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Kinetics and Mechanism of Silver(III) Reduction by Azide Ion in Aqueous Alkaline Media

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The reaction between the tetrahydroxoargentate(III) ion and azide ion proceeds via formation of a monoazidosilver(III) complex, which undergoes internal two-electron redox only after reaction with an additional N_3^-. Formation of $Ag(OH)_3N_3^-$ from $Ag(OH)_4^-$ and N_3^- obeys the full rate law for for reversible associative substitution by both solvent and ligand paths. Two parallel paths also occur in the redox step, both requiring adjacent azide groups prior to electron transfer. Final products are $Ag(I)$ and N_2. Three kinetic determinations of the equilibrium constant for $Ag(OH)_3N_3^-$ are in reasonable agreement with the value of 0.38 ± 0.14 obtained spectrophotometrically (25 °C, $\mu = 1.2$ M). The result that the nucleophilicity of N_3^- toward $Ag(III)$ is slightly less than that of OH^- is in agreement with previous observations for isoelectronic $Pd(II)$.

Introduction

Kinetic and spectral evidence has been obtained indicating the formation of azido (or hydrazido) complexes as intermediates in the oxidation of hydrazoic acid by aquametal cations of Mn(III),[1-3] Co(III),[4-6] and Ce(IV).[7] Indeed, stable azide complexes are known[8,9] for a number of transition metals despite the high thermodynamic instability of hydrazoic acid and azide ion ($E° = -3.4$ and -3.1 V for the N_2/N_3^- and N_2/HN_3 couples, respectively).[10] Various mechanisms have been proposed for the oxidation of HN_3 by metal cations depending upon the particular metal involved and the specific conditions employed. However, the involvement of more than one azide molecule in the redox step seems to be possible for each of the aquametal cations.

Decomposition of azide complexes that are kinetically stable may, in some cases, be initiated photochemically. A particularly interesting example[11] of this is the photoinduced reductive elimination of *cis*-$Pt(N_3)_2(PPh_3)_2$. During the course of this reaction, no azide radicals could be detected. Instead, Volger et al. observed the formation of an intermediate that can be attributed to the transient formation of hexazine (or hexazabenzene, N_6). A similar intermediate was not obtained for the photoinduced reductive elimination of *trans*-$Pt(N_3)_2$-$(CN)_2^{2-}$. In the latter case, azide radicals were, indeed, produced.[12]

Previous studies involving thermal reduction of simple metal ions by hydrazoic acid have dealt only with one-electron oxidants and were carried out in acidic media. We have chosen to study the oxidation of azide ion in alkaline media by the two-electron oxidant $Ag(OH)_4^-$.

$Ag(OH)_4^-$ can be prepared conveniently by anodic oxidation of silver metal in aqueous sodium hydroxide.[13,14] It has a half-life for reduction by the solvent to AgO of ca. 90 min at room temperature in 1.2 M sodium hydroxide. Its stability

decreases markedly with increasing temperature and decreasing hydroxide ion concentration.[13,15]

The results of the present study are consistent with the formation of a monoazidosilver(III) complex followed by reaction with additional azide in the redox step. Furthermore, the complexation reaction between $Ag(OH)_4^-$ and N_3^- obeys a rate law for associative substitution in which forward and reverse rate constants are significant for both the solvent and ligand paths.

Experimental Section

Solutions. All solutions were prepared with doubly distilled water. All other chemicals were reagent grade. $Ag(OH)_4^-$ was prepared in 1.2 M sodium hydroxide (Fisher) by electrolysis of silver foil (Handy and Harman) as previously described.[14] Stock azide solutions were prepared by dissolving solid sodium azide (Sigma) in aqueous sodium hydroxide and sufficient sodium perchlorate to obtain a total ionic strength, μ, of 1.2 M. Sodium azide solutions used in kinetic experiments were prepared by dilution of a stock solution with appropriate quantities of 1.2 M sodium perchlorate and sodium hydroxide. All solutions were adjusted to an ionic strength of 1.2 M or were prepared so as to obtain an ionic strength of 1.2 M on mixing in the stopped-flow apparatus. Sodium perchlorate used for ionic strength adjustments was prepared by neutralization of standard perchloric acid (Fisher) with sodium hydroxide.

Kinetics. Kinetic experiments were carried out with an Aminco-Morrow stopped-flow apparatus[14] at 25 °C and $\mu = 1.2$ M. When solutions of $Ag(OH)_4^-$ and alkaline sodium azide were mixed in the stopped-flow apparatus, a rapid decrease in transmittance was observed in the wavelength region from 350 to 450 nm, followed by a slower increase as shown in Figure 1. Both reactions were monitored primarily at 410 nm where the greatest relative change in absorbance is observed. The initial [Ag(III)] was varied from ca. 8.0×10^{-4} to 2.0×10^{-5} M with the initial [N_3^-] being in a minimum 20-fold excess. The difference in the time scales for the two parts of this reaction was sufficiently large that the kinetics of each could be treated separately. For both reactions pseudo-first-order plots were linear over several half-lives. Neither variations in initial [Ag(III)] nor wavelength had any noticeable effect on observed rate constants.

Complexation Studies. The initial absorbance change (Figure 1) can be attributed to the formation of a monoazidosilver(III) intermediate. A spectrum of this complex was determined in the stopped-flow apparatus in the wavelength region from 260 to 450 nm by using [N_3^-] = 0.55 M and [OH^-] = 0.12 M. Extension of the absorbance data below 260 nm was precluded by the large background absorbance due to the high [N_3^-] required to give significant fractions of $Ag(OH)_3N_3^-$ (vide infra). The spectrum is compared to that of $Ag(OH)_4^-$ in Figure 2.

Tests for Intermediates. To test for the possibility of free-radical intermediates, a series of sodium azide solutions of sufficient concentration to result in 15-40% complexation were mixed with solutions of $Ag(OH)_4^-$. The resulting solutions, while still yellow, were added to acrylonitrile (6% v/v). No precipitation of white polyacrylonitrile could be observed even after several hours, indicating the absence of

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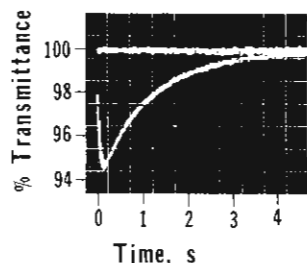(15) Kirschenbaum, L. J.; Mrozowski, L. *Inorg. Chem.* **1978**, *17*, 3718.

Figure 1. Oscilloscope trace of a stopped-flow experiment at 25 °C and $\mu = 1.2$ M. Concentrations: $[\text{Ag(OH)}_4^-] = 1.0 \times 10^{-4}$ M; $[\text{N}_3^-]$ = 0.55 M; $[\text{OH}^-] = 0.12$ M.
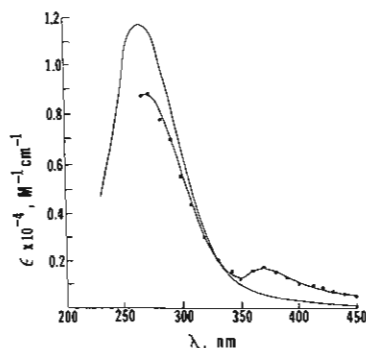

Figure 2. Comparison of the UV–visible spectra of $\text{Ag(OH)}_3\text{N}_3^-$ (■) and Ag(OH)_4^- (—).

any radicals capable of initiating acrylonitrile polymerization.

Similar solutions of Ag(OH)_4^- and NaN_3 were mixed and immediately frozen in liquid nitrogen. EPR spectra were recorded on a Bruker ER-200 spectrometer at 250 K. After the accumulation of five scans, there was no resonance due either to free radicals or to Ag(II).[16]

Product Analysis. Analysis of gaseous products was carried out by using a GOW-MAC series 550-P gas chromatograph fitted with a 3 ft $\times$ $^1/_8$ in. column packed with 5A molecular sieve. The oxidation of N_3^- to nitrogen was confirmed by monitoring the N_2/O_2 peak ratio.[1] No additional peaks were observed.

Results and Treatment of Data

Stoichiometry. When solutions of Ag(OH)_4^- and NaN_3 are mixed, the disappearance of the yellow color of Ag(OH)_4^- is followed by the appearance of a colorless gas. In addition, depending upon the particular $[\text{N}_3^-]$ and $[\text{OH}^-]$ employed, a precipitate (brown-black or white) was often obtained. These observations are consistent with the overall stoichiometry given by eq 1. For moderate $[\text{N}_3^-]$ and $[\text{OH}^-]$, a white precipitate

$$\text{Ag(OH)}_4^- + 2\text{N}_3^- \rightarrow \text{Ag(I)} + 4\text{OH}^- + 3\text{N}_2 \quad (1)$$
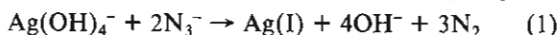
of AgN_3 was obtained. At high $[\text{N}_3^-]$ and low $[\text{OH}^-]$, no precipitate was detected, presumably because of the formation of higher order Ag(I) azide complexes. Under conditions of high $[\text{OH}^-]$ ($[\text{OH}^-] > 0.9$ M) and low $[\text{N}_3^-]$, a dark precipitate of primarily Ag_2O resulted. This dark solid dissolved completely in dilute aqueous ammonia, indicating the absence of any elemental silver. However, when a weighed sample was dissolved in 0.5 M HNO_3 containing an excess of bipyridyl, a brown solution was obtained, the spectrum of which corresponded to that of the Ag(II) bipyridine complex.[17] We conclude from the absorptivity of such solutions that a maximum of 10% of the initial Ag(III) precipitates as AgO by either reaction with solvent, reaction between Ag(III) and Ag(I), surface catalysis, or another minor side reaction.

For $[\text{N}_3^-]$ sufficiently small to make quantitative stoichiometric measurements, the reduction of Ag(OH)_4^- to AgO by the solvent would compete with eq 1. Similarly, the instability

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Table I. Kinetic Data for the Formation of $\text{Ag(OH)}_3\text{N}_3^-$ (25 °C and $\mu = 1.2$ M)

$[\text{OH}^-]$, M	$[\text{N}_3^-]$, M	k_c, s^{-1}	k_{calcd},[a] s^{-1}
0.125	1.10	39	39
0.125	0.55	21	22
0.125	0.275	14	14
0.125	0.11	9.0	8.9
0.125	0.055	7.0	7.3
0.30	0.55	19	19
0.30	0.275	14	14
0.30	0.11	12	12
0.30	0.055	11	11
0.60	0.55	23	23
0.60	0.275	20	20
0.60	0.11	19	18
0.60	0.055	17	17
0.90	0.275	27	27
0.90	0.11	25	25
0.90	0.055	24	24
0.90	0.0275	24	24

[a] Based on eq 5 and the parameters in Table II.

of Ag(OH)_4^- during degassing prior to gas chromatographic analysis made impossible an accurate knowledge of $[\text{Ag(OH)}_4^-]$ at the time of mixing. Therefore, quantitative stoichiometric measurements were not possible. However, gas chromatographic analysis of the gaseous product of this reaction did show a 2–3-fold increase in the N_2/O_2 peak height ratio over that of air. Under similar conditions using either Ag_2O or AgO, no such increase was observed. Thus, we are still able to conclude that nitrogen is produced, consistent with eq 1.

Complexation Studies. The maximum value of absorbance relative to the absorbance of silver(III) at zero time (Figure 1) was found to be proportional to $[\text{N}_3^-]/[\text{OH}^-]$, suggesting the reversible formation of the intermediate complex, $\text{Ag(OH)}_3\text{N}_3^-$. Furthermore, the first part of the reaction is sufficiently faster than the second that we are able to treat this absorbance change as being due to the formation of an equilibrium mixture of Ag(OH)_4^- and $\text{Ag(OH)}_3\text{N}_3^-$ with the total silver(III) concentration ($[\text{Ag(III)}]_T$) essentially equal to the initial concentration of Ag(OH)_4^- ($[\text{Ag(OH)}_4^-]_0$). Thus, the total absorbance (A_T) at this point, for a given $[\text{N}_3^-]$ and $[\text{OH}^-]$ can be defined as in eq 2, where ϵ_{app} is the apparent

$$A_T = \epsilon_{app}[\text{Ag(III)}]_T$$
$$= \epsilon_{\text{Ag(OH)}_4^-}[\text{Ag(OH)}_4^-] + \epsilon_{\text{Ag(OH)}_3\text{N}_3^-}[\text{Ag(OH)}_3\text{N}_3^-] \quad (2)$$

extinction coefficient. Combining eq 2 with the equilibrium expression (3) and rearranging leads to eq 4. Plots of

$$K_{cx} = \frac{[\text{Ag(OH)}_3\text{N}_3^-][\text{OH}^-]}{[\text{Ag(OH)}_4^-][\text{N}_3^-]} \quad (3)$$

$$\frac{[\text{OH}^-]}{[\text{N}_3^-]} = \frac{\epsilon_{\text{Ag(OH)}_3\text{N}_3^-}}{(\epsilon_{\text{Ag(OH)}_4^-} - 1)}K_{cx}\left[\frac{1}{(\epsilon_{app}/\epsilon_{\text{Ag(OH)}_4^-}) - 1}\right] - K_{cx} \quad (4)$$

$[\text{OH}^-]/[\text{N}_3^-]$ vs. $1/[(\epsilon_{app}/\epsilon_{\text{Ag(OH)}_4^-}) - 1]$ at 410 nm where the relative change in ϵ is greatest were linear as predicted by eq 4 and led to $K_{cx} = 0.38 \pm 0.14$ and $\epsilon_{\text{Ag(OH)}_3\text{N}_3^-} = (1.0 \pm 0.2) \times 10^3$ M^{-1} cm^{-1} at 410 nm. The results of this analysis were combined with the wavelength dependence for the construction of the spectrum in Figure 2. The complex has absorption maxima at $\sim$270 nm ($\epsilon = (8.7 \pm 0.4) \times 10^3$ M^{-1} cm^{-1}) and 370 nm ($\epsilon = (1.5 \pm 0.1) \times 10^3$ M^{-1} cm^{-1}).

Kinetics of $\text{Ag(OH)}_3\text{N}_3^-$ Formation. The formation of $\text{Ag(OH)}_3\text{N}_3^-$ in the initial phase of the reaction is first order in $[\text{Ag(III)}]_T$ throughout the concentration range of this study. Values of the observed pseudo-first-order rate constants, k_c,
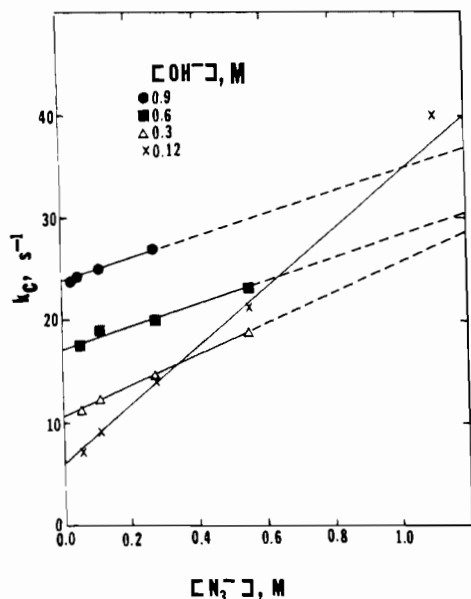
Figure 3. Plots of pseudo-first-order rate constants for complexation, k_c, vs. $[N_3^-]$ at 25 °C and $\mu = 1.2$ M at various $[OH^-]$.

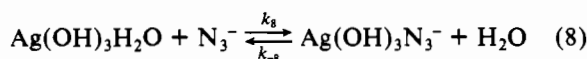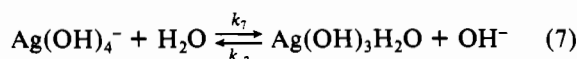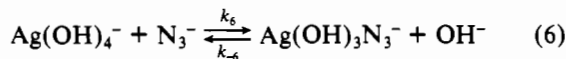**Table II.** Kinetic and Equilibrium Parameters for the Formation of $Ag(OH)_3N_3^-$ (25 °C, $\mu = 1.2$ M)^a

$$k_6 = A_1 = 7.3 \pm 1.5 \text{ M}^{-1} \text{ s}^{-1}$$
$$k_{-6} = A_2 = 22.2 \pm 0.8 \text{ M}^{-1} \text{ s}^{-1}$$
$$k_7k_8/k_{-7} = A_3 = 2.8 \pm 0.5 \text{ s}^{-1}$$
$$k_{-8} = A_4 = 3.5 \pm 0.5 \text{ s}^{-1}$$
$$K_{cx} = k_6/k_{-6} = 0.33 \pm 0.10$$
$$K_{cx} = k_7k_8/k_{-7}k_{-8} = 0.78 \pm 0.20$$
$$K_{cx}(\text{from } A_\infty) = 0.38 \pm 0.14$$

^{a} Based on eq 9 and the assumption that $k_{-7}[OH^-] \gg k_8[N_3^-]$.

for this process are given in Table I. The data indicate that the reaction is dependent on both the concentrations of N_3^- and OH^-. Figure 3 demonstrates that plots of k_c vs. $[N_3^-]$ are linear with slopes that are inversely proportional to $[OH^-]$ and intercepts that are directly proportional to $[OH^-]$. A plot of the slopes of the $[N_3^-]$ dependence vs. $1/[OH^-]$ yielded a straight line with slope $S = 2.8 \pm 0.5 \text{ s}^{-1}$ and an intercept $I = 7.3 \pm 1.5 \text{ M}^{-1} \text{ s}^{-1}$. A plot of the intercepts of the $[N_3^-]$ dependence vs. $[OH^-]$ was also linear with a slope $S' = 22.2 \pm 0.8 \text{ M}^{-1} \text{ s}^{-1}$ and an intercept $I' = 3.5 \pm 0.5 \text{ s}^{-1}$. This analysis leads to the empirical expression (5) for the observed pseu-

$$k_c = A_1[N_3^-] + A_2[OH^-] + A_3\frac{[N_3^-]}{[OH^-]} + A_4 \quad (5)$$

do-first-order rate constants for the formation of $Ag(OH)_3N_3^-$, where $A_1 = 7.3 \pm 1.5 \text{ M}^{-1} \text{ s}^{-1}$, $A_2 = 22.2 \pm 0.8 \text{ M}^{-1} \text{ s}^{-1}$, $A_3 = 2.8 \pm 0.5 \text{ s}^{-1}$, and $A_4 = 3.5 \pm 0.5 \text{ s}^{-1}$. The mechanism shown in eq 6–8 is consistent with eq 5. By placing the aqua complex

$$Ag(OH)_4^- + N_3^- \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} Ag(OH)_3N_3^- + OH^- \quad (6)$$

$$Ag(OH)_4^- + H_2O \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} Ag(OH)_3H_2O + OH^- \quad (7)$$

$$Ag(OH)_3H_2O + N_3^- \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} Ag(OH)_3N_3^- + H_2O \quad (8)$$

in steady state, eq 9 is obtained. If reaction 7 is in equilibrium

$$k_c = k_6[N_3^-] + k_{-6}[OH^-] + \frac{k_7k_8[N_3^-] + k_{-7}k_{-8}[OH^-]}{k_{-7}[OH^-] + k_8[N_3^-]} \quad (9)$$

and/or $k_8[N_3^-] < k_{-7}[OH^-]$, eq 9 and the empirical rate law (5) are of the same form. The relationship between the empirical constants in eq 5 and the constants of the proposed

Table III. Kinetic Data for the Reduction of $Ag(OH)_3N_3^-$ (25 °C, $\mu = 1.2$ M)

$[OH^-]$, M	$[N_3^-]$, M	k_d, s^{-1}	k_{calcd},^{a} s^{-1}
0.125	1.20	2.7	2.7
	0.90	2.0	2.0
	0.80	1.6	1.8
	0.70	1.4	1.4
	0.60	1.1	1.2
	0.55	1.0	1.0
	0.45	0.77	0.75
	0.40	0.66	0.62
	0.35	0.54	0.52
	0.30	0.42	0.39
	0.275	0.38	0.34
	0.25	0.31	0.29
	0.20	0.21	0.20
	0.15	0.12	0.12
	0.10	0.062	0.062
0.20	1.00	1.6	1.6
	0.90	1.5	1.4
	0.80	1.2	1.2
	0.70	0.97	0.94
	0.60	0.70	0.74
	0.55	0.57	0.55
	0.45	0.45	0.46
	0.35	0.30	0.30
	0.20	0.11	0.12
	0.10	0.036	0.037
0.30	0.90	1.1	0.98
	0.80	0.84	0.81
	0.70	0.67	0.65
	0.60	0.48	0.50
	0.55	0.39	0.44
	0.45	0.27	0.25
	0.35	0.17	0.20
	0.275	0.11	0.13
	0.20	0.070	0.076
	0.11	0.028	0.029
0.60	0.55	0.19	0.19
	0.45	0.12	0.16
	0.35	0.077	0.100
	0.275	0.060	0.066
	0.20	0.037	0.039
	0.11	0.020	0.017
	0.055	0.011	0.0096
0.90	0.275	0.051	0.045
	0.11	0.016	0.013
	0.055	0.010	0.0087
	0.0275	0.0080	0.0075

^{a} Based on eq 11 and the parameters of Table IV.

mechanism (eq 6–8) are shown in Table II. Recalculated values of k_{calcd} are given in Table I. Of the two values of K_{cx} resulting from this analysis, we favor the value obtained as the ratio of k_6/k_{-6} since this value is in good agreement with that determined spectrophotometrically and since the analysis of the kinetic data for the decomposition reaction (vide infra) yielded a value of K_{cx} much less than 1.0. In addition, eq 6 is the principal complexation path for most of our experiments.

Redox Kinetics. The second part of this reaction corresponds to silver(III) reduction. Under the conditions of this study, it is first order in $[Ag(III)]_T$ with pseudo-first-order rate constants, k_d, as given in Table III. The equilibrium shown in eq 6 can be presumed to be maintained throughout the second part of the reaction. Therefore, we may express the rate of decomposition of the monoazido complex in terms of total silver(III) as shown in eq 10, where $[Ag(OH)_3N_3^-] = \alpha[Ag(III)]_T$, $[Ag(OH)_4^-] = (1 - \alpha)[Ag(III)]_T$, and $\alpha = K_{cx}[N_3^-]/(K_{cx}[N_3^-] + [OH^-])$.

$$\text{rate (redox)} = k_d[Ag(III)]_T =$$
$$k_d'[Ag(OH)_3N_3^-] = \alpha k_d'[Ag(III)]_T \quad (10)$$

As shown in Figure 4, there is a complex dependence of k_d on both the concentrations of N_3^- and OH^-. Plots of k_d vs.
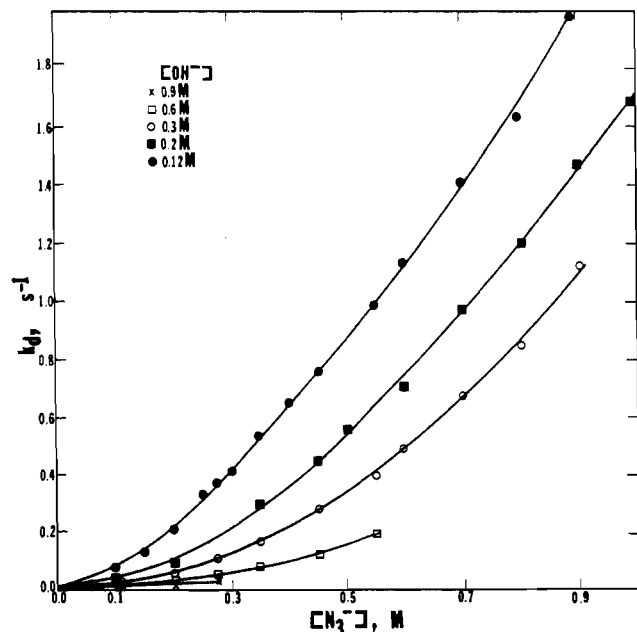
Figure 4. Plots of pseudo-first-order rate constants for redox, k_d, vs. $[N_3^-]$ at 25 °C and $\mu = 1.2$ M at various $[OH^-]$.

$[N_3^-]$ were nonlinear for all $[OH^-]$, as were plots of k_d vs. $[N_3^-]^2$, $k_d/[N_3^-]$ vs. $[N_3^-]$, and log k_d vs. log $[N_3^-]$. However, when k_d' (i.e., k_d/α) was plotted vs. $[N_3^-]$, a series of reasonably straight lines was obtained. The slopes of these lines are inversely proportional to $[OH^-]$. Deviations from linearity are observed only under conditions of high $[OH^-]$ and low $[N_3^-]$. This indicates the presence of a path that is important only at the highest $[OH^-]$ and consequently the lowest $[N_3^-]$. These deviations can be satisfactorily accounted for by eq 11.

$$k_d = \frac{B_1[N_3^-]^2/[OH^-] + B_2[N_3^-]^2 + B_3[OH^-]}{K_{cx}[N_3^-] + [OH^-]} \quad (11)$$

With the use of a nonlinear least-squares program, all the kinetic data in Table III were fit to eq 11 with deviations generally less than 10%. The results are $B_1 = (4.7 \pm 0.6) \times 10^{-2}$ s^{-1}, $B_2 = (4.4 \pm 0.2) \times 10^{-1}$ s^{-1}, $B_3 = (7.0 \pm 2.0) \times 10^{-3}$ s^{-1}, and $K_{cx} = 0.2 \pm 0.10$. Values of k_d were recalculated from the above parameters and are shown in Table III as k_{calcd}.

Under the conditions of most of our experiments, the first two terms of eq 11 predominate. These can be attributed to two parallel paths, both involving the reaction of $Ag(OH)_3N_3^-$ with a second azide. The third term may also be written in terms of $Ag(OH)_3N_3^-$. However, this latter formulation suggests paths leading back to starting material, not to redox, and hence are unacceptable. The simplest interpretation of the third term seems to be an accelerated decomposition of $Ag(OH)_4^-$ in the stopped-flow apparatus. This phenomenon is a common problem, especially for slower runs, and is probably due to Ag(III) decomposition by surface catalysis by solid products and/or at the walls of the cell.

By combining eq 10 and 11 we may write

$$\text{rate} = k_a[Ag(OH)_3N_3^-][N_3^-]/[OH^-] + k_b[Ag(OH)_3N_3^-][N_3^-] + k_x[Ag(OH)_4^-] \quad (12)$$

It seems most reasonable that the redox process involves a simultaneous two-electron transfer in an activated complex having two adjacent azides. This is consistent with the product analysis and the absence of any evidence of either Ag(II) or free-radical intermediates in the EPR and polymerization experiments.

Two kinetically indistinguishable pathways may be written to account for each of the two azide-dependent terms of eq

Table IV. Kinetic and Equilibrium Parameters for the Reduction of $Ag(OH)_3N_3^-$ (25 °C, $\mu = 1.2$ M)^a
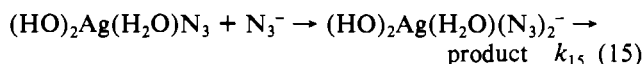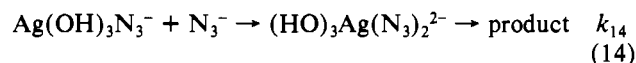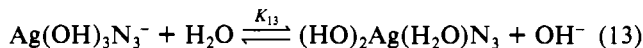
$$k_a = K_{13}k_{15} \text{ or } K_{16}k_{16} = 0.22 \pm 0.04 \text{ s}^{-1}$$
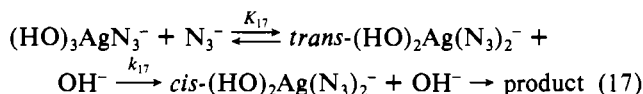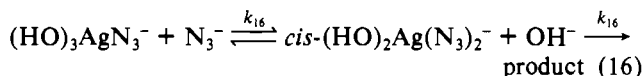$$k_b = k_{14} \text{ or } K_{17}k_{17} = 2.1 \pm 0.2 \text{ M}^{-1}\text{ s}^{-1}$$
$$K_{cx} = 0.21 \pm 0.10$$

^{a} From eq 11.

12. In eq 14 and 15, redox occurs within a five-coordinate intermediate formed by azide attack on $Ag(OH)_3N_3^-$ and its conjugate acid (eq 13). Alternatively, the mechanism could

$$Ag(OH)_3N_3^- + H_2O \xrightarrow{K_{13}} (HO)_2Ag(H_2O)N_3 + OH^- \quad (13)$$

$$Ag(OH)_3N_3^- + N_3^- \rightarrow (HO)_3Ag(N_3)_2^{2-} \rightarrow \text{product} \quad k_{14} \quad (14)$$

$$(HO)_2Ag(H_2O)N_3 + N_3^- \rightarrow (HO)_2Ag(H_2O)(N_3)_2^- \rightarrow \text{product} \quad k_{15} \quad (15)$$

involve formation of cis- and trans-diazido complexes with an OH^--catalyzed trans to cis isomerization required before redox can occur (eq 16 and 17). Resolution of the empirical rate parameters (eq 11) in terms of the constants of eq 12-17 yields the values given in Table IV.

$$(HO)_3AgN_3^- + N_3^- \xrightarrow{k_{16}} cis\text{-}(HO)_2Ag(N_3)_2^- + OH^- \xrightarrow{k_{16}} \text{product} \quad (16)$$

$$(HO)_3AgN_3^- + N_3^- \xrightarrow{K_{17}} trans\text{-}(HO)_2Ag(N_3)_2^- + $$
$$OH^- \xrightarrow{k_{17}} cis\text{-}(HO)_2Ag(N_3)_2^- + OH^- \rightarrow \text{product} \quad (17)$$

Discussion

The reduction of $Ag(OH)_4^-$ by azide ion in alkaline media takes place via an intermediate azido complex. Similar intermediates have been observed or postulated in the oxidation of hydrazoic acid by aquametal cations of Mn(III),[1,2] Co(III),[5] and Ce(IV).[7] However, in contrast to these labile aquametals in which the complexation equilibrium is established during mixing, the kinetics of the complexation and redox steps in the present system could be studied independently.

The kinetics of $Ag(OH)_3N_3^-$ formation reflect reversible complexation in which both the "ligand" and "solvent" paths contribute significantly under our conditions. This behavior has been reported for only one other system, that being the ligand-exchange reaction of $Pd(dien)Br^+$ with inosine.[18] In that system the authors were able to conduct their study over a sufficiently extensive range of concentrations to allow accurate determination of all rate parameters. We were unable to do this because of (i) competition between redox and complexation, (ii) the small spectral changes encountered at low concentrations of azide, and (iii) the spontaneous decomposition of $Ag(OH)_4^-$.

Thus, it must be pointed out that the values of the rate constants in the third term of eq 9 are subject to rather large uncertainties due to their interdependence and the fact that the ligand path predominates for most of our experiments. In addition, although the data are in good agreement with eq 6, the assumption that $k_{-7}[OH^-] \gg k_8[N_3^-]$ requires k_7 to be significantly greater than the value of 0.6–2.5 s^{-1} suggested by other work.[19,20]

In the reaction of $Pd(dien)Br^+$ with inosine, the appearance of the full rate law for both paths was attributed to the very low reactivity of inosine toward both the parent complex and the solvolysis product.[18,21] In the present system, which involves the competition of OH^- and N_3^- for Ag(III), an

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equilibrium constant of ca. 0.38 was obtained. This suggests that the reactivity (or nucleophilicity) of N_3^- and OH^- toward Ag(III) is similar.

Thiosulfate[20] has an equilibrium constant for complexation with $Ag(OH)_4^-$ 4 orders of magnitude greater than that obtained here. This further suggests that OH^- and N_3^- are relatively poor nucleophiles for Ag(III), with the order of nucleophilicity being $S_2O_3^{2-} >> OH^- \geq N_3^-$. The same order has been observed for Pd(II), which is isoelectronic with Ag(III). Thus, the appearance of both ligand and solvent paths in this system and an equilibrium constant near unity are not unexpected.

The rates of OH^- substitution in $Ag(OH)_4^-$ has been determined for a variety of substrates including thiosulfate,[20] periodate,[22] tellurate[22] and ethylenediamine.[19] A wide range of substitution rates has been observed that parallels that found for Pd(II). The largest rate constants have been obtained for the softer[23] ligands such as thiosulfate (ca. $10^4 \ M^{-1} \ s^{-1}$), whereas the slowest substitution rates have been observed for relatively hard ligands such as azide ion ($k_6 = 7.3 \ M^{-1} \ s^{-1}$).

The mechanism proposed for the reduction of silver(III) by azide ion (eq 13–17) involves reaction of the intermediate azido complex with a second molecule of azide. Under the conditions of this study, this occurs by two parallel paths. These reactions may involve either five-coordinate intermediate (eq 13–15) or ligand replacement (eq 16–17). Previous studies have shown that electron transfer within a five-coordinate intermediate can occur in silver(III) reactions.[19,24,25] However, since formation of both *cis*- and *trans*-diazido complexes would also be expected, neither alternative can be eliminated. In any case, the most striking feature for both parts of the redox mechanism is that adjacent azides seem to be required for electron transfer. This suggests a transition state involving a seven-membered cyclic Ag–N_6 species and/or a neutral N_6 molecule. This would allow for the direct formation of Ag(I) and nitrogen, consistent with the product analysis, EPR, and polymerization experiments. A recent study[11] of the decomposition of *cis*-$Pt(N_3)_2(PPh_3)_2$ has, indeed, provided spectral evidence for the intermediate formation of neutral cyclic hexazine, N_6.

Kinetic studies of the reaction of HN_3 with the aquametal ions of Mn(III),[1–3] Co(III),[4–6] and Ce(IV)[7] have given rise to several postulated mechanisms and a certain amount of controversy. For example, both $N_3\cdot$ and $H_2N_6^+\cdot$ have been suggested as intermediates in the Co(III) system under comparable conditions. The Mn(III) reaction seems to involve either a one-electron or two-electron mechanism (involving a Mn(IV) intermediate) depending on $[HN_3]$. The outer-sphere reductions of $Ni(bpy)_3^{3+}$ [26] and $Co(Me_6[14] \ diene)^{3+}$ [27] involve direct N_3^- (even in acid media) oxidation to $N_3\cdot$. In spite of the high thermodynamic instability of N_3^- relative to N_2, the reaction of $Ag(OH)_4^-$ with N_3^- is one of the slowest studied to date. Indeed, under comparable [azide] (HN_3 or N_3^-), it is slower than any of the above reactions, all of which were studied in acid media. Furthermore, the overall redox rate in this system has no detectable contribution from the unimolecular decomposition of $Ag(OH)_3N_3^-$. Our observations suggest that the presence of two adjacent molecules of N_3^- in the activated complex facilitates electron transfer by offering a path with a smaller energy barrier than required for the formation of $N_3\cdot$.

Nevertheless, in contrast to the reaction with hydrogen peroxide,[24] the two-electron reduction of Ag(III) by N_3^- is a relatively slow reaction since some degree of electronic rearrangement and formation of a N–N bond is still necessary.

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Notes

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Unusual EPR Spectrum of $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$: Effect of Magnetic Dipole Coupling with Slow Electron Exchange

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EPR spectroscopy provides a powerful method of investigating metal–ligand bonding and magnetic interactions in transition-metal complexes. Most work in the latter area has involved dimers in which the unpaired electrons exchange between the metal ions more rapidly than on the EPR time scale. In the case of the most widely studied metal, copper(II), sophisticated computer simulation programs have been developed to investigate the way in which the characteristic seven-line spectra of such systems depend upon factors such as the metal–metal separation and the relative orientation of the complexes in the dimer.[1] Magnetic dipole interactions can also significantly affect EPR spectra even when the rate of electron exchange is relatively slow; it is interactions of this type that produce the relatively broad lines observed for pure, as opposed to magnetically dilute, compounds.[2] When the crystal structure of a pure compound is such that each metal has only a few paramagnetic neighbors, magnetic dipole splittings of this kind may sometimes be resolved. Recently, the EPR spectra of single crystals of several copper(II) and vanadyl(IV) complexes have been interpreted in this manner.[3–7] The line shapes observed for these systems, which are quite different from those seen for dimers involving rapid electron exchange, are generally quite complex, ranging from five[5] to nine[6,7] lines in the case of the copper(II) compounds, with the

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