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Kinetics and Mechanism of the Silver(II)–Phosphorous Acid Reaction

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The oxidation of phosphorous acid by silver(II) in perchloric acid solution takes place by two independent paths. Aside from acid dependence, the rate law is $-0.5\mathrm{d}[\mathrm{Ag(II)}]/\mathrm{d}t = k_1[\mathrm{H_3PO_3}] + k_2[\mathrm{Ag(II)}]^2[\mathrm{Ag^+}]^{-1}[\mathrm{H_3PO_3}]$. The rate-determining step proposed for the first path involves the dissociation of $\mathrm{H^+}$ from a P–H bond, generating a reactive intermediate with a lone pair of electrons on phosphorus. The value of k_1 is in reasonable agreement with the previously known rate constant for deuterium exchange with the P–H bond of phosphorous acid. For the second path the reaction of silver(III) with phosphorous acid is suggested as the rate-determining step. However the reaction of silver(II) with a monomeric phosphorus(IV) species, as an alternative possibility for the rate-determining step, is not completely ruled out.

Introduction

Silver(II) is a particularly strong oxidizing agent in aqueous solution ($\mathrm{Ag^{2+}}$–$\mathrm{Ag^+}$ reduction potential $E° = +1.98$ V[1,2]). A review of the chemistry of silver(II) and silver(III) is available.[3]

Kinetic investigations of several redox reactions of silver(II) have been reported previously. These display an interesting range of mechanistic behavior. For several reducing agents the rate-determining step is a simple bimolecular electron transfer to silver(II). Examples include the transition metal ions V(IV), Mn(II), Fe(II), Co(II), and Ce(III),[4] and the nonmetal oxyanion dithionate ($\mathrm{S_2O_6^{2-}}$).[5]

On the other hand, the oxidation of water by silver(II) in acidic solution ($\mathrm{HClO_4}$,[6,7] $\mathrm{HNO_3}$,[8,9] and $\mathrm{H_3PO_4}$[10]) proceeds by a mechanism involving silver(III) as a reactive intermediate, formed by the rapid disproportionation of silver(II): 2Ag(II) = Ag(I) + Ag(III). The equilibrium lies far to the left.[1,6,7,11–13] The silver(II)–silver(I) exchange reaction also proceeds *via* this disproportionation.[14,15] One limiting form of the rate law for the silver(II)–thallium(I) reaction suggests a similar mechanism in which thallium(I) reacts with silver(III) in the rate-determining step. However detailed analysis supports a more elaborate mechanism involving thallium(II) and $\mathrm{NO_3}$ radical, but not silver(III), as intermediates.[16]

The purpose of the present research is to study the kinetics and mechanism of another redox reaction of silver(II) with particular attention to possible involvement of silver(III). For phosphorous acid ($\mathrm{H_3PO_3}$), the reducing agent selected, the possibility of tautomerism is related to interesting mechanistic features in several reactions previously investigated.[17–22]

Experimental Section

Materials.—Solutions of Ag(II) were generated by electrolysis[1,5,23] of $\mathrm{AgClO_4}$ in perchloric acid, using a rotating platinum anode and a cathode isolated by a sintered-glass frit. Typically the electrolysis of 150–250 ml of 0.3 *M* $\mathrm{AgClO_4}$ in 3 *M* $\mathrm{HClO_4}$ utilized a current of 40–100 mA.

The Baker and Adamson $\mathrm{H_3PO_3}$ used was recrystallized for many of the runs. Water was purified by ion exchange or by distillation from alkaline permanganate. Other reagent grade chemicals were used without further purification. The $\mathrm{NaClO_4}$ used in adjusting ionic strength was either added as such or formed by addition of NaOH to the solution.

Kinetics.—Reactions were followed at 470 mμ, the band maximum of Ag(II), using a Beckman DB spectrophotometer with a Beckman or Sargent recorder. The extinction coefficient of Ag(II) was taken as 140 M^{-1} $\mathrm{cm^{-1}}$ at the band maximum.[6] For temperature control, water from a constant-temperature bath was circulated through the cell compartment. Temperatures in Tables II and III were measured at the bath and may have averaged 0.2–0.4° higher in the cell compartment.

Reactions were initiated by mixing five or ten parts of Ag(II) solution to one part of $\mathrm{H_3PO_3}$ solution. Typically $\mathrm{Ag^+}$ and $\mathrm{H^+}$ concentrations after completion of reaction were determined by potentiometric titration of an aliquot of the reaction mixture with $\mathrm{Cl^-}$ and $\mathrm{OH^-}$, after tenfold dilution with water to retard any net reduction of $\mathrm{Ag^+}$ to Ag metal by $\mathrm{H_3PO_3}$. Concentrations of $\mathrm{H_3PO_3}$ are based on titration of stock solutions with $\mathrm{OH^-}$, together with the appropriate dilution factor.

A relationship used in analyzing the data from a single kinetic run is $(1/T)(\mathrm{d}T/\mathrm{d}t) = -2.303(\mathrm{d}A/\mathrm{d}t) = k_a + k_bA^2$, where T denotes transmittance. Plots of $(1/T)(\Delta T/\Delta t)$ *vs.* A^2 were satisfactorily linear for 2 half-lives ($A^2 = 0.18$–0.01) for most of the runs. Upward deviations of $(1/T)(\Delta T/\mathrm{d}t)$ observed at low A^2 were not investigated in detail. Values of k_a and k_b were deter-

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mined by linear least-squares analysis of the $(1/T)(\Delta T/\Delta t)$ *vs.* A^2 data over the linear portion of the run, using 0.05 as the ΔT increment.

Stoichiometry.—To study the stoichiometry of the Ag(II)–H_3PO_3 reaction, an excess of phosphorous acid solution was added to a known initial amount of stirred silver(II) solution. (In one of the determinations, approximate concentrations were 0.38 M Ag^+, 2.9 M H^+, 6.1×10^{-3} M Ag(II), and 2.3×10^{-2} M H_3PO_3 after mixing.) On completion of reaction, a sample of the reaction mixture was diluted 15-fold with water, Ag^+ was removed by titration with chloride, and H^+ was neutralized with base. The amount of phosphate formed was determined colorimetrically by the heteropoly blue method.[24] Contribution of phosphorous acid to the measured absorbance was corrected for by the use of a standard curve, assuming additive contributions of phosphate and phosphorous acid. In some cases an aliquot of the product solution was heated to 100° for 30 min in 1 M $HClO_4$ prior to the colorimetric analysis, with the aim of at least partially hydrolyzing any hypophosphate ($H_2P_2O_6^{2-}$) which might be present.[25]

Results

Stoichiometry.—The ratio of moles of phosphate formed to moles of silver(II) initially present was determined for several runs, on the assumption that all of the absorbance in the heteropoly blue procedure was due to additive contributions from orthophosphate and phosphorous acid. In a set of four samples from two reaction mixtures, this stoichiometric ratio was 0.43 ± 0.08; heating each sample 30 min in 1 M $HClO_4$ prior to colorimetric analysis gave 0.44 ± 0.09. A set of twelve and a set of six samples from six reaction mixtures gave 0.38 ± 0.03 and 0.39 ± 0.02 for the stoichiometric ratio, before and after the 30-min heating in 1 M H^+, respectively. On the basis of the known rate constants for the acid hydrolysis of hypophosphate at lower temperatures,[25] at 100° in 1 M H^+ the half-life of hydrolysis of hypophosphate to H_3PO_3 and H_3PO_4 should be 25–42 min. Though we did not study experimentally the behavior of hypophosphate in the colorimetric procedure, it is unlikely that hypophosphate would give exactly the same absorbance as the phosphate and phosphorous acid which would be formed from it on hydrolysis. Since heating the samples in 1 M H^+ for 30 min has no appreciable effect on the stoichiometric ratio, apparently little or no hypophosphate is formed in the reaction of silver(II) with phosphorous acid. The stoichiometric ratios are reasonably close to the value of 0.5 which should hold if phosphate is the product. Thus it appears that the major reaction taking place is $2Ag(II) + H_3PO_3 + H_2O = 2Ag^+ + H_3PO_4 + 2H^+$.

Kinetics.—To determine whether the extinction coefficient of Ag(II) in perchloric acid media[6] is applicable in the presence of H_3PO_3, absorbance values were extrapolated back to the time of mixing to obtain A_0. Using the integrated form $A_0 = C_1 \tan [\tan^{-1} (A/C_1) + C_1C_2(t - t_0)]$, extrapolated values of A_0 were averaged over a substantial portion of the run [$C_1 = (k_a/k_b)^{1/2}$ and $C_2 = k_b/2.303$]. The expected value A_1 for the initial absorbance was determined from the measured absorbance of the Ag(II) solution prior to mixing, together with the dilution factor on mixing with H_3PO_3. For a set of 36 runs, the average value of A_0/A_1 is 1.00 ± 0.04. This agreement justifies using the value reported for perchloric acid solutions (140 ± 7 M^{-1} cm^{-1})[6] for the extinction coefficient of Ag(II) in these reaction mixtures.

The k_a and k_b terms in the rate law for an individual run represent parallel paths, respectively, zero and second order with respect to silver(II). Rate constants for the second-order path were corrected for the rate of oxidation of water by silver(II),[6] a 4–10% correction in most cases, larger below 0.02 M H_3PO_3.

TABLE I

REACTION ORDERS

Species	Concn range for species, M	Runs[a]	Order: $[Ag(II)]^0$ path	Order: $[Ag(II)]^2$ path
H_3PO_3	0.020–0.050	II: 1–4	1.09 ± 0.04	1.12 ± 0.06
Ag^+	0.10–1.00	III: 4, 7–11	0.10 ± 0.02	−0.86 ± 0.02
H^+	1.92–4.04	III: 2–6	0.31 ± 0.08	−1.49 ± 0.15

[a] Numbers refer to line entries in Table II or III.

Reaction orders with respect to H_3PO_3, Ag^+, and H^+, determined separately for the zero- and second order silver(II) paths, are presented in Table I. The orders with respect to H^+ are least certain. Maintaining constant ionic strength by replacing H^+ with Na^+ may not result in sufficiently constant activity coefficients at these concentrations. Moreover generation of Ag(II) at 1 M H^+ gave difficulty. Aside from acid dependence, the rate law can be written as

$$-0.5 \frac{d[Ag(II)]}{dt} = k_1[H_3PO_3] + k_2 \frac{[Ag(II)]^2[H_3PO_3]}{[Ag^+]}$$

Rate constants are tabulated in Tables II and III for 75 kinetic runs, as a function of ionic strength (I), $[H^+]$, and temperature. For 41 of the runs, the values of k_1 and k_2 were determined by a Runge–Kutta numerical integration[26] of the pair of simultaneous differential equations for $-d[Ag(II)]/dt$ and $-d[H_3PO_3]/dt$ within a kinetic run, systematically adjusting the rate constants to give the best fit, in the least-squares sense, with observed A values. Concentrations other than [Ag(II)] and $[H_3PO_3]$ were assumed constant during the run. This Runge–Kutta analysis was carried out when initial time and absorbance data were available. For the remaining 34 runs, values for k_1 and k_2 result from k_a and k_b as outlined above. Initial concentrations of Ag(II) were generally in the range $(3\text{–}11) \times 10^{-3}$ M, based on initial absorbances recorded for the 41 Runge–Kutta runs.

Average values (and probable errors) for the rate constants at 25° are $k_1 = (4.7 \pm 0.4) \times 10^{-5}$ sec^{-1} and $k_2 = 1.6 \pm 0.2$ M^{-1} sec^{-1} at 3.0 M H^+ and $I = 3.4$ M (Table II, lines 1–11) and $k_1 = (4.9 \pm 0.5) \times 10^{-5}$ sec^{-1} and $k_2 = 1.6 \pm 0.2$ M^{-1} sec^{-1} at 3.1 M H^+ and $I = 4.2$ M (Table III, lines 7–14).

Activation parameters can be evaluated from data at bath temperatures of 25.0–32.0° (Table II, lines 7–14).

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TABLE II

RATE CONSTANTS[a] AT

$[H^+] = 3.0 \pm 0.1\ M$ and $I = 3.4 \pm 0.1\ M$

Temp, °C	$10[Ag^+]$, M	$10^2[H_3PO_3]$, M	10^5k_1, sec^{-1}	k_2, $M^{-1}\ sec^{-1}$	No. of runs
25	3.0	2.0	4.3	1.7[b]	2
	3.0	3.0	4.2	1.8	2
	3.0	3.9	4.4	1.8	2
	2.9	5.0	4.7	1.9	3
	3.0	5.0	5.1	1.3[c]	4
	3.0	6.0	5.1	1.2[b]	2
	1.6	5.0	4.1	1.6[c]	2
	2.0	5.0	4.5	1.9	2
	2.4	5.0	4.5	1.5	2
	3.2	5.0	5.7	1.8	2
	3.9	5.0	4.8	1.8	2
28	3.0	6.0	6.5	1.5[b]	1
32	3.0	6.0	10.4	1.9	3
	3.8	5.0	9.3	2.7	3

[a] For duplicate runs, average values are tabulated. [b] Beginning of rate constants determined from k_a and k_b. [c] Beginning of rate constants determined from Runge–Kutta numerical integration.

TABLE III

RATE CONSTANTS[a] AT

$I = 4.2 \pm 0.1\ M$ AND 25°

$[H^+]$, M	$10[Ag^+]$, M	$10^2[H_3PO_3]$, M	10^5k_1, sec^{-1}	k_2, $M^{-1}\ sec^{-1}$	No. of runs
2.0	2.7	5.0	3.8	3.3[b]	3
1.9	3.0	3.9	3.9	3.6	2
2.4	3.0	6.0	5.6	2.1	3
3.2	3.0	6.0	5.6	1.3	3
3.7	3.0	3.9	5.0	1.2	2
4.0	2.9	5.0	5.7	1.1	3
3.1	1.0	5.0	4.6	1.3[c]	4
3.1	2.5	5.0	5.1	1.5	4
3.1	6.0	5.0	5.4	1.9	4
3.1	9.8	5.0	5.4	1.9	3
3.1	10.0	5.0	5.6	2.0	4
3.0	1.0	1.0	3.0	1.1	2
3.0	2.5	0.50	5.0	0.9	2
3.0	2.5	1.0	4.3	1.4	2
3.3	2.5	1.0	3.8	1.2	2

[a] For duplicate runs, average values are tabulated. [b] Beginning of rate constants determined from k_a and k_b. [c] Beginning of rate constants determined from Runge–Kutta numerical integration.

These are $\Delta H_1^{\ddagger} = 18 \pm 2$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = -16 \pm 5$ cal deg^{-1} mol^{-1} for the k_1 path and $\Delta H_2^{\ddagger} = 4 \pm 4$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -43 \pm 15$ cal deg^{-1} mol^{-1} for the k_2 path (with standard deviations indicated).

Discussion

Two parallel paths for the silver(II)–phosphorous acid reaction are indicated by the experimental rate law. The term $k_1[H_3PO_3]$, with k_1 increasing somewhat with acidity, suggests for the first reaction path a mechanism similar to that suggested for the phosphorous acid–iodine reaction.[17] In acidic solution with A as the oxidizing agent, we have

$$H_3PO_3 + H^+ \rightleftharpoons H_4PO_3^+ \qquad \text{(rapid)}$$

$$H_4PO_3^+ \rightleftharpoons (HO)_3P\colon + H^+ \qquad \text{(rate determining)}$$

$$(HO)_3P\colon + A \longrightarrow \text{products} \qquad \text{(rapid)}$$

The rate law for the H_3PO_3–Hg^{2+} reaction also fits such a mechanism.[18,19] Similarly Haight[21] has found that in the reaction of H_3PO_3 with Cr(VI), the rate-determining step is the loss of H^+ from the P–H bond of an anhydride of H_3PO_3 and Cr(VI). The high reactivity assumed for species with a lone pair of electrons on phosphorus is supported by the rapid rate observed[22] for the oxidation of triethyl phosphite by Cr(VI).

The rate of deuterium exchange between the P–H bond of H_3PO_3 and the solvent has been measured in D_2O–DCl solution.[17] For the phosphorous acid–iodine reaction, ratios of oxidation rate to exchange rate as high as 0.3 were observed, the similarity in rates supporting the mechanism proposed for the oxidation.[17] For the silver(II)–phosphorous acid reaction, from the observed temperature dependence one can estimate $k_1 = (3.3 \pm 0.3) \times 10^{-5}$ sec^{-1} at 3.0 M H^+ and 22°. Interpolating the exchange data,[17] $k = 5.2 \times 10^{-5}$ sec^{-1} at 3.0 M D^+ and 22°. Since the solvent is slightly different (H_2O–H^+ *vs.* D_2O–D^+), the agreement is reasonable. Thus although the acid dependence is somewhat uncertain experimentally, the data as a whole support a mechanism in which dissociation of H^+ from the P–H bond is the rate-determining step for the first reaction path.

The second term in the rate law is of the form $k_2[Ag(II)]^2[Ag^+]^{-1}[H_3PO_3]$, k_2 decreasing with increasing acidity. A possible mechanism for the second reaction path (aside from acid dependence) is

$$2Ag(II) \rightleftharpoons Ag^+ + Ag(III) \qquad \text{(rapid)}$$

$$Ag(III) + H_3PO_3 + H_2O \longrightarrow Ag^+ + H_3PO_4 + 2H^+ \qquad \text{(rate determining)}$$

As discussed in the Introduction, similar mechanisms involving the disproportionation of Ag(II) have been proposed for the oxidation of water by Ag(II)[6–10] and for the Ag^+–Ag(II) exchange reaction.[14,15]

An alternative possibility can also be written for the second path, indicating only the oxidation states

$$Ag(II) + P(III) \rightleftharpoons P(IV) + Ag(I) \qquad \text{(rapid)}$$

$$Ag(II) + P(IV) \longrightarrow P(V) + Ag(I) \qquad \text{(rate determining)}$$

Since this alternative mechanism leads to the same form for the second term in the rate law, it cannot be entirely ruled out. A monomeric P(IV) species would however be somewhat unusual, though the existence of As(IV) as a reaction intermediate has been inferred.[27–30]

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