)_2O$, 115-10-6; $(C_2H_5)_2O$, 60-29-7; THF, 109-99-9.

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Kinetics of the Reduction of the Tetrahydroxoargentate(III) Ion by Arsenite

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The reaction of $Ag(OH)_4{}^-$ with arsenite ion to give Ag(I) and arsenate in strong base was studied by stopped-flow spectrophotometry. The reaction was found to fit a second-order rate law in which all three arsenite species present, $H_2AsO_3{}^-$, $HAsO_3{}^{2-}$, and $AsO_3{}^{3-}$, participate. Second-order rate constants for the three paths at 25 °C and $\mu = 1.2$ M are respectively $k_1 = (6.2 \pm 1.0) \times 10^3\ M^{-1}\ s^{-1}$, $k_2 = (3.7 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$, and $k_3 = (1.8 \pm 0.5) \times 10^4\ M^{-1}\ s^{-1}$. In order to evaluate the activation parameters, the temperature dependence of the deprotonation of arsenite by $[OH^-]$ was studied. The equilibrium parameters are ΔH_2(for $H_2AsO_3{}^- + OH^- \rightleftarrows HAsO_3{}^-$) = 5 ± 1 kcal/mol and ΔH_3(for $HAsO_3{}^{2-} + OH^- \rightleftarrows AsO_3{}^{3-}$) = −2 ± 7 kcal/mol ($\mu = 1$ M). The redox reaction appears to proceed by a one-step oxygen atom transfer. Two kinetically indistinguishable mechanisms are discussed: one involving initial attack of an As(III) oxygen at an axial silver(III) site and the other involving initial interaction between the arsenic and a bound hydroxyl. Differences in activation parameters are indicative of a larger barrier to redox for $AsO_3{}^{3-}$ compared to those for the other two arsenite species. The dependence of the reaction rate on ionic strength supports the formulation of the Ag(III) species as the mononegatively charged ion $Ag(OH)_4{}^-$.

Introduction

The complex $Ag(OH)_4{}^-$ is a square-planar d^8 system that is conveniently prepared by the electrochemical oxidation of a silver-foil anode in NaOH solution.[1-3] The complex is metastable and has a half-life of about $1^1/_2$ h in 1.2 M NaOH at room temperature. The lifetime of the complex and the maximum concentration obtainable depend on the OH^- concentration.[1,2]

Kinetic studies of the oxidation of arsenite by transition-metal complexes in alkaline media have been carried out for a limited number of systems such as $Fe(CN)_6{}^{3-}$,[4] $Mo(CN)_8{}^{3-}$,[5] $W(CN)_8{}^{3-}$,[6] and $Pt(Cl)_6{}^{2-}$.[7] The pH ranges employed for all these studies are such that the monoanion $H_2AsO_3{}^-$ is the predominant form of As(III). The reaction rates for the above-mentioned complexes all show a linear dependence on base concentration, which is accounted for by a mechanism in which the dianion is the reactive species. The rates of reduction of these complexes are many orders of magnitude less than that of $Ag(OH)_4{}^-$, which can react readily by an inner-sphere mechanism.

In their Raman study of the structure of arsenite ions in basic solution, Loehr and Plane[8] noted that at no $[OH^-]$ does $HAsO_3{}^{2-}$ exist unaccompanied by significant fractions of $H_2AsO_3{}^-$ and/or $AsO_3{}^{3-}$. A recent report on the third dissociation constant of arsenous acid indicates that it has a p*K* value only 0.5 unit greater than that of the second dissociation constant.[9] The present kinetic study supports the presence of three stoichiometrically significant arsenite species in the range $0.1 \leq [OH^-] \leq 1.2$ M.

Experimental Section

Reagents. The chemicals used were all of reagent grade. $Ag(OH)_4{}^-$ solutions were prepared as previously described[3] by using doubly

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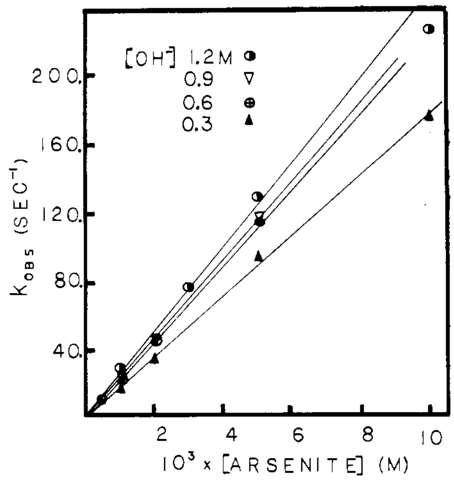

Figure 1. First-order plots of arsenite dependence at 25 °C and μ = 1.2 M.

distilled water and low-carbonate NaOH (50% solution). Arsenite stock solutions were made by exact weighing of sodium arsenite ($NaAsO_2$; Baker and Adamson). New stock solutions were prepared every 5–10 days to minimize variations in concentration due to air oxidation. This effect has been found to be small even for highly basic solutions. $NaClO_4$ solutions for ionic strength adjustment were prepared from NaOH and $HClO_4$. The solutions were filtered, electrolyzed to remove oxidizable species, and degassed with nitrogen.

Procedure. All kinetic runs were made with arsenite in large excess on an Aminco-Morrow stopped-flow apparatus with a thermostated reaction cell.[3,10] The reaction was followed by monitoring the decay of the $Ag(OH)_4^-$ absorbance (maximum at 267 nm, extinction coefficient 1.17×10^4 M^{-1} cm^{-1}).[2,3] The absorbance of arsenite at this wavelength is negligible. Reaction traces were photographed from a Tektronix 564B storage oscilloscope with a C-12 camera. A Graf/Pen sonic digitizer was employed to reduce the data to digital form. Computations were performed on the Itel NAS/7 computer at the URI Computer Center. The reaction was found to obey pseudo-first-order kinetics for all conditions of this study. A linear least-squares computer program was used to obtain rate constants (k_{obsd}), which were generally reproducible to within ±5% for duplicate runs. Determination of individual rate and activation parameters was achieved by nonlinear regression and by graphical methods as described in the results section. Silver(III) preparations that were allowed to decompose partially before use tended to give somewhat larger than expected rate constants, apparently due to catalysis by solid reduction products. Otherwise, rate constants were independent of initial [Ag(III)]. The rate data reported here have been selected to minimize catalytic effects.

Results and Treatment of Data

Reaction Stoichiometry. The stoichiometry of the reaction with excess As(III) was determined by measuring the loss of As(III) from a 1×10^{-3} M solution after addition of 2.2×10^{-4} M $Ag(OH)_4^-$ in 1.2 M NaOH. After acidification of the reaction mixture, titration with standard $KMnO_4$ showed that 1 mol of As(III) was oxidized to As(V)/mol of Ag(III) consumed (±5%). Small quantities of a brown-black precipitate that dissolved readily in dilute HNO_3 were collected by filtering unacidified portions of the reaction mixture. This solid appears to be Ag_2O, as would be expected from the complementary two-electron-transfer reaction

$$\mathrm{Ag(III)} + \mathrm{As(III)} \rightarrow \mathrm{Ag(I)} + \mathrm{As(V)} \qquad (1)$$

Because of the solubility of Ag(I) (1.5×10^{-4} M as $Ag(OH)_2^-$ in 1.2 M NaOH)[11] the amount of Ag(I) recovered (as determined by Volhard titration)[12] was only a fraction of $[Ag(III)]_0$.

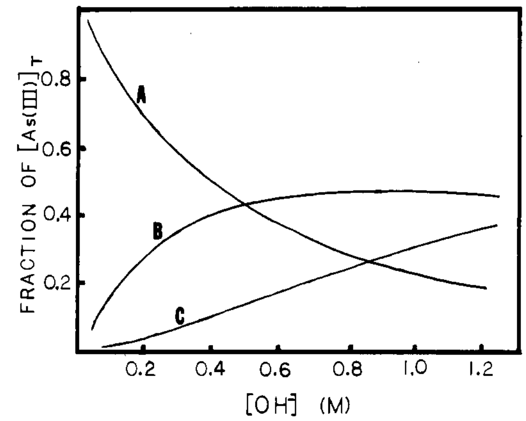

Figure 2. Speciation of arsenite ion (based on data from ref 9): A = $H_2AsO_3^-$; B = $HAsO_3^{2-}$; C = AsO_3^{3-}. Ordinate is fraction of total arsenite.

The stoichiometry under conditions of excess $Ag(OH)_4^-$ was measured by taking the difference between initial and final absorbances of a kinetic trace at 267 nm. The value for Δ[Ag(III)] thus obtained when compared with the amount of arsenite reacted also indicated a stoichiometry of 1:1 within experimental error for $[Ag(III)]_0 = 5.0 \times 10^{-5}$ M and $[As(III)]_0 = 1 \times 10^{-5}$ and 2.5×10^{-5} M.

Kinetics. The dependence of the reaction rate on arsenite ion concentration was studied at 25 °C and μ = 1.2 M with initial concentrations of $1 \times 10^{-5}\ \mathrm{M} \leq [Ag(OH)_4^-]_0 \leq 5 \times 10^{-5}$ M and $1 \times 10^{-3}\ \mathrm{M} \leq [As(III)] \leq 1 \times 10^{-2}$ M. As illustrated in Figure 1, the reaction is first order in total [As(III)] with a definite but nonlinear [OH⁻] dependence. Comparison of the absorbance at $t = 0$ with the absorbance of a nonreacting aliquot of Ag(III) indicates that there is no significant preassociation reaction within the mixing time of the stopped-flow apparatus (2 ms). Several runs were made in solutions that contained added As(V). This addition had no effect on the observed kinetics.

Hydroxide Ion Dependence. The range of basicity under which reactions of the tetrahydroxoargentate(III) ion can be conveniently studied corresponds to a region of changing speciation for the arsenite ion. Thus, the following arsenite equilibria are relevant to our kinetic experiments:

$$H_2AsO_3^- + OH^- \rightleftarrows HAsO_3^{2-} + H_2O \quad K_2 = K_{a2}/K_w \qquad (2)$$

$$HAsO_3^{2-} + OH^- \rightleftarrows AsO_3^{3-} + H_2O \quad K_3 = K_{a3}/K_w \qquad (3)$$

Figure 2 contains a distribution diagram for the various As(III) species at μ = 1 M using the values of pK_{a2} = 13.5 and pK_{a3} = 14.0[9] and pK_w = 13.8.[13]

The behavior of k_{obsd} with [OH⁻] and the speciation of arsenite (Figure 2) in this range of [OH⁻] suggest the overall rate law given by eq 4 in which (i) k_2 alone, (ii) k_1 and k_2,

$$-\mathrm{d[Ag(III)]}/\mathrm{d}t = k_{obsd}[\mathrm{Ag(III)}] = (k_1[H_2AsO_3^-] + k_2[HAsO_3^{2-}] + k_3[AsO_3^{3-}])[\mathrm{Ag(III)}] = \left(\frac{k_1 + k_2K_2[OH^-] + k_3K_2K_3[OH^-]^2}{1 + K_2[OH^-] + K_2K_3[OH^-]^2}\right)[\mathrm{As(III)}]_T[\mathrm{Ag(III)}] \qquad (4)$$

or (iii) k_1, k_2, and k_3 may be significant. Our analysis of the rate data is based on the following considerations:

(i) The ratios of the values of k_{obsd} at e.g. [OH⁻] = 0.1 M and [OH⁻] = 0.4 M are less than the ratios of the fractions of $HAsO_3^{2-}$ at corresponding [OH⁻]'s. This suggests that k_1 is not negligibly small; i.e., the value of k_{obsd} is not simply

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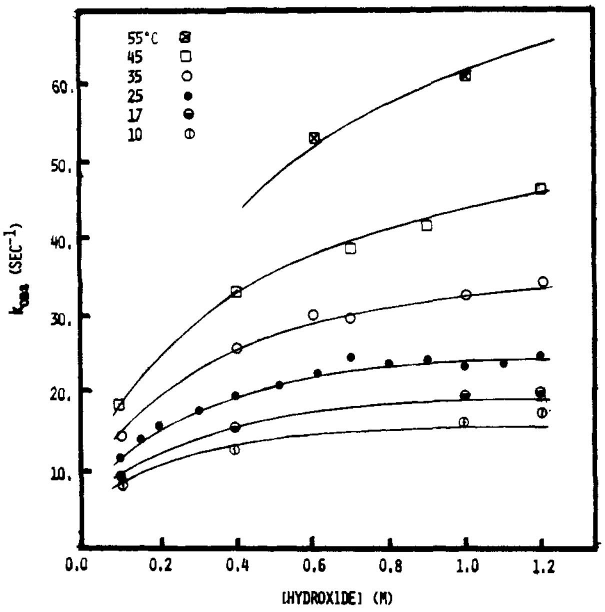

Figure 3. Variation of k_{obsd} with temperature and [OH$^-$] at μ = 1.2 M. Solid lines were calculated from rate constants at 25 °C and derived activation parameters (eq 6).

proportional to [$HAsO_3^{2-}$]. (Note that a significant contribution from the k_3 term at the lower [OH$^-$] would reinforce this conclusion.)

(ii) The presence of AsO_3^{3-} in stoichiometrically significant quantities at high [OH$^-$] is required by an analysis of the data at 25 °C. Although k_{obsd} seems to level off at highest [OH$^-$], treatment of the data as resulting from a single equilibrium would require pK_{a2} to be about 0.5 unit lower than reported[8,13] (cf. data for higher temperatures and next section).

(iii) Since both $HAsO_3^{2-}$ and $H_2AsO_3^-$ react and AsO_3^{3-} is present in significant quantities at [OH$^-$] > 0.6 M, a small but nonzero contribution from the k_3 term is necessary in order to account for the fact that the rate does not decrease at the highest hydroxyl concentrations (cf. Figures 2 and 3).

When the rate data were fit by nonlinear regression to a rate law with three species present but AsO_3^{3-} not reacting, the residuals, $k_{calcd} - k_{obsd}$ showed that this model is unsatisfactory. When only rate constants at [OH$^-$] ≤ 0.6 M were used, a good fit of k_1 and k_2 was obtained since [AsO_3^{3-}]/[As(III)]$_T$ is small in this range. However, extrapolation of these data to higher [OH$^-$] resulted in an underestimation of the net rate constant that was proportional to the fraction of AsO_3^{3-} at the corresponding hydroxyl concentrations. For these reasons, hypothesis iii, that no term in eq 4 can be neglected, appears to be the only tenable one. However, the specific range of hydroxyl ion required for stabilization of Ag(III) along with the proximity of the second and third pK's for As(III) deprotonation limits our ability to determine all three rate constants with similar precision.

At low [OH$^-$], where the fraction of AsO_3^{3-} is small, k_{obsd} can be approximated by eq 5. Under these conditions, a plot

$$k_{obsd} \cong \left(\frac{k_1 + k_2K_2[OH^-]}{1 + K_2[OH^-]}\right)[As(III)]_T \tag{5}$$

of $k_{obsd}(1 + K_2[OH^-])$ vs. [OH$^-$] resulted in estimates of k_1 = 6.5 × 10^3 M^{-1} s^{-1} and k_2 = 3.3 × 10^4 M^{-1} s^{-1} at 25 °C and μ = 1.2 M. The values of k_1, k_2, and k_3 obtained by a nonlinear least-squares fit of all the data at 25 °C to eq 4 were k_1 = (6.5 ± 1) × 10^3 M^{-1} s^{-1}, k_2 = (3.7 ± 0.3) × 10^4 M^{-1} s^{-1}, and k_3 (1.9 ± 0.4) × 10^4 M^{-1} s^{-1}. In the next section, we will refine these values to account for the change in speciation from 20 to 25 °C.

Table I. Hydroxide Ion and Temperature Dependence for the Reaction between $Ag(OH)_4^-$ and Arsenite at μ = 1.2 M ([As(III)]$_T$ = 1.0 × 10^{-3} M)

temp, °C	[OH$^-$], M	k_{obsd}, s^{-1}	k_{calcd},[a] s^{-1}
10	0.1	7.8	7.8
	0.4	12.5	12.5
	1.0	16.0	15.3
	1.2	17.3	15.4
17	0.1	8.6	9.2
	0.4	15.2	15.3
	1.0	19.8	18.7
	1.2	20.5	18.9
25	0.1	11.5	11.3
	0.15	13.7	13.1
	0.2	15.7	14.7
	0.3	17.3	17.2
	0.4	19.2	19.1
	0.5	20.1	20.4
	0.6	22.8	21.5
	0.7	24.9	22.3
	0.8	23.7	23.0
	0.9	24.2	23.4
	1.0	23.3	23.7
	1.1	23.4	23.9
	1.2	25.0	24.0
35	0.1	14.2	14.2
	0.4	26.2	25.2
	0.6	29.7	28.7
	0.7	29.2	30.0
	1.0	32.8	32.3
	1.2	34.1	33.2
45	0.1	17.4	18.0
	0.4	33.0	33.5
	0.7	38.7	40.8
	0.9	41.3	43.9
	1.2	47.5	47.1
55	0.6	53.5	50.7
	1.0	62.0	61.3

[a] k_{calcd} based on activation parameters and rate constants summarized in Table II.

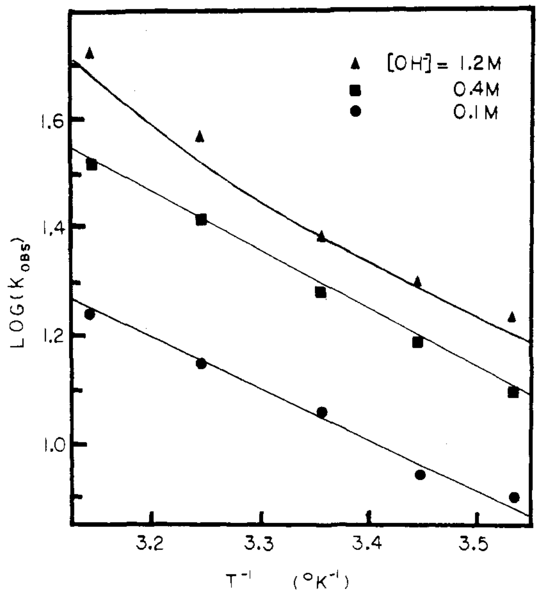

Figure 4. Arrhenius plots at μ = 1.2 M. Note especially the curvature at high[OH$^-$] indicating the participation of k_3. Solid lines were calculated by using apparent values of E_{a1} = E_{a2} = 4 kcal/mol and E_{a3} = 9 kcal/mol and assuming constant speciation.

Temperature Dependence. Because of the complexity of the rate law and its temperature dependence, several approaches were required for the determination of the activation parameters. Table I lists rate data for several OH$^-$ concentrations

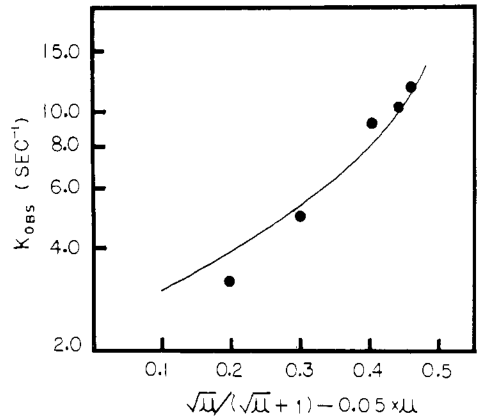

Figure 5. Ionic strength dependence of the reaction between $Ag(OH)_4^-$ and As(III). [Ag(III)] = 5×10^{-5} M; $[As(III)]_T = 1 \times 10^{-3}$ M. The solid line was calculated by assuming a 1− charge on Ag(III) and an ionic strength dependence on protolytic equilibria as predicted in ref 17a.

in the temperature range 10–55 °C. Arrhenius plots of the data (Figure 4) are linear at $[OH^-] = 0.1$ and 0.4 M, indicating that k_1 and k_2 have similar activation energies.[14] However, the data at 1.2 M OH^- (where the trianion is about 35% of the total arsenite at 25 °C) show a definite curvature, which we attribute to a temperature dependence for the reaction between $Ag(OH)_4^-$ and AsO_3^{3-} significantly different from that with the other two arsenite moieties.

The relative contribution of each reaction to the overall rate is a function of both the rate constant as given in eq 6[15] and

$$k_i = \frac{RT}{Nh} e^{\Delta S_i^{\ddagger}/R} e^{-\Delta H_i^{\ddagger}/RT} \qquad (6)$$

the relative fraction of each arsenite species at a given temperature. The resolution of activation parameters for k_1, k_2, and k_3 is, thus, complicated by the lack of published data on the second and third ionization enthalpies (ΔH_{a2} and ΔH_{a3}) of arsenous acid. As an initial approximation, it was assumed that the difference between both of these values and the ionization enthalpy of water (ΔH_w = 13.7 kcal/mol at μ = 1 M[13]) is equal to zero. Thus, if $\Delta H_1 = \Delta H_2 = 0$ (where $\Delta H = \Delta H_a - \Delta H_w$; subscripted as in eq 2), the speciation of arsenite would be independent of temperature. Under this set of conditions, the k_{obsd} data were fit to a function of three parameters corresponding to $\Delta H_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, and $\Delta H_3^{\ddagger}$ as defined in eq 7 where

$$k_i = k_i^{25 °C}\left(\frac{T}{298}\right) \exp\left[-\Delta H_i^{\ddagger}\left(\frac{1}{T} - \frac{1}{298}\right)/R\right] \qquad (7)$$

the entropy factor of eq 6 has been eliminated as a variable in each case since the individual rate constants at 25 °C had been determined independently. The values thus obtained ($\Delta H_1 = \Delta H_2$ = 3.7 kcal/mol, ΔH_3 = 9.4 kcal/mol) were in substantial agreement with those estimated from Figure 4.

The above analysis presumed that K_{a2} and K_{a3} do not vary with temperature. In order to increase the reliability of our results, we undertook to determine ΔH_2 and ΔH_3 (see eq 2 and 3) by measuring spectral changes exhibited by arsenite as a function of $[OH^-]$ and temperature. Quantitative data were taken at 247 nm and μ = 1 M as in the work of Ivakin et al.[9] Results at three temperatures are displayed in Figure 6. Note that the absorbance shows no temperature dependence at $[OH^-] = 0.012$ M where $H_2AsO_3^-$ is the only arsenite species present but that a large temperature variation exists at other hydroxide concentrations. Peak position also varied with both temperature and $[OH^-]$, indicating changes in speciation.

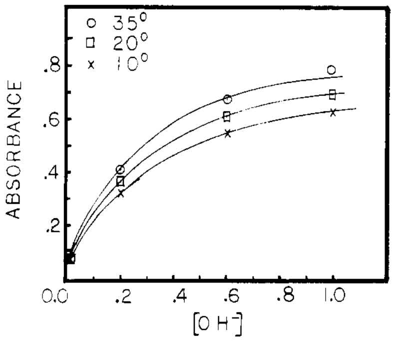

Figure 6. Temperature dependence of arsenite ion equilibria at μ = 1.0 M. Absorbances were measured at 247 nm as a function of $[OH^-]$. Solid lines were calculated from extinction coefficients, K_2 and K_3 determined at 20 °C, ΔH_2 = 5 kcal/mol, and ΔH_3 = −2 kcal/mol.

Extinction coefficients of the three arsenite species at 247 nm were determined at 20 °C from the measured absorbances and the equilibrium constants of ref 9. The resulting values are $\epsilon(H_2AsO_3^-) = 6 \pm 1$ M^{-1} cm^{-1}, $\epsilon(HAsO_3^{2-}) = 105 \pm 3$ M^{-1} cm^{-1}, and $\epsilon(AsO_3^{3-}) = 60 \pm 5$ M^{-1} cm^{-1}. From these values, speciation at other temperatures was calculated. This allowed estimation of K_{a2} and K_{a3} as a function of temperature. A reliable estimate of $\Delta H_2 = 5 \pm 1$ kcal/mol was thus obtained. Although the presence of a second equilibrium is clearly indicated by the variation of absorbance with temperature at $[OH^-] = 1.0$ M, the similarity between $\epsilon(HAsO_3^{2-})$ and $\epsilon(AsO_3^{3-})$ and the restricted range of $[OH^-]$ where AsO_3^{3-} is appreciable give rise to large uncertainties in K_{a3}. Hence, an acceptable estimate of ΔH_3 was not possible. However, the uncertainty in ΔH_3 (the above analysis gives $\Delta H_3 = -2 \pm 7$ kcal/mol) does not significantly affect the analysis of the kinetic data for the reactions of $H_2AsO_3^-$ and $HAsO_3^{2-}$ with silver(III).

Refinement of the estimates of k_1, k_2, and k_3 to reflect the change in speciation from 20 °C yielded final values for the 25 °C data of $k_1 = (6.2 \pm 1) \times 10^3$ M^{-1} s^{-1}, $k_2 = (3.7 \pm 0.4) \times 10^4$ M^{-1} s^{-1}, and $k_3 = (1.8 \pm 0.5) \times 10^4$ M^{-1} s^{-1}. The kinetic data (Table I) were then treated according to eq 4 and 7 (vide supra) by using these values of the rate constants at 25 °C and the value ΔH_2 = 5 kcal/mol and by varying ΔH_3 within the experimentally acceptable range.

A reliable value of $\Delta H_2^{\ddagger} = 2.5 \pm 0.8$ kcal/mol results from this treatment. The calculated value of $\Delta H_3^{\ddagger}$ is, as would be expected, very much dependent on ΔH_3 and is approximately $\Delta H_3^{\ddagger} = (11 \pm 1) - \Delta H_3/2$ kcal/mol. Since $H_2AsO_3^-$ is a major contributor to the rate only at low $[OH^-]$, the best value of $\Delta H_1^{\ddagger}$ was obtained as follows. Temperature-dependent values of k_1 were determined by subtraction of the k_2 term in eq 5 at $[OH^-] = 0.1$ M, where there is no influence from either AsO_3^{3-} or the uncertainty in ΔH_3. Equation 7 was then employed to give $\Delta H_1^{\ddagger} = 2.3 \pm 1.0$ kcal/mol, where the error reflects the uncertainty in both k_{obsd} and $\Delta H_2^{\ddagger}$.

The best estimates of the activation enthalpies are given in Table II(i) along with values of $\Delta S_i^{\ddagger}$ calculated from eq 6. Temperature-dependent rate constants (Table II(ii)) were calculated from eq 7 with the tabulated values of $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ for k_1 and k_2. Because of the uncertainty of ΔH_3, the values of k_3 listed in the table contain the combined effect of $\Delta H_3^{\ddagger}$ and the temperature-dependent variation in the fraction of AsO_3^{3-}. The parameter $\Delta H_3^{\ddagger}$(apparent) = 11 kcal/mol was employed in this calculation. The last column in Table I

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(14) The apparent activation energies obtained are about 4 kcal/mol for both OH^- concentrations but contain a contribution from the temperature dependences of K_2 and K_3 (vide infra).

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Table II. Activation Parameters and Temperature-Dependent Rate Constants for the Reactions between $Ag(OH)_4^-$ and Arsenite Ions at $\mu = 1.2$ M

(i) Activation Parameters[a]

enthalpies, kcal/mol	entropies, cal/deg mol
$\Delta H_1^\ddagger = 2.3 \pm 1.0$	$\Delta S_1^\ddagger = -33.6 \pm 3.5$
$\Delta H_2^\ddagger = 2.5 \pm 0.8$	$\Delta S_2^\ddagger = -29.5 \pm 2.7$
$\Delta H_3^\ddagger \simeq 11\ (\pm 1) - \Delta H_3/2$	$\Delta S_3^\ddagger \simeq -2 \pm 8$

(ii) Rate Constants[b]

temp, °C	$10^{-3}k_1$, $M^{-1}\ s^{-1}$	$10^{-4}k_2$, $M^{-1}\ s^{-1}$	$10^{-4}k_3$,[c] $M^{-1}\ s^{-1}$
10	5.1 ± 0.9	2.9 ± 0.3	0.7 ± 0.3
17	5.5 ± 0.9	3.3 ± 0.3	1.1 ± 0.3
25	6.2 ± 1.0	3.7 ± 0.3	1.8 ± 0.5
35	7.1 ± 1.2	4.2 ± 0.4	3.3 ± 1.1
45	7.9 ± 1.6	4.8 ± 0.6	5.8 ± 2.5
55	8.8 ± 2.0	5.4 ± 0.7	9.9 ± 4.5

[a] $\Delta S_i^\ddagger$ calculated from k_i at 25 °C and $\Delta H_i^\ddagger$ (eq 6). [b] 25 °C values determined from eq 4, all others from eq 7, and $\Delta H_1^\ddagger$, $\Delta H_2^\ddagger$, and $\Delta H_3^\ddagger$(apparent) = $\Delta H_3^\ddagger - \Delta H_3/2 = 11$ kcal/mol. [c] Except for the value at 25 °C, these are apparent values that do not include changes in fraction of AsO_3^{3-} with temperature.

contains recalculated values of the overall first-order rate constant.

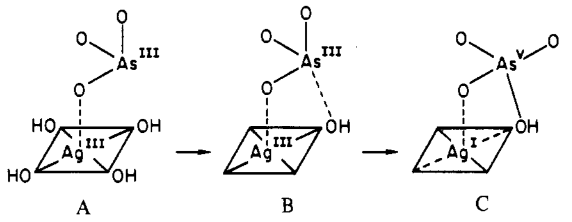
Ionic Strength Variation. The formulation of silver(III) as the tetrahydroxo monoanion has been based mainly on polarographic data that indicate a loss of two hydroxo ligands as Ag(III) is reduced to Ag(I), which exists as $Ag(OH)_2^-$ in basic solution.[1,2] Therefore, in spite of the complexity due to the arsenite equilibria and the high ionic strength, we decided to carry out an ionic strength dependence for the present system in order to confirm this assignment.

For these experiments, the ionic strength was varied between 0.065 and 1.2 M. Basicity was kept constant at $[OH^-] = 0.1$ M except for the experiment at $\mu = 0.065\ M = [OH^-]$ for which k_{obsd} was corrected for the $[H_2AsO_3^-]/[HAsO_3^{2-}]$ ratio appropriate to 0.1 M OH^-. A Davies equation[16] plot of log k_{obsd} vs. $\mu^{1/2}/(\mu^{1/2} + 1) - 0.05\mu$ was nearly linear with a slope of 2.2. Since both $H_2AsO_3^-$ and $HAsO_3^{2-}$ are the major contributors to the rate law under these conditions, a changing slope between 1 and 2 would be expected (assuming [Ag(III)] = $[Ag(OH)_4^-]$) after correction for the ionic strength dependence of the arsenite equilibria. Application of an ionic strength correction to K_2 and K_3[17a] does indeed indicate that the observed rate constant variation can be explained by the reaction of mononegative $Ag(OH)_4^-$ with the mono- and dianions of arsenous acid; i.e., the overall rate is enhanced by both an increase in k_1 and k_2 and a shift toward greater fractions of $HAsO_3^{2-}$ with increasing μ. Figure 4 summarizes the fit of the ionic strength variation when these factors are taken into consideration.

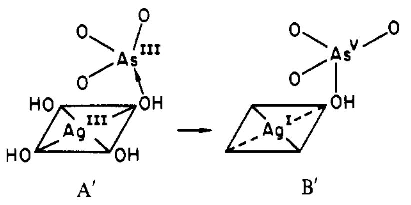
Discussion

Arsenite ion is known to form complexes with polyols[18] and might be expected to do the same with polyhydroxo complexes of metals. Similarly, oxoanions such as periodate and tellurate are effective ligands for Ag(III).[1-3,19] For the present system, however, we find no evidence, either spectral or kinetic, for significant concentrations of an intermediate complex.

Scheme I



Scheme II



In the reaction between $Ag(OH)_4^-$ and HO_2^-, a change in stoichiometry was observed from $\Delta[Ag(III)]:\Delta[HO_2^-] = 1$ at excess HO_2^- to 2 at excess $Ag(OH)_4^-$.[20] This provides evidence for a mechanism involving two one-electron transfers with a silver(II) intermediate. In the absence of excess reductant, free Ag(II) is removed from solution by polymerization[21] and subsequent precipitation of AgO. The fact that there is no significant stoichiometry change in the present system is an indication that the reaction between silver(III) and arsenic(III) does not involve transients with intermediate oxidation states.

Alkaline arsenic(III) oxidations by transition-metal ions in which As(IV) has been postulated as an intermediate have a characteristic kinetic feature in that the $H_2AsO_3^-$ ion is quite unreactive compared to the $HAsO_3^{2-}$ species.[4] Indeed, the rate-determining step in the oxidation of As(III) at a gold electrode appears to require a one-electron transfer from the dianion even when the monoanion is the principal species.[22] Even highly reactive one-electron oxidants such as Mn(III) and Ce(IV) react very slowly with As(III). Hence, analytical determinations involving As(III) often require a catalyst.[17,23] On the other hand, even mild two-electron oxidants often react rapidly with As(III).[17b,24] The reaction between As(III) and Tl(III) has been shown to proceed by a single two-electron redox step.[24] For the Ag(III)–As(III) system, we observe a quite rapid reaction in which the reactivities of the mono- and dianions of As(III) are similar.

Thus, we conclude, from both kinetic stoichiometric observations, that this reaction involves a complementary one-step redox process within an activated complex of formula $[(OH)_4Ag{\cdot}AsO_3H_n]^{4-n}$ (n = 2, 1, 0). It seems likely, as has been found for many other two-electron reactions,[15b,25] that reaction proceeds via oxygen atom transfer. In particular, oxygen atom transfer has been verified by isotopic exchange in the As(III)–BrO_4^- system.[26]

Two kinetically indistinguishable pathways that account for our results may be written. Scheme I involves attack by an arsenite oxygen on an axial site of the square-planar Ag(III) complex. In Scheme II, three-coordinate As(III) undergoes

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nucleophilic attack by a hydroxyl ligand followed by oxygen transfer in either a singly bridged or chelated (as in Scheme I) intermediate.

Both of these mechanisms depend on the expansion of the As(III) coordination sphere with the fourth oxygen in the product As(V) deriving from $Ag(OH)_4^-$. While the possibility of the solvent being an oxygen source cannot be discounted, the transfer of a hydroxyl ligand to arsenic involving donation of its electron pair to silver(III) via the empty $d_{x^2-y^2}$ orbital (which is oriented in the equatorial plane of the complex) appears reasonable. The formation of a four-coordinate As(III) intermediate resulting from nucleophilic attack by H_2O has been postulated in the oxygen-exchange reaction of aqueous arsenite ion[27] and provides a convenient precursor to tetrahedral arsenate.

Support for the possibility that redox occurs through a five-coordinate intermediate as in Scheme I is provided by the results of other $Ag(OH)_4^-$ reactions. For example, the presence of third-order terms in the reaction with ethylenediamine[28] and HO_2^- [20] implies the formation of a five-coordinate transient.[29] Activation parameters for silver(III) complexation reactions have been interpreted in terms of an associative mechanism for ligand exchange.[3]

For simple redox systems, ΔS^* often correlates well with the charge type of the reactants. Thus, one might expect a progressively more negative ΔS_i^* for the silver(III)-arsenite reaction as the charge on arsenic(III) decreases. A recent compilation of activation parameters by Cannon, however, contains a number of examples that do not fit this generalization even for simple, one-electron transfers.[30] Our reaction is likely to proceed by (i) ion association, (ii) axial attack by negative arsenite on the positive Ag(III) center, (iii) changes in bond lengths of the reactants and restructuring of their solvation spheres, and (iv) an electron-transfer step involving the rupture of a silver-oxygen bond. In spite of the uncertainties resulting from a poorly determined value of ΔH_3, it is clear that the activation parameters for the k_3 path are significantly different from those for k_1 and k_2. Thus, it seems that the relative importance of these factors is changed by the final deprotonation of As(III).

It has been suggested that the reason for the proximity of the second and third deprotonations of arsenous acid is that there is an electronic stabilization associated with the dissociation of the third proton.[9] The Raman study of Loehr and Plane[8] of the arsenite system show that all three anions have the same pyramidal geometry in solution. This study also confirmed that there are no polymeric arsenite species in strongly basic media. It seems unlikely, then, that ions so similar should react by different mechanisms.

In the cases of the mono- and dianions the rate seems to be due to the formation of the oxygen-bridged precursor complex (A or A′), which is then followed by a fast redox process.[31] This is consistent with a large negative activation entropy as observed. In fact, at lower ionic strength, ΔS^* should be even more negative.[32] The difference in activation parameters for AsO_3^{3-} compared to those for $H_2AsO_3^-$ and $HAsO_3^{2-}$ probably arises from an increased barrier to redox (steps (iii) and/or (iv)) in the fully deprotonated species. The enthalpy of activation for the trianion reaction is more than twice that of the others, suggesting a large energy barrier to the transfer of two electrons. It is possible that this difference in reactivities has the same origin as the "anomalous" pK_{a3} of arsenous acid.

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Registry No. $Ag(OH)_4^-$, 23172-26-1; $H_2AsO_3^-$, 14102-45-5; $HAsO_3^{2-}$, 21581-64-6; AsO_3^{3-}, 15502-74-6.

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Kinetics of the Reaction of Chromium(II) with (3-Cyano-2,4-pentanedionato-*N*)pentaamminecobalt(III): Intramolecular Electron Transfer between Cobalt(III) and Chromium(II)

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The complex $[(NH_3)_5CoNCacac]^{2+}$, where NCacac = 3-cyano-2,4-pentanedionate, reacts with chromium(II) by way of a binuclear intermediate $[(NH_3)_5CoNCacacCr]^{4+}$ followed by inner-sphere intramolecular electron transfer. The formation constant for the precursor complex is 58 L mol⁻¹ at 25 °C and 1.00 mol L⁻¹ ionic strength, with thermodynamic parameters $\Delta H = -7.1 \pm 0.5$ kcal mol⁻¹ and $\Delta S = -14 \pm 3$ cal deg⁻¹ mol⁻¹. The kinetic parameters for the intramolecular electron transfer in the precursor complex are $k_{is} = 7.3 \times 10^2$ s⁻¹, $\Delta H^* = +8.4 \pm 0.5$ kcal mol⁻¹, and $\Delta S^* = -17 \pm 2$ cal deg⁻¹ mol⁻¹. This example of intramolecular electron transfer in Co(III)-Cr(II) systems will be discussed in relation to other systems.

Introduction

The study of electron-transfer reactions between metal ions involves analysis of several discrete steps along the reaction pathway.[1-3] For most of the reactions studied, separation of these steps is not possible; however, in a few cases the intramolecular electron-transfer step may be separated.[4-7] This

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