Kinetics of the Oxidation of Water by Silver(II) Ions complexed with 2,2′-Bipyridine in Aqueous Nitrate Media

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The kinetics of the oxidative decay of silver(II) ions complexed by 2,2′-bipyridine (bipy) when present in aqueous acidic media have been investigated. The reaction is found to be second order in $[Ag^{II}]$ and zero order in $[H^+]$ with an inverse dependence on $[Ag^I]$. From a detailed consideration of the experimental data, including the overall enthalpy and entropy of activation, it is concluded that Ag^{III} is not involved as an intermediate and that the essential redox step consists of the interaction of two molecules of $[Ag(bipy)(OH)]^+$ formed in the hydrolysis of $[Ag(bipy)]^{2+}(aq)$, which has been found to be the active bipy complex of Ag^{II} involved in the oxidation of substrate ligands added to aqueous solutions.

In the investigation of the kinetics of the oxidation of substrate ligands by transition-metal cations of high redox potential, a limit is often placed on the reactivity of the substrates which can be employed by the oxidation of the aqueous medium by the cation. In some cases the kinetics of this latter reaction have also been investigated, despite the difficulties encountered through the presence of irremovable traces of oxidisable impurities in aqueous media. Examples of such investigations involving aquacations are aquacobalt(III) ions[1] and aquasilver(II) ions[2] in aqueous perchlorate media and aquasilver(II) ions[2] in aqueous nitrate media. In both these cases complex kinetic equations were found to be obeyed, which necessarily involve some speculation concerning the mechanism of the oxidation.[1–3] In our recent kinetic investigations[4–7] of the oxidation reactions of silver(II) ions complexed by 2,2′-bipyridine (bipy), we found a limitation imposed on the reactivity of the substrate by the oxidation of water by the silver(II)–bipy complexes. As some preliminary observations have been recorded about the spectral changes involving these complexes in aqueous nitrate media in the absence of added substrate solutes,[8] we decided to investigate the kinetics of this reaction under the conditions where we have already investigated the equilibria between the silver(II)–bipy complexes[9] and the kinetics of the oxidation of added substrates,[4–7] to compare with the kinetics found[2] for the oxidation of water by silver(II) ions complexed by water molecules.

Experimental

The decay of $[Ag^{II}]$ was followed spectrophotometrically at 450 nm using the thermostatted cell compartment of a Unicam SP800 spectrophotometer with a Honeywell chart recorder or of a Unicam SP6-500 spectrophotometer with digital display. Initial concentrations of Ag^{II} of *ca.* 2×10^{-4} mol dm^{-3}, prepared as described previously,[4–7,9] were used with an excess of 2,2′-bipyridine over that required to complex the Ag^{II} of 4.0×10^{-3} mol dm^{-3}.[9] AnalaR nitric acid was used and silver(I) concentrations were added using AnalaR silver nitrate, the ionic strength was maintained at 1.00 mol dm^{-3} by adding AnalaR sodium nitrate. Water was distilled once in an all-glass still; subsequent purification is not very effective,[1] and experience suggested[1] that removal of trace impurities in an initial reaction with Ag^{2+} was a better procedure.

Results and Discussion

Order of Reaction in $[Ag^{II}]$ *and in* $[H^+]$.—The decay of $[Ag^{II}]$ was first examined in solutions at 25 °C containing varying concentrations of nitric acid, with the ionic strength adjusted to 1.00 mol dm^{-3} with added $NaNO_3$, without any added silver nitrate, and keeping the excess $[Hbipy^+] = 4 \times 10^{-3}$ mol dm^{-3}. One of the difficulties encountered in achieving high reproducibility of rate constants in such reactions is the possibility of the highly oxidising cation reacting with traces of impurities present in the solution or added to it with one of the salts.[1] In most of the cases with $[H^+] = 0.05$–1.00 mol dm^{-3} first-order plots of log (absorbance) against time produced curves, whereas plots of the reciprocal of the absorbance (D) against time were linear. Examples of the latter plots are shown in the Figure. Values for the observed second-order rate con-

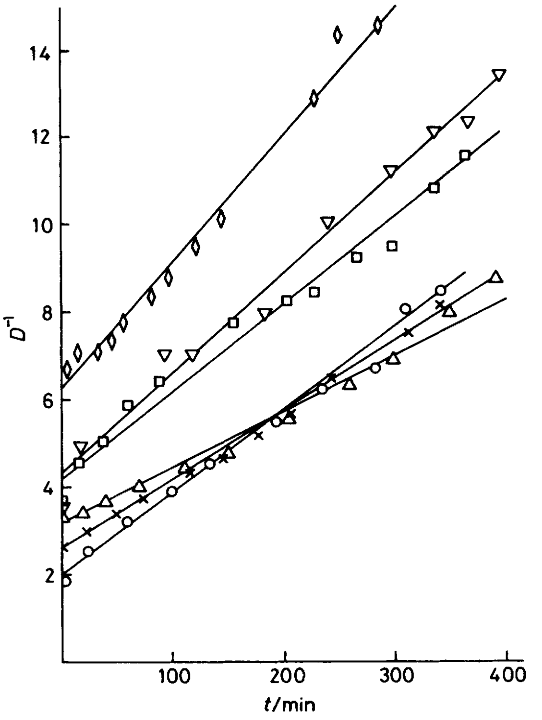

Figure. Plots of the reciprocal of the absorbance D against time at 25 °C for the decay of silver(II) complexed with bipy at a constant ionic strength of 1.00 mol dm^{-3}, a constant excess $[Hbipy^+]$ of 4.0×10^{-3} mol dm^{-3}, and no added Ag^I ions for $[HNO_3]$ 0.050 (◇), 0.100 (□), 0.200 (△), 0.500 (▽), 0.700 (×), and 1.00 mol dm^{-3} (○)

Table 1. Variation of the observed second-order rate constant with acidity at 25 °C, a constant ionic strength of 1.00 mol dm^{-3}, a constant excess [Hbipy$^+$] of 4.0 × 10^{-3} mol dm^{-3}, and no added Ag^I ions

[HNO$_3$]/mol dm^{-3}	10$^4k_0$/dm^3 mol^{-1} s^{-1}
0.05	2.37
0.05	1.39
0.05	1.40
0.10	0.37
0.10	1.69
0.10	1.43
0.20	1.01
0.50	1.87
0.50	1.69
0.70	2.29
0.70	1.29
1.00	1.87
1.00	1.54
1.00	1.59

Table 2. Variation of the observed second-order rate constant with acidity at 25 °C, a constant ionic strength of 1.00 mol dm^{-3}, a constant excess [Hbipy$^+$] of 4.0 × 10^{-3} mol dm^{-3}, and a constant [Ag^I] of 0.10 mol dm^{-3}

[HNO$_3$]/mol dm^{-3}	10$^4k_0$/dm^3 mol^{-1} s^{-1}
0.10	0.238
0.10	0.234
0.30	0.221
0.30	0.221
0.70	0.263
0.70	0.352
0.70	0.242
0.70	0.277
0.90	0.228

stant k_0, calculated from the slope and equation (1), are given

$$-\mathrm{d}[\mathrm{Ag^{II}}]/\mathrm{d}t = 2k_0[\mathrm{Ag^{II}}]^2 \qquad (1)$$

in Table 1. Given the possibility for interference from trace oxidisable impurities discussed above, Table 1 shows quite good agreement in the values of k_0 over the twenty-fold range of acidity. The mean value $k_0 = (1.6 \pm 0.5) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} suggests that k_0 is invariant with changing [H$^+$].

Similar linear plots for D^{-1} against time were obtained for the decay of [Ag^{II}] in aqueous nitric acid with an added constant concentration of silver(I) ions of 0.10 mol dm^{-3}, and with the ionic strength adjusted to 1.00 mol dm^{-3} with NaNO$_3$, compared with curves for the plots of log D against time. Values for k_0 taken from the slopes of the second-order plots are collected in Table 2: again good agreement is obtained in the [H$^+$] range 0.1—0.9 mol dm^{-3}. The mean, $k_0 = (0.25 \pm 0.04) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, over the nine-fold variation in [H$^+$] supports the invariance of k_0 with changing [H$^+$].

Variation of the Rate Constant with [Ag^I].—Comparison of the mean value of k_0 at 25 °C, without added Ag^I, with that for [Ag^I] = 0.10 mol dm^{-3} suggests that the added silver(I) ions have reduced the rate constant by *ca.* six fold. In view of the dependence of the rate constant found for the oxidation of water by aquasilver(II) ions[2] on added silver(I) ions, this has been investigated in detail at 25 °C by varying [Ag^I] at a constant acidity of 0.50 mol dm^{-3} HNO$_3$ whilst maintaining a constant ionic strength of 1.00 mol dm^{-3} using added NaNO$_3$. Linear plots for D^{-1} against time were found and the values of k_0 in Table 3 show that, despite some variation due to reaction with a trace impurity, there is a pronounced decrease in k_0 as the concentration of silver(I) ions increases. However, it is not possible to decide whether there is an accurate direct variation of k_0 with [Ag^I]$^{-1}$, such as found for the oxidation of water by aquasilver(II) ions, as the mean value of k_0[Ag^I] is $(0.026 \pm 0.016) \times 10^{-4}$ s^{-1} over the complete forty-fold range in [Ag^I] or $(0.029 \pm 0.015) \times 10^{-4}$ s^{-1} over the sixteen-fold range in [Ag^I] obtained by omitting the values of k_0 for [Ag^I] = 0.01 mol dm^{-3}. A plot of k_0 against [Ag^I]$^{-1}$ suggests, however, that there may be a tendency for k_0 towards a limiting value at high [Ag^I]$^{-1}$.

Table 3. Variation of the observed second-order rate constant with [Ag^I] at 25 °C, a constant ionic strength of 1.00 mol dm^{-3}, a constant excess [Hbipy$^+$] of 4.0 × 10^{-3} mol dm^{-3}, and a constant [HNO$_3$] of 0.50 mol dm^{-3}

[Ag^I]/mol dm^{-3}	10$^4k_0$/dm^3 mol^{-1} s^{-1}
0.010	0.89
0.010	0.71
0.025	0.61
0.025	1.29
0.040	0.41
0.040	0.45
0.050	0.54
0.050	0.46
0.100	0.28
0.100	0.36
0.100	0.28
0.400	0.17

Table 4. Variation of the observed second-order rate constant with temperature at a constant ionic strength of 1.00 mol dm^{-3}, a constant excess [Hbipy$^+$] of 4.0 × 10^{-3} mol dm^{-3}, a constant [HNO$_3$] of 0.50 mol dm^{-3}, and a constant [Ag^I] of 0.100 mol dm^{-3}

Temp./°C	10$^4k_0$/dm^3 mol^{-1} s^{-1}
30.0	0.78
30.0	0.88
35.0	1.19
35.0	0.90
40.0	1.72
40.0	1.56

Variation of Rate Constant with Temperature.—Values for k_0, for 0.50 mol dm^{-3} HNO$_3$ and for a constant [Ag^I] = 0.10 mol dm^{-3} at a constant ionic strength of 1.00 mol dm^{-3}, were determined from linear plots of D^{-1} against time at 30, 35, and 40 °C. These are given in Table 4 and also show the influence of impurity in the media, found in the values of k_0 given in Table 3, for the investigation of the variation of rate constant with [Ag^I] at an acidity of 0.50 mol dm^{-3}. A least-squares analysis using all the individual values of ln k_0 for all the k_0 values in Table 4, with varying values for the reciprocal of the absolute temperature and using $k_0 = 0.25 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} at [Ag^I] = 0.10 mol dm^{-3} and 25 °C, produces apparent overall values of $\Delta H^\ddagger = 83 \pm 15$ kJ mol^{-1} for the enthalpy of activation and $\Delta S^\ddagger = -55 \pm 50$ J K^{-1} mol^{-1} for the entropy of activation at 25 °C.

Mechanism of the Oxidation.—Although the degree of reproducibility expected in this type of oxidation, where a transition-metal cation of high redox potential oxidises the solvent medium, is less than that usually found for more rapid redox reactions between two dissolved species, it seems clear from the above that the oxidation of water by aquasilver(II) ions complexed with 2,2′-bipyridine is second order in [Ag^{II}] and zero order in [H$^+$], with an inverse dependence on [Ag^I]^x with $0 < x < 1$. In the oxidation of water by aquasilver(II) ions, Kirwin *et al.*[2a] found an order of two in $[Ag^{II}]$ with an inverse order of two in $[H^+]$ and an inverse order of unity in $[Ag^{I}]$: in addition, the rate constant varied with the concentration of perchlorate ions. These authors explained these orders in terms of a rapid pre-equilibrium, equation (2), producing silver(III)

$$Ag^{II}(aq) + Ag^{II}(aq) \rightleftharpoons Ag^{III}(aq) + Ag^{I}(aq) \quad (2)$$

and silver(I), followed by a rapid hydrolytic equilibrium involving $Ag^{III}(aq)$ as in equation (3), which accounted for the

$$Ag^{III}(H_2O) \overset{K_1}{\rightleftharpoons} AgO^+ + 2H^+ \quad (3)$$

inverse dependence of the observed rate constant on $[H^+]^2$ and on $[Ag^{I}]$. The rate-determining redox step was then the production of oxygen atoms as in equation (4) which dimerised to give molecular oxygen.

$$AgO^+ \longrightarrow Ag^+ + O^{\bullet} \quad (4)$$

A similar mechanism might operate here involving the production of Ag^{III} by the interaction of two species of $[Ag(bipy)]^{2+}$[9] as in equation (5), with or without the loss of

$$[Ag(bipy)]^{2+} + [Ag(bipy)]^{2+} \overset{K}{\rightleftharpoons} Ag^{III} + Ag^{I} \quad (5)$$

bipy from the silver cations, followed by steps similar to or identical with equations (3) and (4) above plus the dimerisation of $O^{\bullet}$ atoms. In addition, the rapid pre-equilibrium (6)[9] will be

$$[Ag(bipy)_2]^{2+} + H^+ \overset{K_h}{\rightleftharpoons} [Ag(bipy)]^{2+} + Hbipy^+ \quad (6)$$

involved, and the rate of decay of $[Ag^{II}]_T$ (subscript T indicates total concentration) will be given by equation (7), where $K_h' = K_h/[Hbipy^+]$ for equation (6) and $[Hbipy^+]$ is the standard

$$\frac{d[Ag^{II}]_T}{dt} = \frac{2k_1K_1K[Ag^{II}]_T{}^2}{[Ag^{I}][H^+]^2\{(K_h'[H^+])^{-1} + 1\}^2} \quad (7)$$

excess added concentration of bipy. If $\{(K_h'[H^+])^{-1} + 1\}^2 \sim (1/K_h'[H^+])^2$, the observed orders will be two for $[Ag^{II}]$, zero for $[H^+]$, and -1 for $[Ag^{I}]$. Against this mechanism is the observed inverse order in $[Ag^{I}]$ being $0 < x < 1$ and the unusual participation of Ag^{III} which is not found in the oxidation of inorganic and organic substrates by Ag^{II} complexed with bipy:[4-7] this latter argument has also been used against the participation of Ag^{III} in the oxidation of water by aquasilver(II) ions, as Ag^{III} is not usually involved in the oxidation of substrate ligands by $Ag^{II}(aq)$.[3] Moreover, with Ag^{III} involved in the rate-determining step, the high positive contribution ΔS_e to the entropy of activation arising from the loss of restricted water in the transition state for the two-electron step (4) should compensate the decrease in entropy ΔS_p arising from the loss of the protons with their subsequent solvation producing $\Delta S^{\ddagger} \geqslant 0$, which contrasts with the negative value found for $\Delta S^{\ddagger}$. Equilibrium (5) cannot involve two $[Ag(bipy)_2]^{2+}$ ions as this will not produce a zero kinetic order in $[H^+]$.

An alternative to the above might be the indiscriminate mutual interaction of $[Ag(bipy)_2]^{2+}$ and $[Ag(bipy)]^{2+}$ in an equilibrium of the type (2) or (5) with the equilibrium constant invariant with the amount of bipy complexed in the interacting ions, followed by a direct two-electron oxidation of a H_2O molecule in the co-ordination sphere of Ag^{III} to produce an $O^{\bullet}$ atom. Again, this would require an exact inverse dependence of one in $[Ag^{I}]$ and produce an overall $\Delta S^{\ddagger} \geqslant$ zero, contrary to observation.

An alternative to the above is the influence of Ag^{I} ions present in the walls of a solvent cage in which the redox process occurs, such as has been invoked[10] to explain the dependence of rate constant on $[Ag^{I}]$ found in the oxidation of secondary alcohols by $Ag^{II}(aq)$ ions[10,11] and by $[Ag(bipy)]^{2+}$.[5] Equilibrium (6) will now be followed by the hydrolysis [equation (8)] of $[Ag(bipy)]^{2+}$ ions. Two of the hydrolytic species will then interact long enough to produce two $OH^{\bullet}$ radicals and two Ag^{I} ions in a solvent cage in separate single-electron transfers, as in equation (9).

$$[Ag(bipy)]^{2+}(aq) \overset{K_2}{\rightleftharpoons} [Ag(bipy)(OH)]^+(aq) + H^+(aq) \quad (8)$$

$$\begin{aligned}
&[Ag(bipy)(OH)]^+ + [Ag(bipy)(OH)]^+ \underset{k'}{\overset{k}{\rightleftharpoons}} \\
&\quad \left\{\begin{matrix} Ag(bipy)(OH)^+ \\ Ag(bipy)(OH)^+ \end{matrix}\right\}_{cage} \rightleftharpoons \left\{\begin{matrix} Ag^+\text{-bipy,}OH^{\bullet} \\ Ag^+\text{-bipy,}OH^{\bullet} \end{matrix}\right\}_{cage} \\
&\qquad \xrightarrow[+2H^+]{k_p} 2Ag^+ + H_2O_2 + 2Hbipy^+ \quad (9)
\end{aligned}$$

The two $OH^{\bullet}$ radicals can dimerise and diffuse out of the cage as H_2O_2, which, in turn, is oxidised as in equation (10) by more

$$2Ag^{II} + H_2O_2 \longrightarrow 2Ag^{I} + 2H^+ + O_2 \quad (10)$$

Ag^{II},[12] which is known to be very rapid.[12] As the Ag^{I} ions in equation (9) can either diffuse out of the cage or induce the back reaction, the contents of the cage will be very sensitive to the presence of Ag^{I} ions in the walls of the cage and thereby with Ag^{I} present in the bulk of the solution. Variations in the concentration of the latter will therefore have considerable influence on the back reaction and the ability of Ag^{I} to diffuse out of the cage into the bulk solution. Applying the stationary-state condition to the contents of the cage, the rate of decay of Ag^{II} will be given by equation (11). A reaction second order in

$$\frac{d[Ag^{II}]_T}{dt} = \frac{4k_pkK_2{}^2[Ag^{II}]_T{}^2}{(k'[Ag^{I}]^x + k_p)\{(K_h'[H^+])^{-1} + 1 + K_2[H^+]^{-1}\}^2[H^+]^2} \quad (11)$$

$[Ag^{II}]$ is predicted with an inverse dependence on $[Ag^{I}]$ if $k_p \ll k'[Ag^{I}]^x$, as found experimentally with $0 < x < 1$. It is likely that $K_2[H^+]^{-1} \ll \{1 + (K_h'[H^+])^{-1}\}$, and, as a plot of $\{(K_h'(H^+])^{-1}\}^2$ against $\{1 + (K_h'[H^+])^{-1}\}^2$ is linear with a slope of 1.08 ± 0.01, using the available data[9] for K_h', equation (11) predicts that k_0 will be independent of $[H^+]$, as found experimentally.

This latter mechanism agrees with all the experimental kinetic orders. Moreover, as it avoids the simultaneous two-electron step which could lead to a high positive ΔS_e for the high loss of restricted water in the process $Ag^{III} \longrightarrow Ag^{I}$ rather than the more diffuse loss obtained with two separate processes $Ag^{II} \longrightarrow Ag^{I}$ with possibly only the first being rate determining, it is in accord with the overall $\Delta S^{\ddagger}$ being found negative, arising from the negative ΔS_p for equation (8). This mechanism is also in accord with the known[4-7] greater oxidative reactivity of $[Ag(bipy)]^{2+}$ compared with $[Ag(bipy)_2]^{2+}$, with the former having the higher redox potential.[9] It should be noted that, if $[Ag(bipy)_2]^{2+}$ is the active species, producing $[Ag(bipy)_2(OH)]^+$ which then operates in an analogous mechanism to that proposed above for $[Ag(bipy)]^{2+}$, the rate of decay of $[Ag^{II}]$ will vary markedly in an inverse manner with changing $[H^+]$. The mechanism proposed, equations (6) and (8)—(10), involving $[Ag(bipy)]^{2+}$ and $[Ag(bipy)(OH)]^+$ is also in accord with the absence[4–7] of any involvement of $\mathrm{Ag^{III}}$ found in the oxidation of substrate ligands by bipy complexes of $\mathrm{Ag^{II}}$. In simplified form, omitting any complexing effects of anions, a similar mechanism [equations (12) and (13)] has been suggested[3] for the oxidation of water by $\mathrm{Ag^{2+}(aq)}$, to explain the inverse second and first orders in $[\mathrm{H^+}]$ and in $[\mathrm{Ag^I}]$ respectively and to avoid any involvement of $\mathrm{Ag^{III}(aq)}$ which does not participate[3] in the oxidation of substrate ligands by $\mathrm{Ag^{2+}}$. As the oxidations of pinacol[6] and 2-hydroxy-2-methylpropanoic acid[7] by $\mathrm{Ag^{II}}$ ions complexed with bipy are known to involve single electron-transfer steps involving the substrate and $\mathrm{Ag^{2+}}$ after all the bipy has been stripped off the latter, reactions (12) and (13) are possible steps in the oxidation of water by the $\mathrm{Ag^{II}}$–bipy complexes after removal of the remaining bipy in (14). However, a detailed consideration of reactions (6), (14), (12), and (13) followed by a very rapid (10) predicts that k_0 for the decay of $[\mathrm{Ag^{II}}]$ will depend on $[\mathrm{H^+}]$, contrary to observation.

$$\mathrm{Ag^{2+}(aq)} \overset{\text{rapid}}{\rightleftharpoons} \mathrm{Ag(OH)^+(aq)} + \mathrm{H^+(aq)} \qquad (12)$$

$$\mathrm{Ag(OH)^+(aq)} + \mathrm{Ag(OH)^+(aq)} \rightleftharpoons \left\{\begin{matrix}\mathrm{Ag(OH)^+}\\ \mathrm{Ag(OH)^+}\end{matrix}\right\}_{\text{cage}} \rightleftharpoons \left\{\begin{matrix}\mathrm{Ag^+,OH^\bullet}\\ \mathrm{Ag^+,OH^\bullet}\end{matrix}\right\}_{\text{cage}} \longrightarrow 2\mathrm{Ag^I(aq)} + \mathrm{H_2O_2} \qquad (13)$$

$$[\mathrm{Ag(bipy)}]^{2+} + \mathrm{H^+(aq)} \rightleftharpoons \mathrm{Ag^{2+}(aq)} + \mathrm{Hbipy^+} \qquad (14)$$

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