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Kinetics of Silver(III) Decomposition in Dilute Acid

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Trivalent silver may be prepared as the $Ag(OH)_4^-$ ion by anodic oxidation of silver metal in strongly basic media.[1,2] At room temperature and in the absence of impurities, $Ag(OH)_4^-$ has a half-life for decomposition of about 100 min in 1.2 M NaOH. The stability of Ag(III) decreases considerably with a half-life of less than 30 min in 0.1 M OH⁻. The products of decomposition in base are solid AgO and oxygen. At pH 11, formation of colloidal solid is complete within a few seconds.[3]

Dissolution of AgO in strong acid yields Ag(II) which is also metastable. Kinetic studies in a variety of acid media indicate that decomposition can occur both by direct reaction between Ag(II) and water and through a second-order disproportionation path in which a silver(III) species is the oxidant.[4–7]

Investigations of Ag(II) reactions with a variety of reducing agents also verify that either Ag(III) or Ag(II) can be the oxidant.[8–10] It seems well established from a variety of studies that trivalent silver exists as AgO^+ in acid solutions with $[H^+]$ between 1.5 and 6 M.[4,5,7,11,12]

We may note, therefore, that, since Ag(III) is already extensively hydrolyzed in strong acid, only a two-proton (or hydroxyl) change distinguishes the species existing in strongly acidic and in basic media as shown by eq 1.

$$Ag(OH)_4^- + 2H^+ \rightleftarrows AgO^+ + 3H_2O \qquad (1)$$

In this paper, we present the results of a kinetic study of the rapid reduction of Ag(III) to Ag(I) initiated by acidification of $Ag(OH)_4^-$ solutions in the stopped-flow apparatus.

Experimental Section

Solutions of $Ag(OH)_4^-$ were prepared by electrolysis of silver foil as previously described.[1,2] Concentrations of NaOH were adjusted, either before or after electrolysis, so that reaction with 1.2 M $HClO_4$ produced the desired excess of acid. $NaClO_4$, prepared from sodium hydroxide and perchloric acid, was used to bring Ag(III) solutions to an ionic strength of 1.2 M. Reagent grade $AgNO_3$ was used for the Ag^+ dependence and was added to the acid solution.

Kinetic experiments were performed in an Aminco-Morrow stopped-flow apparatus. All runs were monitored at the $Ag(OH)_4^-$ absorbance peak (267 nm)[2] using a Beckman hydrogen lamp and power supply and a Hamamatsu R136 photomultiplier tube. Because of the rather large temperature rise accompanying the initial acid–base neutralization, solutions were thermostated at 18 °C. We estimate that all kinetic experiments were conducted within ±0.7° of 25.5 °C.

For each set of kinetic experiments, three or four reaction traces were superimposed on the storage oscilloscope and photographed. First-order plots were generally linear through at least 3 half-lives. In some cases, however, replicate sets of runs performed several minutes apart gave rate constant variations of as much as ±10%. We do not consider variations of this magnitude significant in view of potential problems with temperature control and possible complications caused by colloidal AgO in aged solutions. In fact, this reasonably good reproducibility indicates that decomposition of alkaline $Ag(OH)_4^-$ solutions has little, if any, effect on the reaction under investigation.

Since $Ag(OH)_4^-$ undergoes decomposition even in base, initial silver(III) concentrations were determined periodically in the stopped-flow apparatus. For all experiments reported here, $[Ag(OH)_4^-]$ is between 2.7×10^{-5} and 8.6×10^{-5} M. Final H^+ concentrations were determined by titration of reaction mixtures prepared either by mixing equal volumes of reactants or—to minimize the effect of a slightly different mixing ratio—by collection at the waste port of the stopped-flow apparatus. Each hydrogen ion concentration in the range of 2.5×10^{-3}–0.122 M is sufficiently large to ensure constancy during the course of the reaction.

Table I. Hydrogen Ion Variation[a]

$10^5 \times$ [Ag(III)]$_0$	$[H^+]$	k, s⁻¹	$A_{Ag(OH)_4^-}/A_0$
6.0	0.0025	123	0.28
5.5	0.0030	139	0.30
3.4	0.0030	137	0.21
8.6	0.024	120	0.30
5.8	0.023	149	0.19
7.3	0.061	149	0.27
6.3	0.122	155	0.31
		av 140	av 0.27

[a] Concentrations in M; $\mu = 1.2$ M; $T = 25.5 \pm 0.7$ °C.
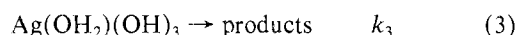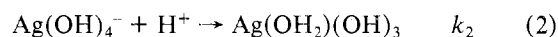
Table II. Silver(I) Dependence at $[H^+] = 0.023$ M[a]

$10^5 \times$ [Ag(III)]$_0$	$10^4 [Ag^+]$	k, s⁻¹	$A_{Ag(OH)_4^-}/A_0$
5.8	0	149	0.19
4.0	1.94	156	0.22
3.1	9.7	151	0.27
2.7	19.4	136	0.24
		av 148	av 0.23

[a] Concentrations in M; $\mu = 1.2$ M; $T = 25.5 \pm 0.7$ °C.

Results and Discussion

Results are given Table I for experiments with no added silver(I) and in Table II for runs with added silver nitrate. Throughout the concentration ranges studied, the reaction is complete within about 25 ms with an average first-order rate constant (weighing each $[H^+]$ and $[Ag^+]$ equally) of 142 s⁻¹ ($\sigma = 13$ s⁻¹). An even faster reaction occurs within the dead time of the apparatus (<2 ms) as evidenced by the fact that initial absorbances, A_0, extrapolated from the first-order plots are only about 25% of values expected for $Ag(OH)_4^-$. The ratios of A_0 to the corresponding absorbance of $Ag(OH)_4^-$ are given in the last column of Tables I and II. This parameter also appears invariant to changes in $[Ag^+]$, $[Ag(III)]_0$, and $[H^+]$, indicating that $Ag(OH)_4^-$ is completely converted to another species in the initial step.

The foregoing observations may be attributed to the mechanism indicated by eq 2 and 3. The second step is rate determining with $k_3 = 142 \pm 13$ s⁻¹.

$$Ag(OH)_4^- + H^+ \rightarrow Ag(OH_2)(OH)_3 \qquad k_2 \qquad (2)$$

$$Ag(OH_2)(OH)_3 \rightarrow \text{products} \qquad k_3 \qquad (3)$$

In acid solution, products of reaction 3 are Ag^+, O_2, and rapidly neutralized hydroxyl ion. Po et al.[7] have raised the possibility that hydrogen peroxide is an intermediate in the AgO^+ path for Ag(II) decomposition, but we can find no evidence for H_2O_2 involvement as either an intermediate or a product.

The postulation that the oxidizing agent is $Ag(OH_2)(OH)_3$ (or the equivalent formulations $Ag(OH)_3(aq)$ or $AgO(OH)$) is based on the following set of arguments which appear self-consistent.

(1) This is the only additional state of Ag(III) hydrolysis possible between 1.5 M H^+ (the lower limit of Kirwin's acid study)[5] and 0.12 M OH^- [2] (cf. eq 1).

(2) If Ag^{3+} is such a strong acid that two protons have been lost even in $[H^+]$ up to 6 M (AgO^+ is equivalent to $Ag(OH)_2^+$), it is not unreasonable to expect the third hydrogen to be ionized at our lowest $[H^+]$ of 2.5×10^{-3} M and, hence (since A_0 is acid independent), throughout our acid range. This behavior is consistent with that of gold(III).[13] Neutral hydroxo complexes exist at detectable levels for a number of other metals,[14] and strong oxidizing agents are often extensively hydrolyzed.[15]

(3) It is very unlikely that the initial rapid reaction involves a change in silver oxidation state since (a) Ag(III) can react
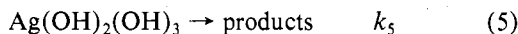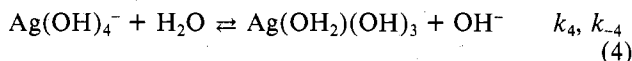
by a two-electron path,[4,5,7,8,10] (b) Ag^+ is the final product and does not absorb at 267 nm, and (c) Ag(II) would either react very slowly by a first-order path[7] or undergo disproportionation which would result in an Ag^+ dependence (cf. Table II). In addition, although Ag(II) is probably deprotonated at these low acidities,[16,17] very rapid reduction of $Ag(OH)_4^-$ to $AgOH^+$ in the initial step would require a rate constant for $AgOH^+$ reduction which is 6 orders of magnitude larger than that reported in ref 7 for the first-order reduction of Ag(II).

(4) Using the equilibrium constant for Ag(II) disproportionation given by Po et al.[7] along with their kinetic data, we estimate a first-order rate constant of about 1 s^{-1} for the reaction of AgO^+ with water. This seems to rule out AgO^+ as the reactant under our conditions since ionic strength differences and the effect of nitrate complexation[16] and hydrolysis of Ag(II) would be insufficient to explain an increase of more than 2 orders of magnitude.

At the low Ag(III) concentrations and short time scale of this study, precipitation of solid $Ag(OH)_3$ does not seem important. However, a small degree of polymerization might be an additional source of the observed experimental deviations.

Since reaction 2 is complete in less than 2 ms, even at 0.0025 M H^+, we are able to estimate that $k_2 > 5.5 \times 10^5 M^{-1} s^{-1}$. We would, in fact, expect this reaction to be even faster with k_2 close to the diffusion-controlled limit.

Spectral measurements and the relative stability of Ag(III) indicate that $Ag(OH)_4^-$ is the only important Ag(III) species in base down to at least 0.1 M OH^-.[1,2] When an $Ag(OH)_4^-$ solution is rapidly brought to pH 11, decomposition occurs within 1 or 2 s at 30 °C.[3] This latter observation is consistent with a mechanism in which formation of $Ag(OH_2)(OH)_3$ is rate determining (eq 4 and 5).

$$Ag(OH)_4^- + H_2O \rightleftharpoons Ag(OH_2)(OH)_3 + OH^- \qquad k_4, k_{-4} \tag{4}$$

$$Ag(OH)_2(OH)_3 \rightarrow products \qquad k_5 \tag{5}$$

Since solid silver oxides are formed under these conditions, k_5 would probably be somewhere between k_2 and $2k_2$ depending on how effectively the conproportionation reaction between Ag(III) and Ag(I) competes with the reduction of Ag(III). The rate constant k_4 has, in fact, been determined from the solvent path for ethylenediamine substitution of Ag(III),[18] and its value of 0.6 s^{-1} is in good qualitative agreement with the decomposition rate at pH 11. Furthermore, the fact that the reverse of reaction 4 suppresses rapid decomposition at 0.1 M OH^- but not at $[OH^-] \approx 10^{-3}$ M leads to a rough estimate of $K_4 \approx 10^{-3}$ M.

Registry No. $Ag(OH)_4^-$, 23172-26-1.

References and Notes

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Contribution from the Nuclear Research Center "Demokritos", Athens, Greece

¹¹⁹Sn Mössbauer Spectroscopy of Polynuclear Dithiooxalate Copper(I)–Tin(IV) Complexes

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The dithiooxalate ligand, $(C_2S_2O_2)^{2-}$, dto, has the important property of acting as a multifunctional complexing agent.[1-4] The dianionic ligand may be O,O, S,S, or O,S bonded to a variety of metal ions according to the particular preference of the metal for "hard" or "soft" ligands. In addition, under appropriate conditions, the ligand may coordinate to more than one metal ion forming polynuclear complexes. A series of such complexes containing Sn(IV) and Cu(I) centers has been recently described by Coucouvanis and Leitheiser.[5] The complexes are of the general type $M[(O_2C_2S_2)Cu(PPh_3)_2]_n$: $M = Cl_4Sn^{IV}$, $CH_3Cl_3Sn^{IV}$, $(CH_3)_2Cl_2Sn^{IV}$, $n = 1$, I; $M = Cl_2Sn^{IV}$, CH_3ClSn^{IV}, $(CH_3)_2Sn^{IV}$, $n = 2$, II; $M = CH_3Sn^{IV}$, $ClSn^{IV}$, $BrSn^{IV}$, $n = 3$, III.

I , X = Cl , CH_3

II , X = Cl , CH_3

III , X = Cl , Br , CH_3

L = PPh_3
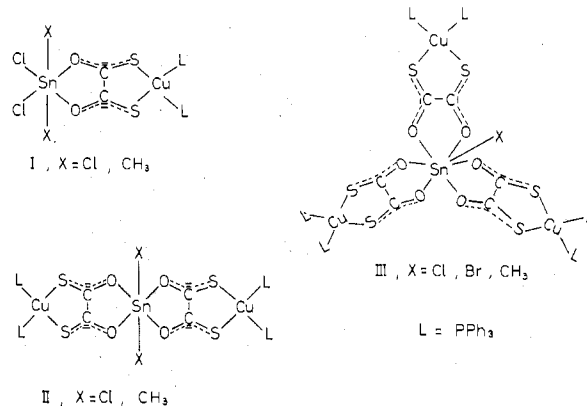
The mode of coordination of the dithiooxalate ligands toward Cu(I) and Sn(IV) and conceivable structures of the complexes were deduced from infrared and NMR spectroscopy. In this note we report on the ¹¹⁹ᵐSn Mössbauer spectra of the above polynuclear complexes; the spectra assist in determining the stereochemistry at the tin site and also in determining the bonding properties of the dithiooxalate ligand toward tin.

Experimental Section

Samples of the complexes were supplied by Professor Coucouvanis. Their preparation and characterization has been reported.[5] Mössbauer spectra were measured on a constant-acceleration spectrometer. Absorbers were maintained at 80 ± 2 K and a source of Ba¹¹⁹SnO₃ was used at room temperature. The spectrometer was calibrated periodically by using the magnetic hyperfine spectrum of an iron-foil absorber. Relative errors were less than ±0.5 mm/s. The parameters were obtained by a least-squares computer fit of the data. In comparing the isomer shifts of different compounds, we assume that the shifts of SnO_2 and $BaSnO_3$ are identical.