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Kinetics and Mechanism of the Oxidation of the Hypophosphite Ion by the Tetrahydroxoargentate(III) Ion

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The kinetics of oxidation of hypophosphite ion to phosphite by the tetrahydroxoargentate(III) ion, $Ag(OH)_4^-$, has been studied in strong base by stopped-flow spectrophotometry. The measured 1:1 stoichiometry is consistent with a two-electron change, which is equivalent to an oxygen atom transfer from Ag(III) to $H_2PO_2^-$ as in the case of arsenic(III) and sulfite ion oxidations. The reaction is pseudo first order in [silver(III)] disappearance with $k_{obsd} = (a + b[OH^-])[H_2PO_2^-]$, where $a = 0.069 \pm 0.014$ dm^3 mol^{-1} s^{-1} and $b = 1.13 \pm 0.02$ dm^6 mol^{-2} s^{-1} at 25 °C and $\mu = 1.58$ mol dm^{-3}. Reaction with $D_2PO_2^-$ is considerably slower ($a_H/a_D = 2.46$; $b_H/b_D = 8.2$), indicating that P–H bond breaking is the rate-determining step. The activation parameters for the [OH$^-$]-independent and -dependent paths are $\Delta H_a^{\ddagger} = 82 \pm 10$ kJ mol^{-1}, $\Delta S_a^{\ddagger} = 10 \pm 32$ J K^{-1} mol^{-1} and $\Delta H_b^{\ddagger} = 39 \pm 5$ kJ mol^{-1}, $\Delta S_b^{\ddagger} = -114 \pm 16$ J K^{-1} mol^{-1}, respectively. The ionic strength dependence of the rate reflects competition between the second- and third-order paths. The proposed mechanism involves the formation of an intermediate between an axial site on $Ag(OH)_4^-$ and $H_2PO_2^-$. The intermediate undergoes redox by two modes—both internal and OH$^-$ assisted—which involve the deprotonation of the P–H bond in the rate-determining steps. Comparison with results of other oxoanion oxidations by silver(III) suggests a common mechanism involving oxygen atom transfer from $Ag(OH)_4^-$ to an axially bound reductant.

Introduction

The kinetics of reactions of hypervalent metal ions in solution, stabilized through complexation with various ligands, is a subject to recent interest. For example, both Ni(III) and Ni(IV) are obtainable as complexes of macrocycles[1] as is Ag(II).[2] Cr(V) is stabilized by tertiary α-hydroxy acids[3] and Mn(III) with bipyridine.[4] The simplest source of tervalent silver in solution is the square-planar tetrahydroxoargentate(III) ion. In strong base, the complex is metastable and decomposes at room temperature and [OH$^-$] = 1.2 mol dm^{-3} with a half-life of approximately 1.5 h.[5] Ag(III) is stabilized in alkaline medium by periodate and tellurate ions.[5] Tetraglycine[6] and dimethylglyoxime[7] complexes of some stability have been prepared from $Ag(OH)_4^-$.

We have been studying the mechanism of oxidation of various inorganic reducing agents by $Ag(OH)_4^-$. The results obtained so far indicate that silver(III) is reduced through a variety of mechanisms. In the oxidations of azide[8] and thiosulfate,[9] transient Ag(III)-substrate complexes could be detected. In other cases the redox occurs within a five-coordinate intermediate.[10,11] In the oxidation of oxoanions such as arsenite[12] and sulfite,[13] five-coordinate intermediates are also possible, and a two-electron redox step, probably an oxygen atom transfer, is involved. It was therefore of interest to extend this study to know if the oxygen atom transfer mechanism is a general feature of the oxidations of oxoanions.

Hypophosphorous acid exists in two tautomeric forms. The predominant form, in which P is tetracoordinated, is known as the "inactive" form whereas the form in which P is tricoordinated is called the "active" form ($K_{eq} \sim 10^{-12}$).[14] The structures of both "inactive" and "active" forms of hypophosphite ion are shown in eq 1.

$$ \text{inactive form} \rightleftharpoons \text{active form} \qquad (1) $$
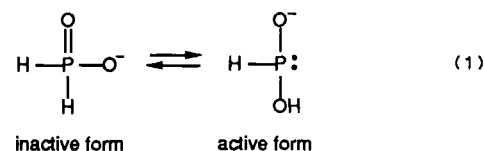
A number of studies have been carried out on the exchange of phosphorus-bonded hydrogen with deuterium in both acidic[15–18] and basic media.[19] The exchange is slow, indicating strong P–H rather than P–O–H bonds, and intermediate species $H_4PO_2^+$ and HPO_2^{2-} have been postulated. In the case of the basic experiments, the rate law had a first-order dependence on [OH$^-$] up to [OH$^-$] = 1 mol dm^{-3}. Thus, we may conclude that the equilibrium amount of HPO_2^{2-} is small under these conditions and that the (composite) second pK of H_3PO_2 is above 14.

Although there have been numerous studies on the oxidation of H_3PO_2 in acid,[20–25] very few studies have been made in basic solution. The oxidations by peroxodisulfate[26] and RuO_4^- [27] and the Cu(II)-catalyzed oxidation by hypobromite ion[28] have been reported. Internal redox in a hypophosphito derivative of Co(III), $(NH_3)_5Co(O_2PH_2)^{2+}$, exhibits an [OH$^-$] dependence and a large deuterium isotope effect, $k_H/k_D = 4.0 \pm 0.5$, indicating that proton removal from phosphorus is rate determining.[29]

The oxidation of hypophosphite in alkaline medium is of interest for various reasons (a) to test the involvement of doubly depro-

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Table I. Stoichiometry of the Reaction $Ag(OH)_4^- + H_2PO_2^-$ at Room Temperature and [NaOH] = 1.2 M

$10^4[Ag(III)]$, M	$10^2[NaH_2PO_2]$, M	$10^4[H_3PO_3]$ found, M	$\Delta[H_3PO_3]/$ $\Delta[Ag(III)]$
3.6	4.75	4.16	1.16
3.0	3.80	3.12	1.04
2.4	2.85	2.70	1.13
			av 1.11 ± 0.05

tonated H_3PO_2 as different rate dependences have been observed, (b) to learn whether the inactive $\rightleftharpoons$ active tautomerism is involved in the mechanism, and (c) to determine whether it is oxidized by Ag(III) via an oxygen atom transfer mechanism as is the case with other oxoanions.[12,13] The results for the oxidation of hypophosphite ion by $Ag(OH)_4^-$ in alkali solution are presented here.

Experimental Section

Solutions. Sodium hypophosphite solutions were prepared by neutralizing a purified 50% sample of hypophosphorous acid (Fisher) with sodium hydroxide. The sample was first quantitatively analyzed for hypophosphorous and phosphorous acids by the method of Jones and Swift.[30] The sample was found to be 9.22 and 0.1 mol dm^{-3} in H_3PO_2 and H_3PO_3, respectively. Although atmospheric oxidation of hypophosphorous acid was not a problem (the above concentrations did not change during the course of study) sodium hypophosphite solutions, prepared for the kinetic runs, were used within 2–3 days. The reaction between $Ag(OH)_4^-$ and $H_2PO_3^-$ is undetectably slow,[13] and hence, the presence of small amounts of phosphite in the hypophosphite solution had no affect on the kinetic results.

A 50 wt % solution of hypophosphorous acid-d_3 (Aldrich) was suitably diluted with deuterium oxide (99.8 atm % D, Aldrich) and standardized. Its solution was converted to the sodium salt and suitably diluted with sodium hydroxide of the desired strength just before the start of the rate measurements to avoid any exchange during the course of the experiments.
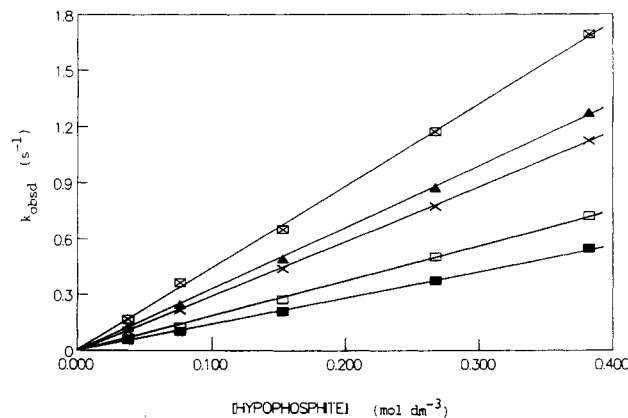
Lithium hydroxide (Matheson Coleman and Bell) was used as supplied. Sodium hydroxide solutions were prepared from 50% (w/w) NaOH (Fisher, Certified reagent) by dilution with distilled water. Concentrations of the alkali solutions were checked by titrations against a standard perchloric acid solution.

Sodium perchlorate solutions, used to adjust the ionic strength, were prepared by neutralizing a weighed amount of sodium carbonate (Fisher, Certified) with a standard perchloric acid solution. The solution was heated to convert any HCO_3^-, if formed, to CO_3^{2-} and to drive out dissolved carbon dioxide and made to the desired volume after cooling. Tests for the presence of CO_3^{2-} with alkaline Ba^{2+} were negative. Lithium perchlorate was prepared by the neutralization of lithium hydroxide solution with standard perchloric acid. The pH in each case was adjusted to 7. The concentration of each solution was determined gravimetrically by evaporating the water from a known volume of aliquots and drying to constant weight.

Tetrahydroxoargentate(III) ion was prepared either in 1.2 mol dm^{-3} sodium hydroxide or lithium hydroxide by electrolysis of a silver foil (Handy and Harman).[5] After electrolysis, the anolyte was quickly filtered through a glass microfiber filter (Whatman, 934-AH) and the clear yellow solution stored in a capped polyethylene bottle. The concentration of Ag(III) solution was checked against its spectrum, which exhibits one broad peak at 267 nm ($\epsilon = 1.17 \times 10^4$ dm^3 mol^{-3} cm^{-1}).

Test for Free Radical. Acrylonitrile (6% v/v) was added during the course of the reaction.[8] No precipitation of white polyacrylonitrile appeared even after several hours. This result is consistent with a one-step, two-electron-transfer mechanism with no free-radical intermediates.

Stoichiometry. Several solutions having known concentrations of Ag(III) were mixed with an excess of $H_2PO_2^-$. The amount of H_3PO_3 produced was estimated as follows.[30] After completion of the reaction, solutions were acidified with perchloric acid to pH $\simeq$ 1 and made to a known volume. A 25 cm^3 aliquot of this solution was added to a known solution of iodine in phosphate buffer, and the pH was adjusted to $\simeq$ 7.3. The reaction mixtures were kept in the dark for about an hour and thereafter acidified with approximately 6 mol dm^{-3} acetic acid solution. The liberated iodine was immediately titrated against a standard thiosulfate solution to a starch–iodine end point. The mean of several such estimations (Table I) yields $\Delta[H_3PO_3]/\Delta[Ag(III)] = 1.11 + 0.05$. Hence the stoichiometric equation of the reaction is as in eq 2.

$$Ag(OH)_4^- + H_2PO_2^- \rightarrow Ag(OH)_2^- + H_2PO_3^- + H_2O \quad (2)$$

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Figure 1. Plots of k_{obsd} versus $[H_2PO_2^-]$: 25 °C (■); 30 °C (□); 35 °C (×); 40 °C (▲); 45 °C (▨). [NaOH] = 1.2 mol dm^{-3}, and $\mu = 1.58$ mol dm^{-3}.
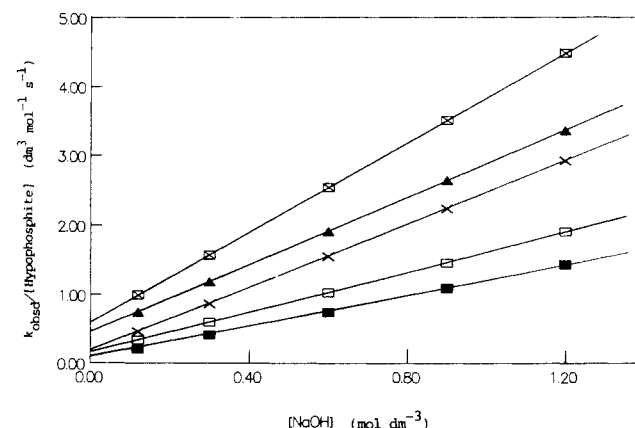
Figure 2. Plots of k_{obsd}/[hypophosphite] versus [OH⁻]: 25 °C (■); 30 °C (□); 35 °C (×); 40 °C (▲); 45 °C (▨). $[H_2PO_2^-] = 0.382$ mol dm^{-3}, and $\mu = 1.58$ mol dm^{-3}.

The relative sluggishness of the Ag(III)–P(I) reaction and the interference of the spontaneous decomposition of Ag(III)[13] precluded determination of the stoichiometry at lower excess of $H_2PO_2^-$ or at excess Ag(III).

Kinetics. All kinetic runs were made with large enough excesses of hypophosphite ion to overcome competition due to the self-decomposition of Ag(III). (Although the half-life of bulk $Ag(OH)_4^-$ preparations is over an hour, significant decomposition occurs within minutes upon mixing it with unelectrolyzed NaOH in the stopped-flow apparatus.) The ionic strength (μ) was maintained at 1.58 mol dm^{-3} for most runs in order to allow appropriate variation of reductant and OH⁻. The kinetic measurements were made (generally at 267 nm) with an Aminco-Morrow stopped-flow apparatus with a thermostated reaction cell.[5] Interference due to hypophosphite absorbance was negligible. The stopped-flow assembly was interfaced to a Radio Shack microcomputer through a Starbuck Data Co. A/D converter.[9] The reaction was first order in Ag(III) for $3 \times 10^{-5} \leq [Ag(HO)_4^-] \geq 1.8 \times 10^{-4}$ mol dm^{-3} and $[H_2PO_2^-]$ in the range 0.0382–0.382 mol dm^{-3}. Replicate runs were generally reproducible to less than ±5%. For several sets of conditions, repetitive spectra were recorded during the course of the reaction on a HP 8451 diode-array spectrophotometer. In no case were any spectral changes present that would indicate the presence of stoichiometrically significant intermediates.

Results

Plots of k_{obsd} vs $[H_2PO_2^-]$ are linear and pass through the origin at all temperatures (Figure 1). The rate also varies linearly with [OH⁻] (Figure 2) leading to the empirical rate law in eq 3.

$$\frac{-d[Ag(OH)_4^-]}{dt} = k_{obsd}[Ag(OH)_4^-]$$

$$k_{obsd} = (a + b[OH^-])[H_2PO_2^-] \quad (3)$$

The least-squares values of a and b are given in Table II wherein are also reported the corresponding values for deuteriohypophosphite. Activation parameters were calculated from eq 4, where
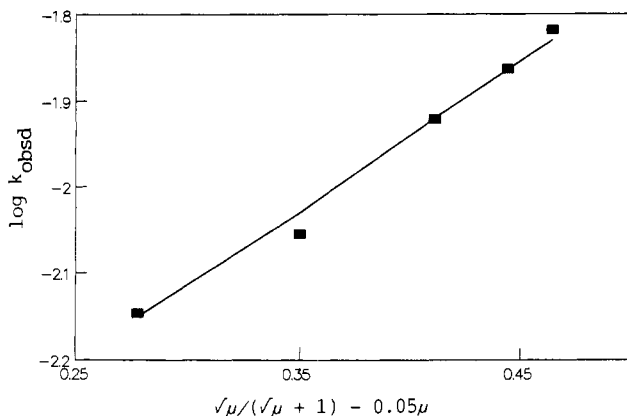
Table II. Values of Intercepts and Slopes of the Linear Plots in Figure 3 at Different Temperatures[a]

temp, °C	intercept (a), dm^3 mol^{-1} s^{-1}	slope (b), dm^6 mol^{-2} s^{-1}
25[b]	0.028 ± 0.01	0.138 ± 0.001
25	0.069 ± 0.014	1.13 ± 0.02
30	0.159 ± 0.015	1.45 ± 0.02
35	0.181 ● 0.039	2.3 ± 0.1
40	0.45 ± 0.03	2.43 ± 0.04
45	0.60 ± 0.02	3.21 ± 0.03

$\Delta H_a^* = 82 \pm 10$ kJ mol^{-1} $\Delta H_b^* = 39 \pm 5$ kJ mol^{-1}
$\Delta S_a^* = 10 \pm 32$ J K^{-1} mol^{-1} $\Delta S_b^* = -114 \pm 16$ J K^{-1} mol^{-1}

[a] See eq 2. [b] Deuteriohypophosphite.

Figure 3. Ionic strength dependence. [$H_2PO_2^-$] = 0.042 mol dm^{-3}, and [OH^-] = 0.12 mol dm^{-3} at 25 °C. Solid line (slope = 1.8) is from the regression analysis. See text for discussion of the "theoretical" fit.

k is a or b and $\mathbf{k}$ and h are the Boltzmann and Planck constants. These are also listed in Table II.
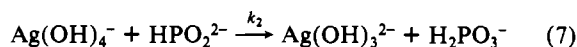
$$k = \frac{\mathbf{k}T}{h} \exp\left(\frac{-\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right) \quad (4)$$

The ionic strength was varied at constant [OH^-] (0.12 mol dm^{-3}) and [$H_2PO_2^-$] (0.042 mol dm^{-3}) between 0.162 and 1.242 mol dm^{-3} by using sodium perchlorate. The plot of log k_{obsd} against $\sqrt{\mu}/(\sqrt{\mu} + 1) - 0.05\mu$, based on the Davies equation,[31] is shown in Figure 3. A linear least-squares fit of the data yields a slope of 1.8.

The parameters a and b in the rate law (eq 3) are expected to give rise, individually, to linear plots with slopes of +1 and +3, respectively. On the basis of experimentally determined values of a and b[OH^-] at 1.58 mol dm^{-3} ionic strength, the composite second-order rate constant was computed. This "theoretical curve" has a gradually changing slope that goes from 1.3 at μ = 0 to about 2.6 at μ = 2 mol dm^{-3}. In the region of our experiments, the calculated curve is close to linear with a slope of 2.0. This is in good agreement with the experimental data.

Discussion

The measured 1:1 stoichiometry, the simple kinetics (first order in both [Ag(III)] and [$H_2PO_2^-$]), and lack of evidence, either kinetic or spectral, of an intermediate species indicate a one-step, two-electron-redox process. The substantial deuterium isotope effect indicates that P–H fission is involved in the rate-determining steps. The mechanism shown in eq 5–7 is analogous to that for
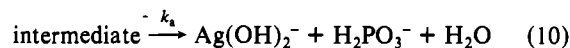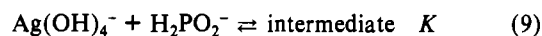
$$Ag(OH)_4^- + H_2PO_2^- \xrightarrow{k_1} Ag(OH)_2^- + H_2PO_3^- + H_2O \quad (5)$$

$$H_2PO_2^- + OH^- \underset{}{\overset{K_2}{\rightleftharpoons}} HPO_2^{2-} \quad (6)$$

$$Ag(OH)_4^- + HPO_2^{2-} \xrightarrow{k_2} Ag(OH)_3^{2-} + H_2PO_3^- \quad (7)$$

the arsenite reaction at low OH^- where both $H_2AsO_3^-$ and $HAsO_3^{2-}$ are stoichiometrically significant.[12]

Equilibrium 6 has been invoked to account for the mechanism of the base-catalyzed exchange of hydrogen on hypophosphite ion,[19] and an equivalent equilibrium was considered in the oxidation of $H_2PO_2^-$ by RuO_4^-.[27] The rate of disappearance of Ag(III) in terms of reactions 5–7 is given by eq 8, which, with the approximation $1 \gg K_2[OH^-]$, is equivalent to eq 3 with $a = k_1$ and $b = k_2K_2$.

$$\frac{-d[Ag(OH)_4^-]}{dt} = \frac{(k_1 + k_2K_2[OH^-])[H_2PO_2^-][Ag(OH)_4^-]}{1 + K_2[OH^-]} \quad (8)$$

The activation energies for proton exchange on hypophosphorous acid and its monoanion have been measured in acidic and basic media. In base,[19] where HPO_2^{2-} is a likely intermediate, ΔH^* = 79 kJ mol^{-1}. In acid,[15] the value is 100 kJ mol^{-1}. The uncatalyzed exchange on H_3PO_2 is second order (ΔH^* = 130 kJ mol^{-1}). The activation enthalpies determined in the present study are large for silver(III) reactions but considerably less than the corresponding values for the exchange reactions. We would expect the enthalpy change for reaction 6 to be similar to the activation barrier for the base-catalyzed exchange reaction. The combination of reactions 6 and 7 therefore should give rise to a value of ΔH^* much greater than the observed value of 39 kJ mol^{-1} and cannot explain the observed kinetics. Although ΔH^* for the uncatalyzed hydrogen exchange on $H_2PO_2^-$ has not been studied, its value is probably far in excess of the measured value of ΔH_a^* of 82 kJ mol^{-1}.

In light of the above, we conclude that both redox paths involve P–H bond breaking within a silver(III)–hypophosphite intermediate. Such intermediates are common for square-planar silver(III). The lack of an inverse [OH^-] dependence is an indication of five-coordinate silver with an axial Ag–O–P bridge. This configuration would, as postulated previously, put the phosphorus in position to accept an oxygen from the Ag(III), which could then receive a pair of electrons directly into the empty $d_{x^2-y^2}$ orbital.[12] Intermediate formation between $Ag(OH)_4^-$ and $H_2PO_2^-$ (eq 9) can be followed by redox either via eq 10 or with assistance from hydroxyl ion as in eq 11.

$$Ag(OH)_4^- + H_2PO_2^- \rightleftharpoons \text{intermediate} \quad K \quad (9)$$

$$\text{intermediate} \xrightarrow{k_a} Ag(OH)_2^- + H_2PO_3^- + H_2O \quad (10)$$

$$\text{intermediate} + OH^- \xrightarrow{k_b} Ag(OH)_3^{2-} + H_2PO_3^- \quad (11)$$

Reactions 9–11 lead to the rate law in eq 12, which reduces to a form similar to eq 3 with $a = Kk_a$, $b = Kk_b$, and $K[H_2PO_2^-] \ll 1$.

$$k_{obsd} = \frac{(Kk_a + Kk_b[OH^-])[H_2PO_2^-]}{1 + K[H_2PO_2^-]} \quad (12)$$

The oxygen involved in bridging is the phosphoryl oxygen. A similar type of oxygen bridging has been considered in the reduction of Cr(V) by H_3PO_2[32] and in the reduction of Ag(III) by other oxoanions.[12,13] An intermediate also appears to be present in the reduction of RuO_4^- by hypophosphite ion.[27]

As previously noted, the [OH^-] rate dependence cannot be adequately explained by the formation of $Ag(OH)_5^{2-}$.[11,33] The principle species of hypophosphite ion, like the acid, has two P–H bonds (see Introduction). This conformation would create a barrier to oxidation since the phosphorus needs to gain a P–O bond. Hence, redox via an oxygen-transfer mechanism would be en-

(31) Davies, C. W. *Ion Association*; Butterworths: London, 1962; p 39.

(32) Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, 25, 4737.

(33) Kirschenbaum, L. J.; Panda, R. K. *Polyhedron* **1988**, 7, 2753.

Scheme I
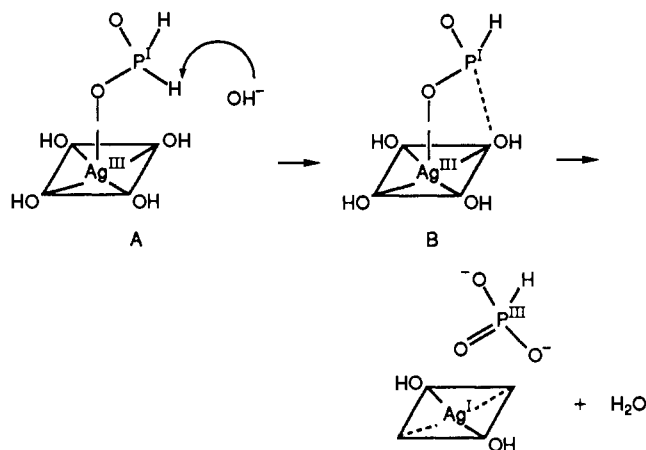
hanced by deprotonation as depicted in Scheme I.

The foregoing analysis permits us to understand the large difference in rates for the silver(III) oxidation of hypophosphite ion compared to the reaction with arsenite.[12] The electrode potential for hypophosphite oxidation is about 0.9 V more favorable than for the As(III)/As(V) couple in basic media;[34] yet the arsenite reaction, under comparable conditions, is over 4 orders of magnitude faster. Ag(III) oxidation of phosphite ion, which also has a P–H bond, could not be detected,[13] even though the redox potential should make that reaction more favorable than the Ag(III)–As(III) reaction. Differences in $\Delta S^{\ddagger}$ for the two paths in the $H_2PO_2^-$ reaction are consistent with (a) a negative contribution for intermediate formation, (b) a positive contribution due to P–H bond breaking, and (c) an additional negative contribution in the [OH⁻]-dependent path.

Raman spectral data indicate that hypophosphite ion has the tetrahedral "inactive" form[35] while arsenite is pyramidal.[36] In using the measured activation enthalpies to favor a mechanism in which there is intimate contact between the Ag(III) and hypophosphite ions, we have ruled out either deprotonation (eq 6) or the inactive–active tautomerization (eq 1), which should have the same activation energy.[19] A similar argument was used to explain the low $\Delta H^{\ddagger}$ for the reduction of RuO_4^- by hypophosphite.[27] We note, in fact, that the rate of tautomerization is much less than the presently observed redox rate.

The isotope effect, $a_H/a_D = 2.5 \pm 0.5$ and $b_H/b_D = 8.2 \pm 0.2$, indicates that P–H bond breaking is the rate-determining process.

The values are comparable to the values 3.13 ± 0.32 and 5–6 for the OH⁻-independent and OH⁻-assisted hypophosphite exchange reaction.[19] The internal redox of $(NH_3)_5Co(O_2PH_2)^{2+}$, which has a one-term rate law,[29] has a value $k_H/k_D = 4.0 \pm 0.5$.

The differences between the rate constants for protio and deuterio compounds involving hydrogen and deuterium bond breaking in the rate-determining step are attributed to differences in zero-point energy. The ratio k_H/k_D can be obtained from eq 13.[37]

$$\frac{k_H}{k_D} = \exp\left(\frac{hc(\nu_H - \nu_D)}{2kT}\right) \quad (13)$$

Using the values of the frequencies $\nu_{P-H} \sim 2400$ cm⁻¹ and $\nu_{P-D} \sim 1700$ cm⁻¹ for free hypophosphite[19] yields $k_H/k_D = 5.5$ at 25 °C; however, we have no way of estimating these frequencies in the intermediate complex. Isotope effects greater than those calculated from eq 13 may be due to tunneling and/or to differences in bending modes, while smaller ratios are usually due to concerted bond making and breaking.[38] In any case it is certain that breaking of the P–H bond in a silver(III)–hypophosphite species is involved in the rate-determining process.

Concluding Remarks

The results of this study give convincing support to our earlier suggestion that silver(III) oxidizes oxoanions via a one-step oxygen atom transfer. In discussing the reactions of $Ag(OH)_4^-$ with other oxoanions,[12,13] we have considered the additional possibility that reactions analogous to eq 9–11 proceed via an initial link between a bound hydroxyl and X (X = As, S, P). In the case of hypophosphite, this seems unlikely because of the two P–H bonds. Comparison of all the oxoanion data suggests a common mechanism. Hence, we conclude that the axially bound intermediate, B in Scheme I, is representative of the arsenite(III) and sulfite reactions as well. The involvement of five-coordinate silver(III) intermediates is well established in both redox and complexation mechanisms.[8,9] Indeed complexation of silver(III) by the nonoxidizable oxoanions, phosphate, arsenate, borate, and carbonate, involve a five-coordinate intermediate of structure similar to species A.[39]

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