Kinetics and Mechanism of Hydrogen Peroxide Oxidation by Silver(III) in Aqueous Alkaline Media

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The oxidation of hydrogen peroxide by Ag^{III} in strongly alkaline media has been studied by stopped-flow spectrophotometry in the temperature range 6—45 °C at a total ionic strength of 1.2 mol dm^{-3} ($NaClO_4$). The reaction is first order in $[Ag^{III}]$, $[HO_2^-]$, and $[OH^-]$ with a third-order rate constant of $(4.2 \pm 0.6) \times 10^5$ dm^6 mol^{-2} s^{-1} at 25 °C. The form of the rate law and the activation parameters ($\Delta H^‡ = 25 \pm 5$ kJ mol^{-1}, $\Delta S^‡ = -113 \pm 5$ J K^{-1} mol^{-1}) suggest the formation of a five-co-ordinate intermediate of the form $[Ag(OH)_4O_2]^{3-}$. Although kinetic results do not distinguish between a one- or two-electron transfer, a change in stoicheiometry from $\Delta[Ag^{III}]/\Delta[HO_2^-] = 1$ at high $[HO_2^-]$ to 2 at excess $[Ag^{III}]$ leads to the conclusion that a bivalent silver intermediate is produced.

The presence of metal—hydrogen peroxide complexes as intermediates has been postulated in the oxidation of H_2O_2 by a number of aquametal ions,[1-6] as well as complexed metal ions [7-11] and, indeed, complexes of H_2O_2, HO_2^-, and O_2^{2-} are well known.[12-14] Previous kinetic studies of peroxide oxidation by simple transition-metal ions have been carried out in acidic media. This paper presents the results of a study of the reaction, in alkaline media, between silver(III) and HO_2^- (which is both a better nucleophile and stronger reducing agent [15] than neutral H_2O_2).

Silver(III) can be conveniently prepared as the tetrahydroxo-anion $[Ag(OH)_4]^-$ in basic media by anodic oxidation of silver metal.[16,17] The half-life for the reduction of $[Ag(OH)_4]^-$ (to AgO) by the solvent is *ca.* 90 min in 1.2 mold m^{-3} NaOH at room temperature. This stability decreases markedly with decreasing $[OH^-]$.[18] Because it is a low-spin, square-planar, d^8 system, $[Ag(OH)_4]^-$ can undergo inner-sphere redox either by a ligand-replacement mechanism or *via* electron transfer in a five-co-ordinate intermediate. Indeed, both of these mechanisms appear to operate simultaneously in the reaction between Ag^{III} and ethylenediamine.[19] Although uncomplexed Ag^{II} is unknown in basic media and solid AgO actually contains stoicheiometric amounts of Ag^I and Ag^{III},[20] silver(III) reductions can involve either one- or two-electron changes. Thus, in contrast to previous studies, we have the possibility for a single-step, complementary two-electron transfer in the present system.

Experimental

Solutions.—The anion $[Ag(OH)_4]^-$ was prepared in 1.2 mol dm^{-3} sodium hydroxide (Fisher) by electrolysis of silver foil (Handy and Harmon) as described previously.[17] All solutions were prepared using doubly distilled water. All other chemicals were reagent grade. Hydrogen peroxide (Matheson, Coleman, and Bell Co.; 30% w/v, stabilizer free) stock solution was standardized prior to use by titration with Ce^{IV} using a ferroin indicator. The concentration of hydrogen peroxide was determined at the time of each kinetic run by acidification of an aliquot of alkaline hydrogen peroxide solution with perchloric acid (Baker and Adamson) followed by addition of excess iron(II) perchlorate at a total $[HClO_4]$ of greater than 1.0 mol dm^{-3}. The Fe^{III} so produced was determined spectrophotometrically at 260 nm *versus* an appropriate blank ($\varepsilon = 2.88 \times 10^3$ dm^3 mol^{-1} cm^{-1}) [21] with a relative error of less than 1%. As a check on this analysis, neutral H_2O_2 solutions were standardized by titration with Ce^{IV} using a ferroin indicator. Concentrations determined by this method agreed with those determined spectrophotometrically to within 1%, indicating minimal decomposition of hydrogen peroxide on dilution in base and or acidification of alkaline solutions with perchloric acid. Sodium perchlorate (1.2 mol dm^{-3}) used for ionic strength adjustments was prepared by neutralization of standard perchloric acid with sodium hydroxide to a final pH of *ca.* 8. Iron(II) perchlorate was prepared by first dissolving barium carbonate (Baker and Adamson) in 1.2 mol dm^{-3} perchloric acid followed by addition of acidified iron(II) sulphate (dissolved $FeSO_4{\cdot}7H_2O$, Baker analyzed). The resulting solution was boiled for *ca.* 20 min, cooled overnight, and filtered. Titanium(IV) sulphate solutions for use in stoicheiometry determinations were prepared [22] by heating anhydrous titanium(IV) oxide (*ca.* 0.5 g) (Fisher) with concentrated sulphuric acid (*ca.* 0.1 dm^3) (Matheson, Coleman, and Bell) at 150 °C for 7 h. After cooling, the solution was diluted to 0.50 dm^3 with H_2O and filtered through a glass fibre filter ($[Ti^{IV}] = 0.01$ mol dm^{-3}, $[H_2SO_4] = 3.5$ mol dm^{-3}).

Kinetics.—Kinetics were performed by stopped-flow spectrophotometry [17] at a total ionic strength of 1.2 mol dm^{-3}. The concentration of Ag^{III} was varied from 4.0×10^{-6} to 5.0×10^{-5} mol dm^{-3} with the concentration of hydrogen peroxide being in a minimum 15-fold excess. The disappearance of $[Ag(OH)_4]^-$ was followed at its absorption peak of 267 nm ($\varepsilon = 1.17 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[17] Although alkaline solutions of hydrogen peroxide absorb at this wavelength, this background absorbance caused no significant problems under our conditions. Oscilloscope traces were photographed from a Tektronix 549 storage oscilloscope using a Tektronix type C-12 oscilloscope camera. Pseudo-first-order plots were linear through at least three half-lives with deviations in replicate determinations of rate constants generally less than 5%. Because of the possibility of involvement by products of slow Ag^{III} decomposition, the order of concentration was varied for each series of hydrogen peroxide dependences. This variation in order had no noticeable effect on observed rate constants, nor were there any differences observed by varying the initial $[Ag(OH)_4]^-$ concentration or the monitoring wavelength. Uncertainty associated with temperature readings was less than 0.2 °C at 25 °C and not greater than 0.5 °C at the extremes (6 and 45 °C) of the temperature-dependence study.

Stoicheiometry.—Attempts to determine the stoicheiometry of this reaction in the presence of excess hydrogen peroxide by quenching with iron(II) perchlorate were unsuccessful. Catalytic decomposition of hydrogen peroxide after completion of Ag^{III} reduction was too rapid even at reduced

Table 1. Stoicheiometry of the reaction between $[Ag(OH)_4]^- + HO_2^-$

Initial ratio $[H_2O_2]_0/[Ag(OH)_4^-]_0$	$\Delta[H_2O_2]/\Delta[Ag(OH)_4^-]$
6 : 1	1.0
4 : 1	1.0
2 : 1	0.9
1 : 1	0.9
1 : 1	1.1
1 : 2	0.6
1 : 4	0.5
1 : 8	0.5

temperatures to obtain reproducible results. The stoicheiometry was, however, determined in two other ways. In the first method, excess $[Ag(OH)_4]^-$ was mixed with hydrogen peroxide in the stopped-flow apparatus. The final $[Ag(OH)_4]^-$ concentration was calculated using the value of the optical density obtained immediately following completion of the reaction and assuming that the hydrogen peroxide had been completely consumed during the reaction. The initial $[Ag(OH)_4]^-$ concentration (8.2×10^{-5} mol dm^{-3}) was obtained spectrophotometrically in the stopped-flow apparatus at the monitoring wavelength of 267 nm by mixing a solution of $[Ag(OH)_4]^-$ with a solution of 1.2 mol dm^{-3} NaOH. Initial hydrogen peroxide concentrations (1.0×10^{-5}—7.7×10^{-5} mol dm^{-3}) were determined spectrophotometrically using iron(II) perchlorate. The stoicheiometry was also determined under conditions of excess peroxide, using Ti^{IV}. This was achieved as follows. Given volumes of $[Ag(OH)_4]^-$ and basic H_2O_2 solutions were quickly acidified (pH <1) with 3.5 mol dm^{-3} sulphuric acid and to the acidified reaction mixture was added excess Ti^{IV}. Unreacted hydrogen peroxide was estimated spectrophotometrically at 415 nm as the Ti^{IV}–H_2O_2 complex ($\varepsilon = 731$ dm^3 mol^{-1} cm^{-1}).[23–25] The initial ratio of $[H_2O_2]/[Ag(OH)_4^-]$ was varied between *ca.* 6 : 1 to *ca.* 1 : 1 such that the reactant concentrations were in the range used for kinetic experiments. Initial reactant concentrations were determined spectrophotometrically as described above.

Results and Treatment of Data

The results of the stoicheiometry measurements are given in Table 1. Note that from $[H_2O_2]_0 = [Ag(OH)_4^-]_0$ to a high excess of H_2O_2, the stoicheiometry is 1 : 1 consistent with the overall reaction shown by equation (1). Thus equation (1)

$$[Ag(OH)_4]^- + HO_2^- \longrightarrow [Ag(OH)_2]^- + O_2 + H_2O + OH^- \qquad (1)$$

represents the reaction under the conditions of our kinetic experiments. At excess Ag^{III}, 2 mol of silver are reduced per mol of H_2O_2. This net one-electron change (for silver) could be due either to an initial reduction to bivalent silver or to a two-electron change [equation (1)] followed by the association reaction, equation (2). We note that Ag^{II} does not

$$Ag^I + Ag^{III} \longrightarrow 2\,AgO \qquad (2)$$

persist in basic solution so that formation of a Ag^{II} intermediate would also be followed by formation of the Ag^I–Ag^{III} containing oxide, AgO.[20] The disproportionation of Ag^{II} in the pH region *ca.* 9—10 has been shown to proceed through dimers and higher-order polymers.[26]

The rate of reaction of $[Ag(OH)_4]^-$ with $[Ag(OH)_2]^-$ at concentrations comparable to those expected from reactions (1) and (2) is significantly slower [27] than the observed decrease in Ag^{III} at excess Ag^{III}/HO_2^-. Thus, reaction (2) does not seem to explain the 1 : 2 stoicheiometry unless some other reaction intermediates are involved.

Table 2. Kinetic data at 25 °C and $I = 1.2$ mol dm^{-3}

$10^4[H_2O_2]$/mol dm^{-3}	$[OH^-]$/mol dm^{-3}	$k_{obs.}$/s^{-1}
1.30	1.2	82.0
2.38	1.2	154
3.70	1.2	183
5.20	1.2	287
5.32	1.2	277
7.92	1.2	445
9.30	1.2	480
10.30	1.2	544
1.30	0.75	53.2
3.38	0.75	110
5.40	0.75	200
6.08	0.75	166
10.20	0.75	328
12.90	0.75	383
15.00	0.75	490
1.08	0.45	33.9
2.60	0.45	60.6
5.42	0.45	113
13.40	0.45	256
1.30	0.12	12.2
3.25	0.12	33.0
6.73	0.12	59.2
13.20	0.12	78.0

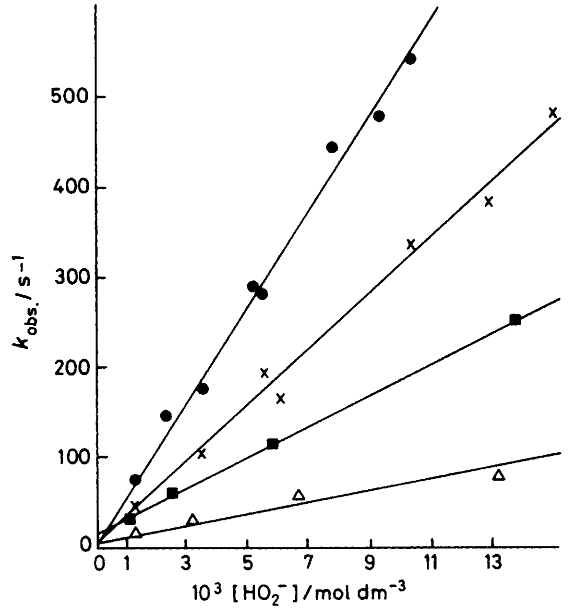


Figure 1. Plots of pseudo-first-order rate constants, $k_{obs.}$, *versus* $[HO_2^-]$ at 25 °C and $I = 1.2$ mol dm^{-3} at various $[OH^-]$: (●), 1.2; (×), 0.75; (■), 0.45; (△), 0.12 mol dm^{-3}

The reaction between hydrogen peroxide and the tetrahydroxoargentate(III) ion is first order in $[Ag^{III}]$ under the conditions of this study. Values of the observed pseudo-first-order rate constants, $k_{obs.}$, are given in Table 2. The data indicate that the reaction is dependent on the concentrations of hydrogen peroxide and hydroxide ion. Figure 1 demon-

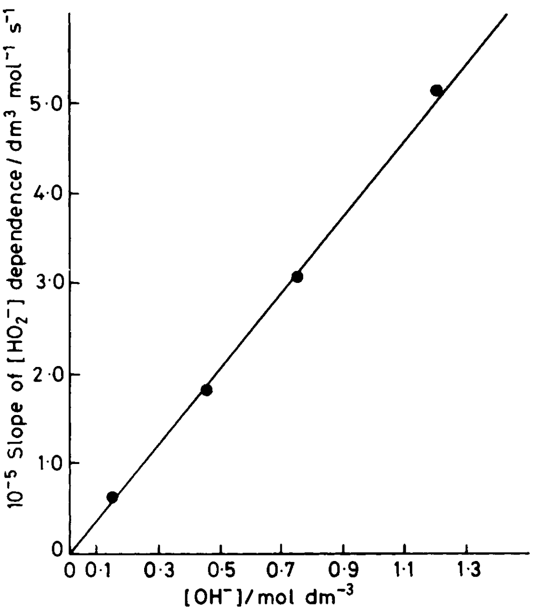


Figure 2. Plot of slopes of $[HO_2^-]$ dependence (from Figure 1) *versus* $[OH^-]$

Table 3. Variation of $k_{obs.}$ with temperature

T/°C	$k_{obs.}/s^{-1}$
6.0	149
14.0	177
25.0	196
35.0	221
45.0	247

Activation parameters $\Delta H^\ddagger = 25 \pm 5$ kJ mol^{-1}, $\Delta S^\ddagger = -113 \pm 5$ J K^{-1} mol^{-1}.

strates that plots of $k_{obs.}$ *versus* hydrogen peroxide concentration are linear with slopes which vary with hydroxide ion concentration and small intercepts which show no regular hydroxide dependence. These intercepts can be attributed to minor side reactions such as that between Ag^{III} and $HO_2^{\cdot -}$ (or $O_2^{\cdot -}$) formed from reactions of HO_2^- with lower-valent silver. A plot of the slopes of the $[HO_2^-]$ plots against $[OH^-]$ is also linear with an intercept that is essentially zero (Figure 2). Thus, this reaction can be described by a simple third-order rate law, equation (3), where $k = (4.2 \pm 0.6) \times 10^5$

$$-d[Ag(OH)_4^-]/dt = k[Ag(OH)_4^-][HO_2^-][OH^-] \quad (3)$$

dm^6 mol^{-2} s^{-1} at 25 °C. Following the oxidation of hydrogen peroxide by silver(III) further decomposition of hydrogen peroxide was observed as evidenced by a very slow increase in the ' infinite ' optical density of kinetic traces. However, these secondary reactions involving silver reduction products were much slower than the reaction with silver(III) and would therefore contribute only minimal error.

Activation studies were carried out in the temperature range 6—45 °C at an ionic strength of 1.2 mol dm^{-3} and hydroxide ion concentration of 1.2 mol dm^{-3}. Hydrogen peroxide concentration was 3.7×10^{-4} mol dm^{-3} and $[Ag(OH)_4^-]$ varied between 2×10^{-5} and 5×10^{-6} mol dm^{-3}. The results are given in Table 3. Enthalpies of activation were determined from a plot of $\ln(k/T)$ *vs.* $1/T$. Activation entropies were calculated from equation (4)[28] using the value of the

$$k = \left(\frac{RT}{Nh}\right)e^{-\Delta H^\ddagger/RT\ \cdot\ \Delta S^\ddagger/R} \quad (4)$$

enthalpy of activation as determined above. The uncertainties in the enthalpy and entropy of activation were estimated to be 5 J mol^{-1} and 5 J K^{-1} mol^{-1} respectively.

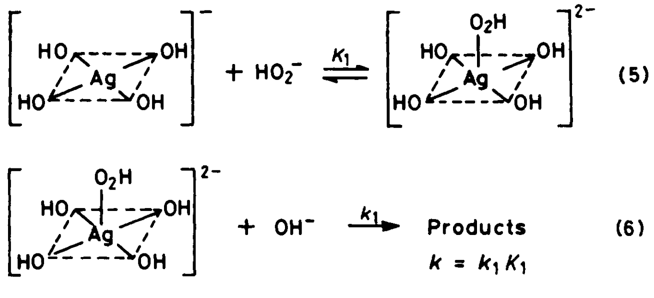
Discussion

The reaction between hydrogen peroxide and the tetrahydroxoargentate(III) ion proceeds *via* a third-order path which is first order in $[OH^-]$. Similar behaviour has been observed in a previous study involving the reduction of Ag^{III} by ethylenediamine.[19] For an outer-sphere redox reaction, no $[OH^-]$ dependence is expected, while if ligand displacement preceded the electron-transfer step an inverse or zero-order hydroxide ion dependence would be predicted.

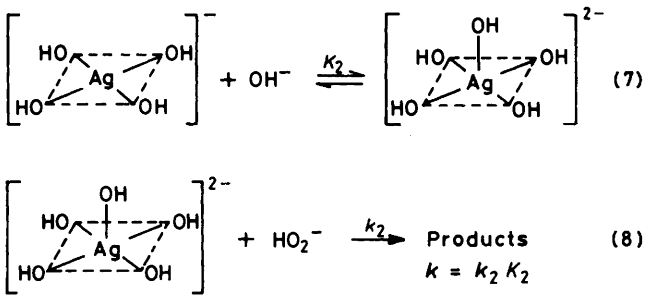
Under the experimental conditions employed in the present study (pH $\geqslant 13$) more than 96% (and usually much more) of the hydrogen peroxide was in the form of HO_2^-. The second pK_a of H_2O_2 (>25) is much too high to explain the third-order path by attack of O_2^{2-} since the resulting second-order rate constant would be greater than the diffusion controlled limit.[29,30]

Thus, the most reasonable explanation for the third-order dependence involves the formation of a five-co-ordinate intermediate which undergoes further reaction prior to, or accompanied by, redox. Two kinetically equivalent mechanisms involving the three reacting species are given in equations (5)—(8). A similar set of alternative reaction sequences have been discussed in connection with the third-order path in the Ag^{III}–ethylenediamine reaction.[19]

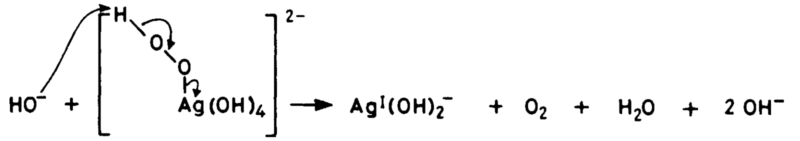
Mechanism (I)



Mechanism (II)



We favour Mechanism (I) for reasons which include the following: (*i*) there is no evidence for any stoicheiometrically significant quantities of Ag^{III} species other than $[Ag(OH)_4]^-$ in the range 0.12 mol dm^{-3} $\lesssim [OH^-] \lesssim$ 12 mol dm^{-3} in the absence of other complexing agents;[16,17] (*ii*) HO_2^- is a much better nucleophile than OH^- and, indeed, many metal ion–hydrogen peroxide reactions, including the reduction of silver(II),[7] occur *via* co-ordinated peroxide intermediates; [1-11] and (*iii*) the deprotonation of HO_2^- should be facilitated by co-ordination to Ag^{III} resulting in a convenient and plausible redox path as shown in equation (9).



(9)

We must now distinguish between the one-step two-electron transfer indicated by equation (9) and the possibility of two successive one-electron steps involving a Ag^{II} intermediate. If a two-step mechanism were operative, deprotonation could occur either before or after the initial reduction as demonstrated by equations (10) and (11), respectively. Since de-

$$[(HO)_4Ag^{III}\text{-}O_2H]^{2-} + OH^- \underset{H_2O}{\overset{-H_2O}{\rightleftharpoons}} [(OH)_4Ag^{III}\text{-}O_2]^{3-} \longrightarrow [(OH)_nAg^{II}\text{-}O_2^{\bullet}]^{(1-n)} + 4-n\,OH^- \quad (10)$$

$$[(HO)_4Ag^{III}\text{-}O_2H]^{2-} \overset{K_{11}}{\rightleftharpoons} [(HO)_4Ag^{II}\text{-}O_2H)] \xrightarrow{OH^-} \text{Products} \quad (11)$$

protonation of co-ordinated $HO_2^{\bullet}$ should be rapid and complete under our conditions (free $HO_2^{\bullet}$ is deprotonated even at pH 7),[31] equation (11) would explain the observed kinetics only if the first step [in equation (11)] were indeed in equilibrium and K_{11} were very small. Since silver(II) (d^9) is labile,[7] these Ag^{II} intermediates would be expected to be quickly solvated and loss of $HO_2^{\bullet}$ or $O_2^{\bullet-}$ should compete with transfer of the second electron. Dissociation of HO_2 and subsequent reaction between Ag^{II} and HO_2^- is inconsistent with the observed $[OH^-]$ dependence. Thus, the immediate product of equation (11) must either be the $Ag^{II}\text{-}O_2^{\bullet-}$ complex indicated in equation (10) or Ag^I and O_2. However, the involvement of free silver(II) *does* seem to be supported by the stoicheiometry measurements at excess Ag^{III} (see below) since neither equation (9) nor a sequence of one-electron exchanges within a single pair of reactants can account for the observed change in $\Delta[HO_2^-]/\Delta[Ag(OH)_4^-]$.

A series of reactions which seems best able to account for the final electron transfer steps as well as the stoicheiometry are given in equations (12)—(14). In the stoicheiometry

$$Ag\text{-}O_2^{\bullet-} \longrightarrow Ag^{II} + O_2^{\bullet-} \quad (12)$$

$$2\,Ag^{II} \longrightarrow Ag^{I} + Ag^{III} \quad (13)$$

$$Ag^{III} + O_2^{\bullet-} \longrightarrow Ag^{II} + O_2 \quad (14)$$

experiments at excess silver(III), the suppression of reaction (13) and the slower overall rate (due to lower $[HO_2^-]$) allows the formation of polymeric species [26] or colloidal AgO which as in the case of polymeric Ce^{IV} [2] oxidizes hydrogen peroxide very slowly.

In order for the rate law to be strictly third order, reaction (14) would have to be either much more rapid than the sequence ending in reaction (12) ($k_1 \geqslant 3 \times 10^7$ dm^3 mol^{-1} s^{-1}) or sufficiently slow that all superoxide ion decayed by the disproportionation reaction, equation (15). However, since reaction (15) ($k_{15} = 6$ dm^3 mol^{-1} s^{-1} [32]) is slower than the overall rate of Ag^{III} disappearance, reaction (14) must be rapid to account for the measured stoicheiometry in both excess HO_2^- and excess Ag^{III} (Table 1). Indeed, $O_2^{\bullet-}$ reacts rapidly with a number of other transition-metal ions.[33] The reaction sequence (5), (10), and (12)—(14) summarizes the result of our analysis.

$$2\,O_2^{\bullet-} + H_2O \longrightarrow HO_2^- + O_2 + OH^- \quad (15)$$

Further support of the proposed mechanism involving the formation of an activated complex of increased co-ordination number and increased negative charge is found in the activation parameters even though the contributions of each step cannot be unambiguously assigned. The rather large negative value of $\Delta S^\ddagger = -113$ J K^{-1} mol^{-1} and the moderate $\Delta H^\ddagger$ of 25 kJ mol^{-1} are similar to those found for reaction of $[Ag(OH)_4]^-$ with negatively charged complexing agents [17] and with arsenite ions.[34] Heyward and Wells [35] pointed out that for aquametal cations *overall* $\Delta S^\ddagger$ values for replacement of a water molecule by H_2O_2 followed by electron transfer tend to be greater than zero. On the other hand, negative $\Delta S^\ddagger$ values are observed for outer-sphere redox and for reactions in which the metal is co-ordinated to multidentate ligands. As in the latter type of complex, the reaction between HO_2^- and $[Ag(OH)_4]^-$ involves a metal whose positive charge is diffused within a complex which in our case has a net negative charge.

The overall redox reaction between $[Ag(OH)_4]^-$ and HO_2^- is more rapid than any other Ag^{III} ligand-exchange process which we have observed to date.[17,19,36] In this study, we have concluded that electron transfer takes place before replacement of bound hydroxide can occur. This is in contrast to the ethylenediamine reaction [19] in which both types of behaviour are indicated by the multipart rate law. The formation of the five-co-ordinate intermediate could be accompanied by not only a change in ligand geometry but also by a shift in electronic configuration from low- to high-spin. Noting that the d_{z^2} orbital in $[Ag(OH)_4]^-$ is filled this change in spin state would present the reducing agent with a half-filled orbital which could then accept one electron to form Ag^{II}. The apparent involvement of silver(II) as the initial product suggests that this path may have a smaller overall barrier than would be needed to make an empty *d* orbital available to accept two electrons. This is in contrast to the reaction between $[Ag(OH)_4]^-$ and As^{III} [34] in which a two-electron change occurs even when Ag^{III} is in excess. In that case, redox takes place through oxygen atom transfer involving an equatorial OH^- that can easily transfer a pair of electrons to the empty $d_{x^2-y^2}$ orbital of Ag^{III}.

In acid solution, the reaction between silver(II) and hydrogen peroxide is very rapid.[7,37] Yet, it seems that the $Ag^{II}\text{-}O_2^{\bullet-}$ complex formed in reaction (10) dissociates before further redox occurs. The large extent of metal-ion hydrolysis in base, coupled with the labile d^9 configuration of Ag^{II}, appears to account for this variation at the two extremes of the acidity scale.

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