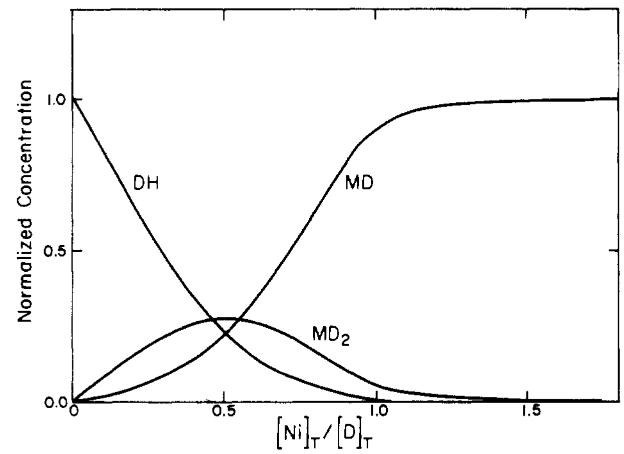

Figure 9. Concentration profiles of dye **3** and its nickel(II) complexes as a function of the *R* ratio. $[D]_T = 8.0 \times 10^{-6}$ M.

The formation constants for **2** and **3** are smaller than those for SV by several orders of magnitude. The K_1 values of **2** and **3** are also smaller than those of several (arylazo)pyrazolones[27] (**5**) by the same amount. Since all the chelates contain one six- and one five-membered ring and the same ligand atoms are involved in all cases, the lower values of K_i for **2** and **3** probably result from steric effects. Space-filling models of **2–4** show steric crowding of the ligand groups in coplanar conformations needed to form the chelates and suggest that bond angles and distances may be distorted in the complexes of these dyes. Table I and Figures 4 and 5 show that the complexes of **2–4** have maximum absorbance at nearly the same wavelength but that the absorptivities of the complexes of **2** and **3** are about 30% lower than those of **4**. This suggests that the dye moieties in the chelates of **2** and **3** are twisted slightly out of coplanarity[28] compared to dye **4**.

Although a number of K_1 values have been published for complexes of metal ions with *o,o'*-dihydroxy azo dyes,[29] there are few published examples of both K_1 and K_2 for the same metal–dye system. The results of Coates and Rigg[4] on SV show that $K_2 < K_1$ by several orders of magnitude for a number of metal ions. Our results for dyes **2** and **3** show that $K_2' < K_1$ by factors of 400 and 1000, respectively. The effect of reducing the difference between the constants on the composition of a system as a function of the molar ratio is seen by comparing Figures 1 and 9. Figure 9 shows the calculated fractions of the various species of **3** as *R* is varied. The comparison shows that as the difference between the *K*'s decreases, the symmetry in the profiles about the *R* ratio of 0.5 decreases and larger excesses of the metal ion are required to completely convert all the dye to the 1:1 complex. A very few data suggest that the replacement of a 2-hydroxyaryl moiety by a 2-pyridyl or an 8-quinolyl moiety decreases the difference in the *K*'s until they are essentially the same.[20,30] In this situation, all symmetry in the molar ratio titrations is lost.[20] As the values of the two *K*'s become more similar, the 1:2 complex becomes increasingly predominant at $R = 0.5$, and a larger excess of metal ion is required for complete conversion to the 1:1 complex.

Registry No. **2**, 94519-58-1; **3**, 94519-59-2; **4**, 94519-60-5.

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Reaction of the Tetrahydroxoargentate(III) Ion with Thiosulfate

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The reaction of $Ag(OH)_4^-$ with thiosulfate ion (T), potentially an eight-electron reductant, was studied over the range 2.5×10^{-6} M ≤ [T] ≤ 0.2 M in 0.6 M NaOH. At lowest [T], reaction via the aquated silver(III) species, $Ag(OH)_3H_2O$, results in a monothiosulfato complex, $Ag(OH)_3S_2O_3^{2-}$, which undergoes internal redox with a rate constant of 0.22 ± 0.03 s^{-1}. The stability constant of the complex is about $(1.4 \pm 0.2) \times 10^4$ and an absorption maximum for the species occurs at 260 ± 5 nm. At [T] > 1.0×10^{-3} M, Ag(III) is reduced by T without hydroxyl replacement. The rate law contains four terms with first- and second-order contributions predominating at high [T]: $-d[Ag(III)]/dt \sim (D[T] + E[T]^2)[Ag(III)]$. At 25 °C and $\mu = 1.2$ M, $D = 158 \pm 30$ M^{-1} s^{-1} and $E = 768 \pm 94$ M^{-2} s^{-1}. The presence of a third-order term is attributed to the reaction of T with a five-coordinate Ag(III)–T species. The principal product at excess T is tetrathionate.

Introduction

The tetrahydroxoargentate(III) ion, $Ag(OH)_4^-$, is a strongly oxidizing square-planar system that can be prepared by the electrochemical oxidation of a silver anode in 1.2 M NaOH.[1,2] The complex is metastable in this medium, decomposing at room temperature with a half-life of approximately 1.5 h.

The hydroxyl ion is a strongly σ-donating ligand in square-planar complexes and, consequently, a poor leaving group in ligand-substitution reactions.[3,4] This increase charge reduction on the metal and partly explains the ability of the hydroxyl group to stabilize the +3 oxidation state of silver. Reductions of silver(III) by potential ligands can occur simultaneously with hydroxyl replacement or within a five-coordinate intermediate.[5,6] In some cases, displacement of hydroxyl by, for example, azide[7] and tetraglycine[8] has resulted in the formation of novel silver(III) complexes.

The decomposition of the monoazido Ag(III) complex to silver(I) and nitrogen requires the participation of a second N_3^- as in other transition-metal oxidations of this ion.[9] A similar pattern is observed in the oxidations of thiosulfate by transition metals that, like Ag(III), act as two-electron oxidants.[10,11]

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We have studied the reaction of $Ag(OH)_4^-$ with thiosulfate ion (abbreviated as T) to see if mechanisms for these ions of greatly different nucleophilicity are similar. We have observed that, in contrast to the azide system, the complexation of Ag(III) occurs only through an aquation path. Furthermore, there is no evidence for dithiosulfato complex formation, and indeed, at excess [T], redox occurs directly without displacement of bound hydroxyl.

Experimental Section

$Ag(OH)_4^-$ was prepared in 1.2 M sodium hydroxide (Fisher 50% solutions) by electrolysis of silver foil (Handy and Harmon) as described elsewhere.[1] All solutions were prepared with doubly distilled water. Sodium perchlorate solution (to maintain constant ionic strength) was prepared by neutralizing perchloric acid with sodium hydroxide. This was filtered at pH 11 to remove traces of Fe(III) before adjusting to pH 8.[12] Sodium thiosulfate (Baker and Adamson, $Na_2S_2O_3 \cdot 5H_2O$) stock solutions were made by weight and standardized by titration with iodine. These were adjusted to 1.2 M ionic strength with sodium perchlorate solution. Fresh thiosulfate stock solutions were prepared every few days to minimize possible decomposition.

Polythionate solutions for comparison with product solutions were prepared by oxidizing thiosulfate with iodine[12] and potassium peroxodisulfate[13] (tetrathionate) and with hydrogen peroxide (trithionate).[14]

Kinetic experiments were performed by stopped-flow spectrophotometry using an Aminco-Morrow stopped-flow apparatus. Oscilloscope traces were photographed from a Tektronix 564B oscilloscope by using a Tektronix Type C-12 camera. Slower reactions were recorded with a Houston Instruments strip-chart recorder. For some runs, kinetic data were acquired with a Starbuck Data Co. analog–digital converter interfaced to the stopped-flow apparatus and a TRS-80 microcomputer, which permitted on-line processing of first-order rate data.

The reduction of first-order data was done with a linear least-squares fitting program operating on the microcomputer. Data from the complex formation reaction were interpreted by an approximate method. A nonlinear least-squares program, operating on the URI Academic Computer Center's Intel NAS/7 computer, was used to fit rate parameters.

The formation of the monothiosulfato–Ag(III) complex was studied under non-pseudo-first-order conditions. Complexation was only faster than reduction for [T] < 5 × 10^{-4} M, and the stability constant of the complex was obtained by measuring the total absorbance change as a function of [T] and [OH^-]. By variation of the wavelength from 240 to 420 nm, a point-by-point spectrum of the complex was obtained. Kinetic measurements were made over the concentration ranges 5×10^{-5} M < $[Ag(III)]_0 \leq 1.5 \times 10^{-4}$ M and 2.5×10^{-6} M ≤ [T] ≤ 2.5×10^{-4} M.

The reduction of Ag(III) by thiosulfate was studied with [T] in at least a 10-fold excess over the range 5×10^{-4} M ≤ [T] ≤ 0.2 M. For runs at excess [T], traces were pseudo first order through at least 3 half-lives, and replicate traces were reproducible to within ±5%. Because the products of the reaction, $S_4O_6^{2-}$ and $Ag^I(S_2O_3)_2^{3-}$, absorb strongly at lower wavelengths, the decomposition was monitored at 300–320 nm rather than at the absorption maximum of $Ag(OH)_4^-$ (267 nm).

Results

Complexation Reaction. When kinetic runs were made at concentrations of ligand less than 1 × 10^{-3} M, a rapid initial decrease in absorbance was found to precede the slower first-order reduction of Ag(III). For an initial silver(III) concentration of 1 × 10^{-4} M, the magnitude of this absorbance change reached a maximum in the range [T] ~ [Ag(III)]. At no wavelength was an absorbance increase observed as in the azide reaction.[7] At [T] > 1 × 10^{-3} M, this reaction, which we attribute to complex formation, became insignificant and altogether indistinguishable from the reduction of silver(III).

The total absorbance change due to complexation at 310 nm $(\Delta A_{310})_{tot}$ was measured by extrapolation of the first-order region to initial time and subtraction of this from the measured initial absorbance (which was equivalent to that of $[Ag(OH)_4^-]_0$). The variation of $(\Delta A_{310})_{tot}$ with [T] in the range 2×10^{-5} ≤ [T] ≤ 2×10^{-4} M with [Ag(III)] = (2.8 ± 0.3) × 10^{-4} M was nearly linear and became saturated at [T] = 5 × 10^{-4} M. The equilibrium constant for complex formation was thus estimated to exceed 1 × 10^4 at 0.6 M OH^-. $(\Delta A_{310})_{tot}$ was also measured for [T] = 2.5 × 10^{-5} M and [Ag(III)] = 6 × 10^{-5} M while [OH^-] was varied from 0.3 to 1.2 M. The inverse dependence of $(\Delta A_{310})_{tot}$ on [OH^-] indicated that one hydroxyl was reversibly replaced by thiosulfate with an overall equilibrium constant of (1.4 ± 0.2) × 10^4. A point-by-point spectrum of the solution after reaction of 1 × 10^{-4} M $Ag(OH)_4^-$ with 1.25 × 10^{-4} M thiosulfate was obtained (Figure 1). After compensation for the $Ag(OH)_4^-$ remaining at equilibrium, the spectrum of the complex was calculated.

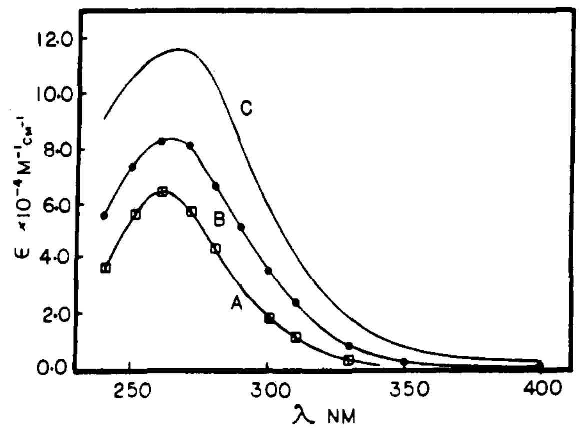

Figure 1. Absorption spectrum of $Ag(OH)_3S_2O_3^{2-}$ in 0.6 M NaOH; μ = 1.2 M. The spectrum (A) is calculated from the plot of the experimental points (B) obtained after the reaction of 1 × 10^{-4} M $Ag(OH)_4^-$ with 1.25 × 10^{-4} M $S_2O_3^{2-}$. The spectrum of $Ag(OH)_4^-$ (C) is shown for comparison.

Table I. Kinetic Data for $Ag(OH)_3S_2O_3^{2-}$ Formation at 25 °C, μ = 1.2 M

(a) Ligand Dependence ($[Ag(OH)_4^-]$ ~ 1 × 10^{-4} M, [OH^-] = 0.6 M[a])

10^5 × $[S_2O_3^{2-}]$, M	$R/[Ag(III)]_0$, s^{-1}	10^5 × $[S_2O_3^{2-}]$, M	$R/[Ag(III)]_0$, s^{-1}
0.25	0.09	2.5	0.96
0.50	0.22	5.0	1.95
1.0	0.47	10	2.5
1.5	0.7	15	2.4
2.0	0.9	25[b]	2.0

(b) Ag(III) Dependence ($[S_2O_3^{2-}]$ = 5 × 10^{-5} M)

$10^4[Ag(III)]_0$, M	$10(\Delta A_{310}/\Delta t)$, s^{-1}
0.5	1.2
1.0	2.2
1.5	2.9

(c) OH^- Dependence ($[S_2O_3^{3-}]$ = 5 × 10^{-5} M)

[OH^-], M	$R/[Ag(III)]_0$, s^{-1}
0.3	2.6
0.6	2.2
1.2	1.4

[a] Data for the first five entries were obtained at 310 nm. Succeeding runs were made at 320 nm. R is $\Delta A/\Delta t$ divided by the difference between the extinction coefficients for $Ag(OH)_4^-$ and $Ag(OH)_3S_2O_3^{2-}$. [b] The direct reaction (see next section) competes with formation at this [T].

Because pseudo-first-order conditions for a kinetic study of this reaction could not be attained, only a semiquantitative approach to the formation kinetics was possible. The rate of change of absorbance, $(\Delta A_{310}/\Delta t)$, following a brief induction period was measured as a function of initial [T] [Ag(III)].

The results are listed in Table I. The rate shows a linear dependence for both reactants that levels off when [T] is greater

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than ~5 × 10^{-5} M. It does not seem reasonable to postulate a highly favorable preequilibrium attack by $S_2O_3{}^{2-}$ since (i) rapid spectral changes are not observed and (ii) such an intermediate in steady-state quantities is necessary to explain the redox kinetics (next section). Thus, we conclude that OH$^-$ replacement occurs via the solvent path

$$Ag(OH)_4{}^- + H_2O \underset{}{\overset{k_1}{\rightleftharpoons}} Ag(OH)_3H_2O + OH^- \qquad (1)$$

$$Ag(OH)_3H_2O + S_2O_3{}^{2-} \overset{k_2}{\rightleftharpoons} Ag(OH)_3S_2O_3{}^{2-} + H_2O \qquad (2)$$

Putting $Ag(OH)_3H_2O$ in the steady state yields the following expression for the complexation rate:

$$\text{rate} = \frac{k_1k_2[Ag(OH)_4{}^-][T]}{k_{-1}[OH^-] + k_2[T]}$$

Although the range of [OH^{-1}] was, of necessity, rather limited, our observation that the rate is independent on [OH$^-$] only at low [T] is consistent with this rate law.

The limiting-rate data from Table I give $k_1 \sim 2.5$ s^{-1}. This value is consistent with the results obtained for the aquation-controlled reduction of silver(III) by ethylenediamine.[6] Further details of our analysis will be deferred to the Discussion.

Complex Decomposition. The complex shows maximum stability when [T] is not in large excess and decomposes according to eq 3. Solutions containing equal quantities of Ag(III) and

$$Ag(OH)_3S_2O_3{}^{2-} \xrightarrow{k_3} Ag(I) + \text{products} \qquad (3)$$

ligand (1 × 10^{-4} M) decomposed by first-order kinetics with an observed rate of 0.13 ± 0.02 s^{-1}. The rate constant, k_3 = 0.22 ± 0.03 s^{-1}, was obtained after correcting for the degree of complexation. Varying [T] in the range 5 × 10^{-5} M ≤ [T] ≤ 2 × 10^{-4} M (for $[Ag(OH)_4{}^-] \sim 5 \times 10^{-3}$ M) causes the rate constant for decomposition to increase from 0.09 to 0.2 s^{-1} due to increased complex formation. However, at [T] > 5 × 10^{-4} M, the rate increases sharply as the direct reduction of $Ag(OH)_4{}^-$ (see next section) becomes more important than the complexation path, which is limited by the rate of reaction 1.

Redox Reaction. (a) Product Analysis. Solutions of silver(III) that had been reduced by reaction with excess thiosulfate ranged in appearance from colorless to pale yellow with varying quantities of a brown-black precipitate. Colorless solutions were generally obtained with the greatest amount of precipitate when the ratio [T]/[Ag(III)]$_0$ did not exceed 5. UV-visible spectra of these colorless solutions (after filtration) revealed only a single peak at 230–240 nm, which was identified as that of $Ag(S_2O_3e_2{}^{3-}$. This peak persisted even for [T]/[Ag(III)] < 1, indicating that, at low [T], thiosulfate can transfer more than two electrons. Indeed, solutions of $Ag(OH)_4{}^-$ were completely reduced to Ag(I) within 1–2 min even with a 4:1 molar ratio of Ag(III) to T. Therefore, it seems likely that some products of the initial reaction with Ag(III) are more reactive than thiosulfate itself (see next section).

The precipitate, when acidified, gave off H_2S, from which we conclude that the precipitate was mainly Ag_2S, as other relevant silver(I) compounds, notably the oxide, are very soluble in the thiosulfate/OH$^-$ medium. Blank solutions of Ag(I) and $S_2O_3{}^{2-}$ in NaOH were completely stable to precipitation of Ag_2S, such as occurs in the commonly used analytical test for thiosulfate ion.[15]

The source of the pale yellow color observed at higher [T] is a silver(I) tetrathionate species. Product solutions and tetrathionate solutions with added silver I (prepared by iodine and peroxodisulfate oxidations of thiosulfate) showed a similar absorbance band at 275 nm. Trithionate solutions were colorless in the presence of silver(I). Silver sulfide precipitates were also observed to occur immediately from peroxodisulfate preparations[13] though not from iodine preparations.

The determination of the reaction stoichiometry at [T]/[Ag(III)] = 10 by titration of unreacted thiosulfate with iodine was not successful. The iodine titer of control solutions was found to be actually slightly less than that of the product solution. This result may be partly accounted for by the decomposition of tetrathionate in base according to eq 4.[16] The occurrence of possible

$$2S_4O_6{}^{2-} + 6OH^- \rightarrow 3S_2O_3{}^{2-} + 2SO_3{}^{2-} + 3H_2O \qquad (4)$$

side reactions from the oxidation of thiosulfate is indicated by the presence of sulfide, and these products may react with more equivalents of I_2 than thiosulfate itself.

(b) Thiosulfate Dependence. The decrease in absorbance from Ag(III) solutions in kinetic runs with at least a 10:1 excess of thiosulfate was first order. Initial absorbances from reaction traces were independent of [T] and equivalent to those obtained by mixing an aliquot of $Ag(OH)_4{}^-$ with water. At the lowest concentrations of T, where initial complexation occurs, k_{obsd} was calculated from the first-order part of the curve.

Plots of k_{obsd} vs. [T] are shown in Figures 2 and 3 for [OH$^-$] = 0.6 M, μ = 1.2 M, and 25 °C. The rate shows deviations from linearity at both higher and lower [T]. A determination of k_{obsd} at [T] = 0.04 M was made with use of Na_2SO_4 (0.4 M) to maintain the ionic strength of the thiosulfate solution while [Na$^+$] was reduced to 1.0 M and [ClO$_4^-$] to 0.6 M after mixing. Its conformity with the data taken in NaClO$_4$ media indicates that reduction in NaClO$_4$ is not a factor in the deviations from linearity at [T] > 0.1 M.

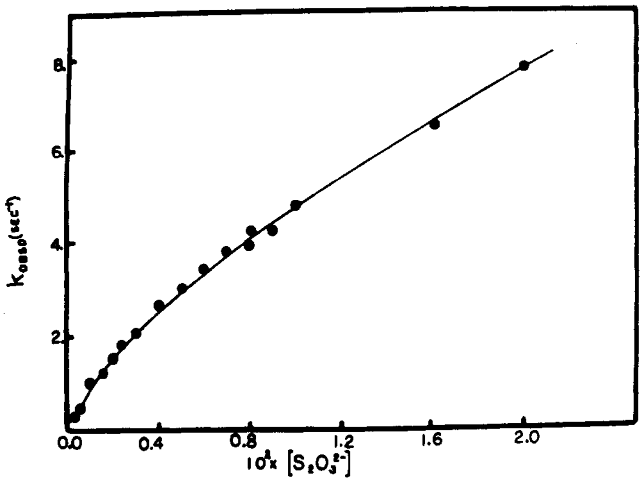

Figure 2. Variation of k_{obsd} with [$S_2O_3{}^{2-}$] at lower [$S_2O_3{}^{2-}$] for μ = 1.2 M, [OH$^-$] = 0.6 M, 25 °C. The solid curve is calculated from eq 5.

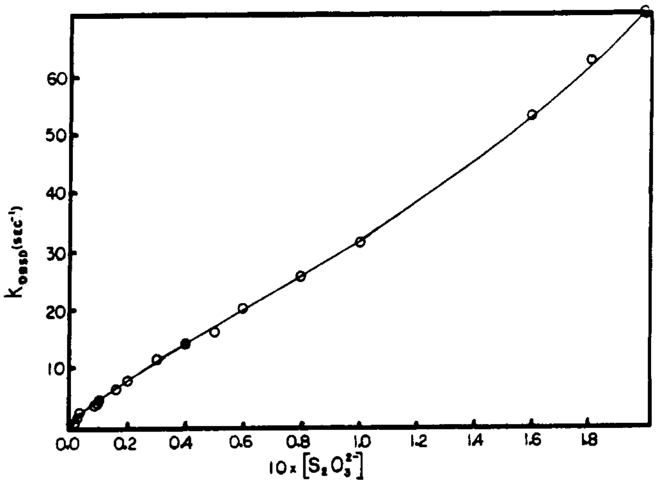

Figure 3. Variation of k_{obsd} with [$S_2O_3{}^{2-}$] at higher [$S_2O_3{}^{2-}$], for μ = 1.2 M, [OH$^-$] = 0.6 M, 25 °C. The solid curve is calculated from eq 5. The solid point (●) was obtained at reduced [Na$^+$] and [ClO$_4^-$] with Na$_2$SO$_4$ used for ionic strength adjustment.

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Table II. Kinetic Dependences for the Redox Reaction

(a) Hydroxide Ion (25 °C, $\mu = 1.2$ M)[a]

$[S_2O_3^{2-}] = 5 \times 10^{-4}$ M		$[S_2O_3^{2-}] = 1 \times 10^{-2}$ M	
$[OH^-]$, M	k_{obsd}, s^{-1}	$[OH^-]$, M	k_{obsd}, s^{-1}
0.9	0.47	0.6	4.7
0.6	0.45	0.3	4.6
0.4	0.44	0.15	4.9
0.2	0.47	0.05	4.7

(b) Ionic Strength[b] (25 °C, $[S_2O_3^{2-}] = 9 \times 10^{-3}$ M)

μ, M	k_{obsd}, s^{-1}	μ, M	k_{obsd}, s^{-1}
1.2	4.0	0.17	2.2
0.66	3.55	0.09	2.07
0.32	2.5		

(c) Temperature ($\mu = 1.2$ M,[a] $[OH^-] = 0.6$ M, $[S_2O_3^{2-}] = 0.05$ M, $[Ag(OH)_4^-] \sim 3 \times 10^{-5}$ M)

T, °C	k_{obsd}, s^{-1}	T, °C	k_{obsd}, s^{-1}
15	22.3	30	30.4
25	18.0	35	42.1

[a] Constant μ maintained with $NaClO_4$. [b] $\mu = [NaOH] + 3[Na_2S_2O_3]$.

The dependence of k_{obsd} on [T] obeys the empirical expression of eq 5. The parameter A is important to the fit only for [T] $< 1 \times 10^{-3}$ M and can be attributed to eq 3. The independently measured value of k_3 was fixed at 0.22 s^{-1}, and B, C, D, and E were evaluated by a nonlinear least-squares fit. This yielded $B = 495 \pm 41$ M^{-1} s^{-1}, $C = 54 \pm 17$ M^{-1}, $D = 158 \pm 28$ M^{-1} s^{-1}, and $E = 768 \pm 94$ M^{-2} s^{-1}. The solid lines in Figures 2 and 3 represent these parameters.

$$\frac{-d[Ag(III)]}{dt} = \left(A + \frac{B[T]}{1 + C[T]} + D[T] + E[T]^2\right)[Ag(III)] = k_{obsd}[Ag(III)] \qquad (5)$$

(c) Hydroxyl, Ionic Strength, and Temperature Dependences. The dependences of k_{obsd} on these conditions are summarized in Table II, parts a–c, respectively. The observed rate is essentially independent of $[OH^-]$. The increase in k_{obsd} with μ is as would be expected of a reaction between anionic species. However, a Davies equation plot[17] showed upward curvature in the range of ionic strengths studied, and a simple charge product could not be evaluated.

Arrhenius plots of the temperature dependence data were also nonlinear, and indeed, the reaction is slightly faster at 15 °C than at 25 °C. Thus the overall rate must consist of opposing kinetic and thermodynamic contributions.[18]

(d) Mechanism. The limiting rate of the complexation reaction (eq 1) prevents the monothiosulfato (or higher) complexes from being precursors in the redox reaction, and although the denominator in the second term of eq 5 suggests an equilibrium constant, observations of the initial absorbance indicate that, over most of the range of [T] studied, $Ag(OH)_4^-$ is the only silver(III) species present in stoichiometrically significant amounts. Equations 6–9 appear to explain this behavior.

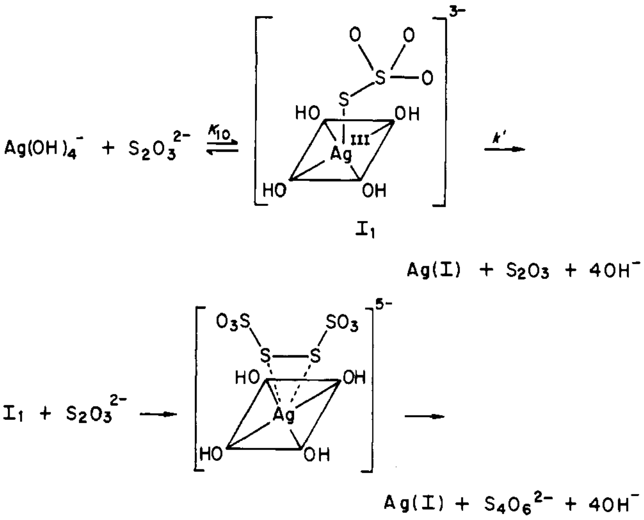
$$Ag(III) + S_2O_3^{2-} \xrightarrow{k_6} Ag(I) + S_2O_3 \qquad (6)$$

$$S_2O_3 \xrightarrow{k_7} S_i \qquad (7)$$

$$S_i + nAg(III) \xrightarrow{k_8} nAg(I) + \text{products} \qquad (8)$$

$$S_2O_3 + S_2O_3^{2-} \xrightarrow{k_9} S_4O_6^{2-} \qquad (9)$$

Scheme I



The species S_2O_3, which is generated by two-electron oxidation of thiosulfate, decomposes in eq 7 to form other reactive sulfur moieties. Designated as S_i, these may include sulfite and the sulfoxylic acid anion, such as are found to occur from the base-catalyzed decomposition of tetrathionate.[14] These species are capable of reducing a total of n equivalents of Ag(III), and they are presumed to react very rapidly with Ag(III) in eq 8. Indeed, second-order rate constants larger than 10^4 M^{-1} s^{-1} are commonly observed for the reactions of $Ag(OH)_4^-$ with simple reductants.[7,19] Application of the steady-state approximation to S_2O_3 gives the second and third terms in eq 5 with $B = nk_6$, $C = k_9/k_7$, and $D = k_6$. The value of $n = B/D \cong 3$ is consistent with the expected value for complete oxidation of S_2O_3 to sulfate.

Edwards and Sorum[13] attributed the presence of sulfides produced as byproducts in the oxidation of thiosulfate by peroxodisulfate to the decomposition of S_2O_3. Reaction 9, which eventually suppresses the decompositon of S_2O_3 and leads to a proposed limiting 1:2 (Δ[Ag(III)]:Δ[T]) stoichiometry, is plausible and consistent with the known properties of thiosulfate, which is an excellent nucleophile for electron-deficient sulfur species (e.g. tetrathionate).[16,20] Tetrathionate behaves as $(S_2O_3)\cdot(S_2O_3^{2-})$ in its reactions with cyanide and sulfite.[16]

The third-order term in eq 5 evidently results from the attack of a second thiosulfate on a species that would otherwise decompose to give the products of eq 6. This process is represented in eq 10 and 11. Thus the value of E in eq 5 is equivalent to $k_{11}K_{10}$.

$$Ag(OH)_4^- + S_2O_3^{2-} \underset{}{\overset{K_{10}}{\rightleftharpoons}} [(OH)_4Ag(S_2O_3)]^{3-} \qquad (10)$$

$$[(OH)_4Ag(S_2O_3)]^{3-} + S_2O_3^{2-} \xrightarrow{k_{11}} Ag(I) + S_4O_6^{2-} + 4OH^- \qquad (11)$$

This type of reductive elimination of tetrathionate from a transient donor–acceptor complex is a mechanistic feature of numerous reactions of $S_2O_3^{2-}$ with metallic and nonmetallic oxidants.[20]

Discussion

Reactions 6, 10, and 11 can be visualized as occurring via the detailed mechanism given in Scheme I where $k_6 = k'K_{10}$. The existence of an Ag(III)·T adduct (I_1) in equilibrium with the reactants is consistent with the third-order term in eq 6 as well as the complex temperature dependence of the reaction. The intermediate I_1 is present in steady-state amounts, and it is likely that K_{10} is small. The absence of a hydroxyl dependence suggests that OH^- is not reversibly displaced from the silver when I_1 is formed. Thus I_1 is depicted in Scheme I as being bound to the axial position of $Ag(OH)_4^-$ by the polarizable sulfur atom.

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Attack by a second thiosulfate suggests the reductive elimination of tetrathionate with transfer of two electron to the metal. Although the silver(III) site is occupied by a bound ligand, $S_2O_3^{2-}$ is an exceptional nucleophile and it has been found to attack axially even with severely hindered $Pd^{II}(Et_4dien)X^+$.[21] Thiosulfate may attack the metal ion at a site adjacent to the bound sulfur atom on I_1 prior to forming a bond with that sulfur. An alternative (or simultaneous) path may involve attack on the bound sulfur atom. A similar mechanism has been postulated in the reaction of thiosulfate with Cr(VI).[10]

A number of mechanisms by which square-planar systems might oxidize a substrate have been discussed in the literature, particularly with regard to Au(III) complexes. These include (i) attack by the reductant on a ligand (e.g. Cl^- or OH^-) with resulting atom transfer,[22,23] (ii) nucleophilic attack on the metal ion with electron transfer occurring in a five-coordinate stage,[5,6] and (iii) electron transfer following ligand substitution.[24] Annibale et al.[22] found that the rates of oxidation of alkyl sulfides to sulfoxides by $AuCl_4^-$ correlated directly with their basicity and inversely with steric hindrance in the alkyl chains. The magnitudes of the stability constants of the respective complexes were inversely related to thse factors, which caused them to conclude that nucleophilic attack was not rate determining in the redox reaction.

Oxidations by $Ag(OH)_4^-$ have been interpreted as being initiated by axial attack on the silver atom.[5,6,19] The absence of an inverse hydroxyl dependence in many Ag(III) oxidations suggests that ligand displacement does not occur or is followed immediately by redox. We have found that the rate at which certain common ligands reduce $Ag(OH)_4^-$ roughly parallels the order of their nucleophilicity[25] (e.g. $S_2O_3^{2-} > SCN^- > NH_3 > N_3^-$[7] $> OCN^- \sim$ bipyridyl). Although some of these results are qualitative,[26] the variation of rates is large (over 3 orders of magnitude) and the order strongly suggests that a nucleophilic attack on silver is rate determining. The polarizability of the sulfur atom greatly enhances its reactivity toward silver(III) as compared to that of azide, even though N_3^- is a stronger reductant.

The species I_1 decomposes by the intramolecular transfer of two electrons. Oxidation of thiosulfate by metal ions frequently results in the production of thiosulfuryl radicals when the metal can act as a one-electron oxidant.[27,28] $Ag(OH)_4^-$ has been shown to act as a one-electron oxidant in its reaction with HO_2^-.[5] However, experiments with added acrylonitrile to detect the presence of thiosulfuryl radicals formed by the reduction of Ag(III) to Ag(II) gave no trace of polymerization. Furthermore, in alkaline media silver(II) is known to form dimeric species (which absorb in the 300-nm range) at nearly diffusion-controlled rates.[29] These species have been found to react sluggishly compared to Ag(III) itself.[30] No secondary reactions of this type were observed in the present system. The production of S_2O_3 (eq 6) also seems consistent with the presence of sulfide byproducts[13] as well as with the evidence (cf. Results, part a) that thiosulfate acts as a multielectron reductant at low [T]. Our conclusion that the competition of reactions 7 and 8 with reaction 9 results in a [T]-dependent mixture of $S_4O_6^{2-}$ and SO_4^{2-} is consistent with the results of Wilmarth et al. for the $Pt(CN)_4(OH)Br^{2-}$ oxidation of thiosulfate.[31]

Axial attack on $Ag(OH)_4^-$ by $S_2O_3^{2-}$ results in an intermediate that undergoes electron transfer faster than hydroxyl replacement. Thus, the formation of detectable quantities of $Ag(OH)_3S_2O_3^{2-}$ occurs only at low [T] and only via an aqua intermediate (eq 1 and 2). The identification of the limiting rate constant for complexation as k_1 is consistent with our conclusions from other work.

A comparison of silver(III) stability in strong base, weak base, and weak acid has led us to postulate a value of the equilibrium constant for eq 1 of $K_1 \sim 10^{-3}$ M; i.e., $pK \sim 11$ for the fourth deprotonation of Ag(III).[32] Thus, k_{-1} ($\sim 10^3$ M^{-1} s^{-1}) seems to be much smaller than the diffusion-controlled limit, which might be expected if eq 1 were a simple Brønsted acid–base reaction. Such dramatic decreases in deprotonation rates have indeed been observed for other thermodynamically favorably reactions in which the acidic proton participates in intramolecular hydrogen bonding.[33] Hydrogen bonding in $Ag(OH)_3(OH_2)$ could be of particular importance because of the small distances in the resulting four-membered ring and the possibility of the extra proton "scrambling" between any two hydroxyls. For the forward reaction, we note that although proton transfer from water to $Ag(OH)_4^-$ is rather slow, direct protonation at low pH is very rapid.[32]

Use of the values $k_1 \sim 2.5$ s^{-1} and $k_1/k_{-1} = K_1 \sim 10^{-3}$ M leads to an estimate of $k_2 \sim 2 \times 10^7$ M^{-1} s^{-1}. Thus, water replacement from $Ag(OH)_3H_2O$ by thiosulfate appears over 400 times faster than replacement of OH^- from $Ag(OH)_4^-$ by periodate ion.[1]

The equilibrium constant for complex formation is large (1.4×10^4 compared to 0.4 for the monoazido complex[7]). This is not unexpected, considering the above factors and the high stability of $Ag(S_2O_3)_2^{3-}$ and species such as the sulfur-bonded $Au(SCN)_4^-$ ($\beta_4 = 10^{45}$ M^{-4}).[34] The formation of the gold(III) thiocyanato complexes from the tetrahalo species[23] involves changes in the intensity of spectral bands without significant change in peak position as in the present system.

The redox stability of the monothiosulfato–Ag(III) complex is surprisingly high, considering that thiosulfate, while coordinated axially, transfers two electrons to Ag(III) faster than it can replace hydroxyl ligand. However, coordination of Au(III) by soft donor ligands generally reduces the Au(III)/Au(I) redox potential,[35] and this is probably an important factor in the Ag(III) system as well. Nord et al.[11] studied the reduction of $Au(S_2O_3)_3H_2O^{5-}$ and concluded that the reduction occurred intermolecularly and is initiated by the attack of excess thiosulfate on that species. Under the conditions for complex formation in the present study (i.e. very low [T]), this mode of reduction probably does not contribute significantly to the rate of decomposition.

Registry No. $Ag(OH)_4^-$, 23172-26-1; $Ag(OH)_3S_2O_3^{2-}$, 94500-11-5; $S_2O_3^{2-}$, 14383-50-7.

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