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Kinetics of the Oxidation of 2-Hydroxy-2-methylpropanoic Acid by Silver(II) Ions Complexed with 2,2′-Bipyridine in Aqueous Nitrate Media

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Stopped-flow traces show that the oxidation of 2-hydroxy-2-methylpropanoic acid (hmpa) by $[Ag(bipy)_2]^{2+}$ proceeds in two consecutive reactions. Both are found to be first order in $[Ag^{II}]$ and first order in [hmpa]. The first rapid reaction is ascribed to complex formation between Ag^{II} and hmpa and the second to a slower redox step. A mechanism is proposed to account for the observed orders in $[Ag^{II}]$, [hmpa] and $[H^+]$ for each reaction and values for the enthalpies and entropies of activation are determined. To investigate the effect on the redox kinetics of oxidatively inert species close to the cation, these are compared with the transition-state parameters for the oxidation of hmpa by aqua-metal cations and for the oxidation of other substrates by metal cations complexed with 2,2′-bipyridine.

Following our spectrophotometric examination[1] of the complexed species of Ag^{II} which exist in aqueous nitric acid containing 2,2′-bipyridine, we have investigated the kinetics of the oxidation of hydrogen peroxide,[2] propan-2-ol[3] and pinacol[4] by such complexed Ag^{II} ions. With the latter two substrates, the kinetics of the oxidation show[3,4] that intermediate complexes with the substrate ligand are involved, but with hydrogen peroxide such intermediate complexes were not detected in the oxidation.[2] Intermediate cation–substrate complexes have been detected in the oxidation of 2-hydroxy-2-methylpropanoic acid (hmpa) by aqua-cations such as Mn^{3+}_{aq},[5] Ce_{aq}[6] and V^{V}_{aq},[7] and the importance of chelation in determining the rate of oxidation has been discussed.[5] We wish, therefore, to compare Ag^{II} complexed with 2,2′-bipyridine with these aqua-cations in the reaction with hmpa. Some kinetic work has also been recorded for the oxidation of iminodiacetic acid and *N*-methyliminodiacetic acid by these complexes involving Ag^{II} and 2,2′-bipyridine.[8]

EXPERIMENTAL

MATERIALS

The $[Ag(bipy)_2]^{2+}$ ion was prepared in aqueous nitric acid by the anodic oxidation of Ag^{I} under nitrogen with sufficient 2,2′-bipyridine added to provide an excess of 4.0×10^{-3} mol dm^{-3} after complexing of the Ag^{II} with two 2,2′-bipyridine molecules.[1-4] 2-Hydroxyl-2-methylpropanoic acid was recrystallized from benzene and dried under vacuum: solutions in water were prepared by weight. All other materials were as described previously.[1-4, 9]

PROCEDURES

Concentrations of the species of Ag^{II} complexed with 2,2′-bipyridine were determined spectrophotometrically using the recorded variation of extinction coefficient with acidity.[1] The product of the oxidation, acetone, was removed by high-vacuum distillation in a closed system with the reaction mixture first neutralized by adding KOH:[3-5,7] the concentration of acetone in the distillate was determined spectrophotometrically as the anion of the 2,4-dinitrophenylhydrazone.[9]

Rates were followed spectrophotometrically at 450 nm using the thermostatted cell compartment of the Unicam SP800 spectrophotometer with a Honeywell chart recorder or of a Unicam SP6-500 with digital display or a Durrum-Gibson stopped-flow spectrophotometer coupled with a Tektronix oscilloscope with a storage screen. The excess 2,2′-bipyridine over $[Ag(bipy)_2]^{2+}$ was always maintained at 4.0×10^{-3}, as in previous investigations involving this complex.[1-4]

RESULTS AND DISCUSSION

STOICHIOMETRY OF THE OXIDATION

Owing to the low rate of the oxidation when $[Ag^{II}] \approx [hmpa] \approx 10^{-4}$ mol dm^{-3}, it is only possible to determine values for $|\Delta[Ag^{II}]|/|\Delta[acetone]|$ with $[hmpa] \gg [Ag^{II}] \approx 10^{-4}$ mol dm^{-3}. The acetone, distilled off such mixtures after neutralizing the nitric acid with KOH, was determined spectrophotometrically and the values for $|\Delta[Ag^{II}]|/|\Delta[acetone]|$ are given in table 1 for initial $[Ag^{II}] \approx 2.5 \times 10^{-4}$ mol dm^{-3}. Table 1 shows that this ratio is not influenced by the presence or absence of molecular oxygen in the reaction mixture. The mean value of $|\Delta[Ag^{II}]|/|\Delta[acetone]|$ is 1.92 ± 0.16 under conditions where the loss of $[Ag^{II}]$ due to reaction with water and acetone is $< 1\%$ of the observed decrease. The stoichiometry is represented by

$$2Ag^{II} + (CH_3)_2COHCOOH \rightarrow 2Ag^{I} + (CH_3)_2CO + H^+_{aq} + CO_2. \qquad (1)$$

VARIATION OF RATE WITH [hmpa] AND [H$^+$] AT 25 °C

The result of the stopped-flow experiment in fig. 1 shows that the decrease of $[Ag^{II}]$ for the reaction of *ca.* 2×10^{-4} mol dm^{-3} of $[Ag(bipy)_2]^{2+}$ with excess $[bipy] = 4.00 \times 10^{-3}$ mol dm^{-3} with ionic strength adjusted to 1.00 mol dm^{-3} by the addition of $NaNO_3$ proceeds through two consecutive reactions. The decrease in optical density at 450 nm was followed on the stopped-flow spectrophotometer over a long period by repeated manual triggering at one minute intervals after the start of the reaction and shows a rapid decrease followed by a much slower decrease. The slower decrease is first order in $[Ag^{II}]$ and the slope of the log plot agrees well (fig. 1) with the slope of a similar plot for the same reaction determined using a conventional spectrophotometer.

Values of the first-order rate constants for the slow decay were determined from linear log plots using conventional spectrophotometry for [hmpa] in the range $(3.0\text{–}15.0) \times 10^{-3}$ mol dm^{-3} for acid concentrations ranging from 0.1 to 1.0 mol dm^{-3}. At any particular acid concentration it was found that the first-order rate constant varied linearly with [hmpa], passing through the origin, as shown in fig. 2. Values for the second-order rate constant k determined from the slopes using the least-squares procedure are given in table 2. It was shown that the first-order rate constant is unaffected by replacing molecular oxygen in the mixture by molecular nitrogen, replacing the added $NaNO_3$ by $LiNO_3$ to maintain the ionic strength at 1.00 mol dm^{-3} or replacing the added $NaNO_3$ partially with added $AgNO_3$, for the same [hmpa] and $[H^+]$.

With initial $[hmpa] \approx 25.0 \times 10$ mol dm^{-3} the fast initial reaction accounts for all the loss of optical density at 450 nm and this decrease can be followed using stopped-flow spectrophotometry. Linear log plots were always found and fig. 3 shows that the first-order rate constant varies linearly with [hmpa] with the plot passing

Table 1. Values of $|\Delta[Ag^{II}]|/|\Delta[\text{acetone}]|$ at various $[HClO_4]$ for an ionic strength of 1.0 mol dm^{-3} at 20 °C

$[HClO_4]$ /mol dm^{-3}	[hmpa] /mol dm^{-3}	initial $[Ag^{II}]$ /10^{-4} mol dm^{-3}	$\frac{|\Delta[Ag^{II}]|}{|\Delta[\text{acetone}]|}$
0.10	0.05	2.20	2.06
0.10	0.10	2.58	2.03[a]
1.00	0.05	2.50	1.89
1.00	0.05	2.50	1.80[a]
1.00	0.10	2.50	1.84

[a] Under nitrogen.

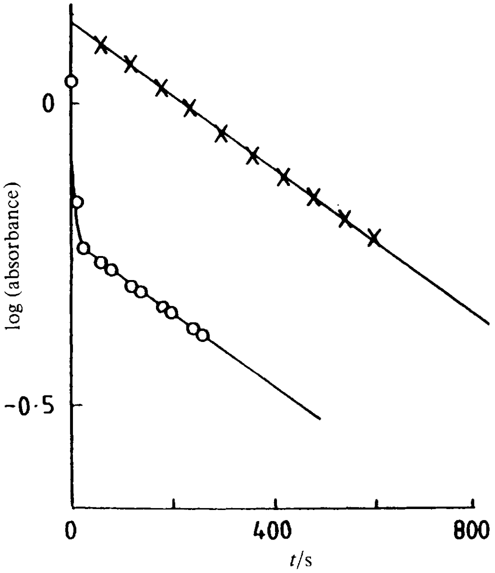


Fig. 1. Comparison of the decrease in absorbance at 450 nm for the reaction of 2×10^{-4} mol dm^{-3} $Ag(bipy)_2^{2+}$ with 5×10^{-3} mol dm^{-3} hmpa at an ionic strength of 1.0 mol dm^{-3}, $[H^+] = 0.20$ mol dm^{-3} and with excess $[bipyH^+] = 4 \times 10^{-3}$ mol dm^{-3} at 25 °C using conventional spectrophotometry (×) and stopped-flow spectrophotometry (○).

through the origin. Values for the second-order rate constants k' determined from the slopes using the least-squares method with [hmpa] in the range 0.05–0.20 mol dm^{-3} at each acidity, except for $[H^+] = 0.1$ mol dm^{-3} where the range was 0.025–0.20 mol dm^{-3}, are given in table 3.

VARIATION OF RATE CONSTANTS WITH TEMPERATURE

The reaction was also found to take place in two stages at other temperatures. The slow step could be followed at 11.5, 19.4 and 30.0 °C and the reaction was found to be first order in $[Ag^{II}]$ and first order in [hmpa] at constant acidity. Values for the second-order rate constant k calculated from the slopes of the plots of the pseudo-

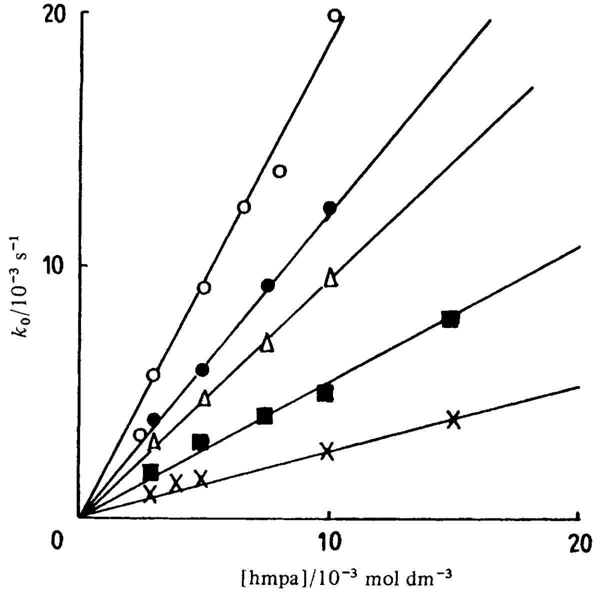


Fig. 2. Plot of the pseudo-first-order rate constant k_0 against [hmpa] for the slow oxidation of hmpa by Ag^{II}bipy complexes at an ionic strength of 1.00 mol dm^{-3} and with excess [bipyH$^+$] = 4.0 × 10^{-3} mol dm^{-3} at 25 °C using the following [H$^+$] (mol dm^{-3}): ×, 0.10; ■, 0.30; △, 0.50; ●, 0.80; ○, 1.00.

Table 2. Values of the second-order rate constant k and a derived function for the redox step at an ionic strength of 1.00 mol dm^{-3} with excess [bipyH$^+$] = 4.00 × 10^{-3} mol dm^{-3}

T/°C	[H$^+$] /mol dm^{-3}	k /dm^3 mol^{-1} s^{-1}	$k(1+K_c h)(1+K'_h h)$ /dm^3 mol^{-1} s^{-1}
11.5	0.100	0.039±0.001	0.042±0.001
11.5	0.300	0.120±0.014	0.148±0.017
11.5	0.500	0.167±0.008	0.233±0.011
11.5	0.800	0.255±0.028	0.42±0.05
11.5	1.00	0.256±0.027	0.47±0.05
19.4	0.100	0.116±0.001	0.126±0.001
19.4	0.300	0.237±0.006	0.299±0.008
19.4	0.500	0.369±0.008	0.53±0.01
19.4	0.800	0.40±0.01	0.70±0.02
19.4	1.00	0.56±0.02	1.07±0.03
25.0	0.100	0.248±0.010	0.271±0.011
25.0	0.300	0.49±0.03	0.63±0.04
25.0	0.500	0.95±0.03	1.40±0.04
25.0	0.800	1.24±0.05	2.25±0.09
25.0	1.00	2.06±0.14	4.12±0.28
30.0	0.100	0.48±0.01	0.53±0.01
30.0	0.300	0.98±0.05	1.27±0.07
30.0	0.500	1.43±0.13	2.16±0.20
30.0	0.800	2.55±0.11	4.7±02
30.0	1.00	3.01±0.04	6.2±0.08

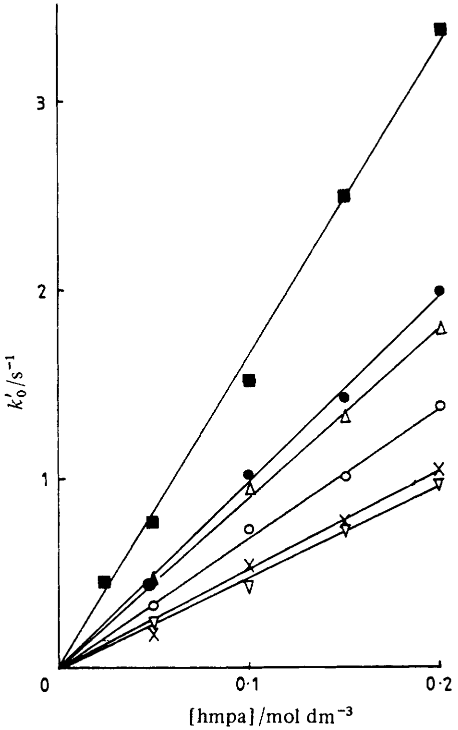


Fig. 3. Plot of the psuedo-first-order rate constant k'_0 against [hmpa] for the rapid initial reaction between hmpa and Ag^{II}bipy complexes at an ionic strength of 1.00 mol dm^{-3} and with excess [bipyH$^+$] = 4.0×10^{-3} mol dm^{-3} at 25 °C using the following [H$^+$] (mol dm^{-3}): ■, 0.10; ●, 0.20; △, 3.30; ○, 0.50; ×, 0.80; ▽, 1.00.

Table 3. Values of the second-order rate constant k' and a derived function for the rapid initial reaction at an ionic strength of 1.00 mol dm^{-3} with excess [bipyH$^+$] = 4.00×10^{-3} mol dm^{-3}

T/°C	H$^+$ /mol dm^{-3}	k' /dm^3 mol^{-1} s^{-1}	$k'(1+K_c h)(1+K'_h h)$ /dm^3 mol^{-1} s^{-1}
25.0	0.100	17.0±0.6	18.6±0.7
25.0	0.200	10.1±0.5	12.0±0.6
25.0	0.300	8.9±0.3	11.4±0.4
25.0	0.500	7.0±0.3	10.4±0.4
25.0	0.800	5.2±0.4	9.3±0.7
25.0	1.00	5.2±0.2	10.4±0.4
10.6	0.100	3.2±0.1	3.4±0.1
10.6	0.300	1.8±0.1	2.2±0.1
10.6	0.500	1.7±0.1	2.4±0.1
10.6	1.00	1.2±0.2	2.2±0.4
38.0	0.100	73±13	82±15
38.0	0.300	35.5±1.9	48.3±2.6
38.0	0.500	23.2±2.3	37.4±3.7
38.0	1.00	23.0±0.3	52.4±0.7

first-order rate constant against [hmpa] using the least-squares procedure are collected in table 2.

The initial rapid stage was followed at 10.6 and 38.0 °C using the stopped-flow technique. Linear log plots were always found and the pseudo-first-order rate constant varied directly with [hmpa] passing through the origin at constant acidity. Table 3 contains values for the second-order rate constant calculated using the least-squares procedure.

MECHANISM OF THE RAPID INITIAL REACTION

It appears likely that the rapid fall in optical density observed when mixing the reactants, as illustrated in fig. 1, can be ascribed to the formation of a complex between $\mathrm{Ag^{II}}$ and hmpa in a similar manner to the intermediate complex found in the oxidation of hmpa by $\mathrm{Mn^{III}_{aq}}$,[5] $\mathrm{Ce^{IV}_{aq}}$[6] and $\mathrm{V^{V}_{aq}}$.[10] The following processes may be involved:

$$\mathrm{Ag(bipy)_2^{2+} + H^+ \overset{K_h}{\rightleftharpoons} Ag(bipy)^{2+} + bipy\,H^+} \tag{2}$$

$$\mathrm{hmpa + H^+ \overset{K_c}{\rightleftharpoons} hmpa\,H^+} \tag{3}$$

$$\mathrm{Ag(bipy)_2^{2+} + hmpa \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} Ag(bipy)_2^{2+}\,hmpa} \tag{4}$$

$$\mathrm{Ag(bipy)_2^{2+} + hmpa \underset{k_{2b}}{\overset{k_{2f}}{\rightleftharpoons}} Ag(bipy)^{2+}\,hmpa + bipy} \tag{5}$$

$$\mathrm{Ag(bipy)^{2+} + hmpa \underset{k_{3b}}{\overset{k_{3f}}{\rightleftharpoons}} Ag(bipy)^{2+}\,hmpa} \tag{6}$$

$$\mathrm{Ag(bipy)^{2+} + hmpa \underset{k_{4b}}{\overset{k_{4f}}{\rightleftharpoons}} Ag^{2+}\,hmpa + bipy.} \tag{7}$$

If it is assumed that the proton transfer equilibria reactions (2) and (3) are very rapid compared with reactions (4)–(7), and if one can neglect the back reaction in our conditions because either $k_{1b} \ll k_{1f}$, $k_{2b} \ll k_{2f}$, $k_{3b} \ll k_{3f}$ and $k_{4b} \ll k_{4f}$ or the concentration of the complexes containing hmpa is kept low by removal in the subsequent redox step, the rate of change in the optical density is given by

$$\text{rate} = \frac{[k_{1f}+k_{2f}+(k_{3f}+k_{4f})\,h]\,[\mathrm{Ag^{II}}]_T\,[\mathrm{hmpa}]_T}{(1+K_h'\,h)\,(1+K_c\,h)} \tag{8}$$

where $h = [\mathrm{HClO_4}]_T$, the subscript T indicates the total concentration of that species, $K_h' = K_h/[\mathrm{bipyH^+}]$ and it is assumed that the contributions of $\mathrm{Ag^{II}}$ complexed with hmpa to $[\mathrm{Ag^{II}}]_T$ are small. Eqn (8) complies with the observed first order in each of $[\mathrm{Ag^{II}}]_T$ and $[\mathrm{hmpa}]_T$, and equating the observed second-order rate constant k with the complex term involving rate and equilibrium constants in eqn (8) gives

$$k'(1+K_h'\,h)\,(1+K_c\,h) = k_{1f}+k_{2f}+(k_{3f}+k_{4f})\,h. \tag{9}$$

Table 3 shows that values for the left-hand side of eqn (9) calculated using the experimental values for k' and K_h'[1] together with[5] $K_2 = 0.1\ \mathrm{dm^3\ mol^{-1}}$ are approximately constant at each temperature in the range $[\mathrm{H^+}]_T = 0.2$–$1.0\ \mathrm{mol\ dm^{-3}}$. This suggests that k_{3f} and k_{4f} contribute little to eqn (9) in this range of acidities. Although these results do not permit one to distinguish between k_{1f} and k_{2f} in eqn (9), where intermediate complexes have been detected[3,4] for other substrates X oxidized by $\mathrm{Ag(bipy)_2^{2+}}$, the dominant intermediate species is $\mathrm{Ag(bipy)X^{2+}}$, suggesting that reaction

(5) may dominate here. A plot of the logarithm of the mean value of the left-hand side of eqn (9) in the range $[H^+]_T = 0.2\text{–}1.0$ mol dm^{-3} against the reciprocal of the absolute temperature gives a straight line, and application of the least-squares procedure gives $\Delta H^* = 78 \pm 3$ kJ mol^{-1} and $\Delta S^* = 34 \pm 11$ J K^{-1} mol^{-1}.

The rise in the value of the left-hand side of eqn (9) at $[H^+] = 0.1$ mol dm^{-3} is the reverse of the change expected if k_{3f} and k_{4f} become significant. It is more likely that this rise at low $[H^+]_T$ is due to the participation of anionic forms of hmpa, which has an acid dissociation constant $K_a \approx 1 \times 10^{-4}$ mol dm^{-3} in this temperature range.[11]

MECHANISM OF THE REDOX REACTION

Following our investigation of the kinetics of the oxidation of pinacol[4] by Ag(bipy)$_2^{2+}$, it is necessary to include all possibilities of Ag^{II} complexed with 2,2′-bipyridine and hmpa as being capable of being involved in the mechanism in the following rate-determining steps:

$$\mathrm{Ag(bipy)^{2+}hmpa} \xrightarrow{k_1} \mathrm{Ag^I + bipy\,H + radical} \tag{10}$$

$$\mathrm{Ag(bipy)^{2+}hmpa^-} \xrightarrow{k_2} \mathrm{Ag^I + bipy + radical} \tag{11}$$

$$\mathrm{Ag^{2+}hmpa} \xrightarrow{k_3} \mathrm{Ag^I + radical + H^+} \tag{12}$$

$$\mathrm{Ag^{2+}hmpa^-} \xrightarrow{k_4} \mathrm{Ag^I + radical} \tag{13}$$

$$\mathrm{Ag(bipy)_2^{2+}hmpa} \xrightarrow{k_1'} \mathrm{Ag^I + bipy\,H^+ + radical + bipy} \tag{14}$$

$$\mathrm{Ag(bipy)_2^{2+}hmpa^-} \xrightarrow{k_2'} \mathrm{Ag^I + 2bipy + radical} \tag{15}$$

with unprotonated 2,2-bipyridine being rapidly protonated in these acidic solutions. The rate-determining reactions (10)–(15) will be preceded by the following rapidly established equilibria:

$$\mathrm{Ag(bipy)^{2+} + hmpa} \overset{\beta}{\rightleftharpoons} \mathrm{Ag(bipy)^{2+}hmpa} \tag{16}$$

$$\mathrm{Ag(bipy)_2^{2+} + hmpa} \overset{\beta'}{\rightleftharpoons} \mathrm{Ag(bipy)_2^{2+}hmpa} \tag{17}$$

$$\mathrm{Ag(bipy)^{2+}hmpa} \overset{K_1}{\rightleftharpoons} \mathrm{Ag(bipy)^{2+}hmpa^- + H^+} \tag{18}$$

$$\mathrm{Ag(bipy)^{2+}hmpa + H^+} \overset{K_2}{\rightleftharpoons} \mathrm{Ag^{2+}hmpa + bipyH^+} \tag{19}$$

$$\mathrm{Ag^{2+}hmpa} \overset{K_3}{\rightleftharpoons} \mathrm{Ag^{2+}hmpa^- + H^+} \tag{20}$$

$$\mathrm{Ag(bipy)_2^{2+}hmpa} \overset{K_1'}{\rightleftharpoons} \mathrm{Ag(bipy)_2hmpa^- + H^+} \tag{21}$$

$$\mathrm{Ag(bipy)_2^{2+}hmpa + H^+} \overset{K_2'}{\rightleftharpoons} \mathrm{Ag(bipy)^{2+}hmpa + bipyH^+}. \tag{22}$$

The radical formed in the rate-determining steps will react very rapidly with more Ag^{II} species to produce Ag^{I} and to produce acetone.[5, 6, 10] The rate of loss of Ag^{II} will then be given by

$$\frac{[2\beta K'_h(k_1 h+k_2 K_1+k_3 K_2 h^2+k_4 K_2 K_3 h)+2\beta'(k'_1+k'_2 K'_1 h^{-1})][Ag^{II}]_T[hmpa]_T}{(1+K'_h h)(1+K_c h)+[hmpa]_T[\beta K'_h(h+K_1+K_2 h^2+K_2 K_3 h)+\beta'(1+K'_1 h^{-1})]}. \quad (23)$$

If the second term in the denominator is much smaller than the first, the observed second-order rate constant is given by

$$k(1+K'_h h)(1+K_c h)=2\beta K'_h(k_1 h+k_2 K_1+k_3 K_2 h^2 +k_4 K_2 K_3 h)+2\beta'(k'_1+k'_2 K'_1 h^{-1}). \quad (24)$$

Fig. 4 shows that plots of the left-hand side of eqn (24) using the experimental values of k and K'_h [1] with $K_c = 0.1$ dm^3 mol^{-1} [5] against h^2 are linear with intercepts on the ordinate. Eqn (24) suggests that the slopes of these plots are $2\beta K'_h k_3 K_2$ with intercepts of $2\beta k_2 K'_h K_1+2\beta' k'_1$.

Note that to produce the term in eqn (24) in h^2 it is essential to include the possibility that $Ag(bipy)_2^{2+}$ and $Ag(bipy)^{2+}$ arising in reaction (2) are both involved in rapid pre-equilibria with hmpa. If only $Ag(bipy)_2^{2+}$ is involved in such a pre-equilibrium, as suggested might be the case from the analysis of the kinetics of the rapid initial change in optical density, by combining the equilibrium

$$Ag(bipy)_2^{2+}+hmpa \overset{\beta''}{\rightarrow} Ag(bipy)^{2+}hmpa+bipy \quad (25)$$

with equilibria reactions (17)–(21), the equation analogous to eqn (24) is

$$k(1+K'_h h)(1+K_c h) = 2\beta''(k_1+k_2 K_1 h^{-1}+k_3 K_2 h+k_4 K_2 K_3)+2\beta'(k'_1+k'_2 K'_1 h^{-1}) \quad (26)$$

and it is not possible to explain the observed linear variation of the left-hand side with h^2. We must therefore conclude that, although the equilibrium constants for equilibria involving $Ag(bipy)^{2+}$ and hmpa are too low in magnitude to show experimentally in eqn (9), they do, nevertheless, operate as pathways towards the redox steps.

The values of $\beta k_3 K_2$ derived from the slopes of fig. 4 are collected in table 4. A plot of $\log \beta K_2 k_3$ against the reciprocal of the absolute temperature is linear and the overall values for ΔH^* and ΔS^* obtained using the least-squares procedure are given in table5. A plot of the logarithm of the intercepts of fig. 4 against the reciprocal of absolute temperature is also linear, suggesting strongly that only one of the terms in $2\beta k_2 K'_h K_1+2\beta' k'_1$ is significant. As in the oxidations of other substrates by $Ag(bipy)_2^{2+}$, $Ag(bipy)^{2+}$ is the bipyridine–silver (II) complex which is oxidatively active and not $Ag(bipy)_2^{2+}$; it is assumed, by analogy, that $\beta' k'_1 \ll \beta k_2 K'_h K_1$, and values for $\beta K_1 k_2$ are also included in table 4. The overall values of ΔH^* and ΔS^* derived from the application of the least-squares procedure to the linear plot of $\log \beta K_1 k_2$ against the reciprocal of absolute temperature are given in table 5.

COMPARISON WITH OTHER CATION+SUBSTRATE REDOX SYSTEMS

INFLUENCE OF OXIDATIVELY INERT SPECIES ADJACENT TO THE CATION

The overall values of ΔH^* and ΔS^* for the oxidation of hmpa by $Ag(bipy)_2^{2+}$ are compared in table 5 with ΔH^* and ΔS^* for the oxidations of hmpa by other metal ions and with those for the oxidation of other organic substrates by $Ag(bipy)_2^{2+}$: the reactions are represented in table 5 by the intermediate complex involved. Initial inspection shows that for a variation in E_0 of between 1 and 2 V for the cations,

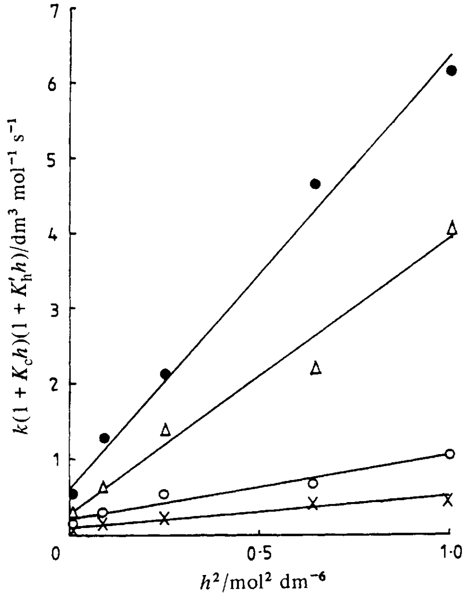


Fig. 4. Plot of the left-hand side of eqn (24) against h^2 for the slow oxidative step between hmpa and Ag^{II}bipy complexes at an ionic strength of 1.00 mol dm^{-3} and with excess [bipyH$^+$] = 4.0 × 10^{-3} mol dm^{-3} at the following temperatures (°C): ×, 11.5; ○, 19.4; △, 25.0; ●, 30.0.

Table 4. Values of $k_3\beta K_2$ and $k_2\beta K_1$ for the oxidation of hmpa by Ag(bipy)$^{2+}$ and Ag$^{2+}_{aq}$ at an ionic strength of 1.00 mol dm^{-3} with excess [bipyH$^+$] = 4.00 × 10^{-3} mol dm^{-3}

T/°C	$k_3\beta K_2$ /dm^6 mol^{-2} s^{-1}	$k_2\beta K_1$/s^{-1}
11.5	0.32 ± 0.05	0.073 ± 0.029
19.4	0.58 ± 0.07	0.135 ± 0.039
25.0	2.23 ± 0.21	0.170 ± 0.113
30.0	3.27 ± 0.18	0.386 ± 0.097

although the values of ΔH^* for any species of 2-hydroxy-2-methylpropanoic acid range only between 58 and 95 kJ mol^{-1}, the values of ΔS^* vary from −64 to +81 J K^{-1} mol^{-1}, but, for the oxidation of un-ionized hmpa, ΔH^* ranges only between 78 and 95 kJ mol^{-1} whilst ΔS^* still varies between −52 and +81 J K^{-1} mol^{-1}. To explain this wide range of ΔS^* values it is necessary to look at the variation of ΔS^* involving two extreme cases: the oxidations of substrate by Ni(bipy)$_3^{3+}$, where little disturbance of the coordination sphere round Ni^{3+} occurs, and oxidations by Ce$^{4+}_{aq}$, where there is considerable disturbance of the coordination sphere around Ce^{4+}.

For oxidations by Ni(bipy)$_3^{3+}$ there are two major contributions to ΔS^* arising from configurational changes in the solvent: first, ΔS^*_e has positive values because of water oriented around Ni(bipy)$_3^{3+}$ being released to the bulk solvent on the change $3+ \rightarrow 2+$ in the transition state; secondly, ΔS^*_p is negative because of restrictions imposed on

Table 5. Comparison of overall values of ΔH^* and ΔS^* for the oxidation of hmpa by Ag(bipy)$^{2+}$ and Ag$^{2+}_{aq}$ with those for the oxidation of other organic ligands by the same ions and with those for the oxidation of hmpa by other aqua-cations

intermediate complex	ΔH^*_{ov} /kJ mol^{-1}	ΔS^*_{ov} /J K^{-1} mol^{-1}	ref.
Ag(bipy)$^{2+}$hmpa$^-$	58 ± 6	-64 ± 39	this work
Ag^{2+}hmpa	95 ± 8	32 ± 56	this work
Ag(bipy)$^{2+}$pin	49.5 ± 0.7	81 ± 5	4
Ag^{2+}pin	45.3 ± 3.3	18 ± 12	4
Ag(bipy)$^{2+}$Pr^{i}OH	88 ± 5	13 ± 15	3
Mn^{3+}hmpa	93	81	5
VO$_2^+$hmpa	78 ± 5	-41 ± 15	10
V(OH$_2^{3+}$)hmpa	82 ± 7	-52 ± 20	10
Ce^{4+}hmpa$^-$	64	22	6

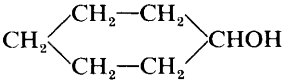
solvent molecules if a proton is released to the solvent. Thus for the oxidations of the uni-negative ions Br$^-$ and N$_3^-$ by Ni(bipy)$_3^{3+}$, where contributions to ΔS^* other than ΔS_e^* are likely to be similar, ΔS^* is *ca.* 0,[12, 13] but for H$_2$O$_2$, where a proton is released to the solvent in the transition state and a negative ΔS_p^* is also involved, ΔS^* has a large negative value.[14]

In contrast to oxidations by Ni(bipy)$_3^{3+}$, oxidations with Ce$^{4+}_{aq}$ involve considerable movement of the molecules contiguous with the metal ion, in this case water molecules; this adds to the possibility of a variation in the entropy of activation. As a consequence of the larger size of Ce^{4+} compared with metal ions of the first transitional series, the coordination number for solvent molecules around Ce^{4+} is greater than six and these loosely packed solvent molecules will have considerable freedom of movement. With Ce^{4+}, therefore, there is a strong tendency to form complexes involving the partial removal of these solvating molecules and for all substrates, HA, oxidation proceeds through an intermediate complex as in

$$\mathrm{Ce^{4+}_{aq} + HA_{aq} \overset{\text{rapid}}{\rightleftharpoons} Ce^{4+}HA_{aq} \longrightarrow Ce^{3+}_{aq} + radical + H^+_{aq}}. \qquad (27)$$

Values of ΔH_{pre} and ΔS_{pre} for the formation of the complex in the rapid pre-equilibrium and values of ΔH^* and ΔS^* for the slow redox step are given in table 6 for a range of HA. If ΔS_c represents the entropy change resulting from the disturbance of oriented water molecules solvating Ce^{4+}, the positive ΔS_c deriving from the release of such water molecules by the complexation of HA with Ce$^{4+}_{aq}$ will contribute to ΔS_{pre}. During the process initial state → transition state for the subsequent redox step involving CeHA$^{4+}_{aq}$, the Ce$^{4+}\cdots$HA distance probably contracts to facilitate electron transfer, with further release of oriented water giving a positive contribution ΔS_c^* to ΔS^*, to which ΔS_e^* and ΔS_p^* must also contribute. Table 5 shows that the larger substrates have the smaller values for ΔS_{pre} because of their low ability to penetrate the aqua-sheath in the initial state, but their larger positive values of ΔS^* arise from the larger positive ΔS_c^* which results from the greater contraction in the Ce$^{4+}\cdots$HA distance to produce the transition state required for electron transfer: correspondingly, the smaller substrates penetrate the aqua-sheath further in the initial state, producing a large positive ΔS_{pre}, and therefore require a smaller contraction of Ce$^{4+}\cdots$HA to achieve the transition state for electron transfer with a smaller ΔS_c^* leading to a negative ΔS^*. For the diols other than pinacol, where only values of ΔH^* and ΔS^*

Table 6. Comparison of values of ΔH_{pre}, ΔS_{pre}, ΔH^* and ΔS^* for the oxidation of HA by Ce^{4+}_{aq} *via* reaction (27)

substrate, HA	ΔH_{pre} /kJ mol^{-1}	ΔS_{pre} /J K^{-1} mol^{-1}	ΔH^* /kJ mol^{-1}	ΔS^* /J K^{-1} mol^{-1}	ref.
$(CH_3)_2CHOH$	67	243	86	−7.5	15
$CH_3CHOHCH_2CH_3$	60	225	73	−48	16
	−5.9	5.9	127	145	16
$(CH_3)_2COH(CH_3)_2COH$	34.3	156	94	67	17
$CH_2OHCH_2CH_2OH$	—	—	73	29.3	18
$CH_3CHOHCH_2CH_2OH$	—	—	64	−16.7	18
$CH_2OHCH_2CH_2CH_2OH$	—	—	73	39.3	18
$CH_2OHCH_2CH_2CH_2CH_2OH$	—	—	123	192	18
$CH_2OHCH_2CH_2CH_2CH_2CH_2OH$	—	—	115	171	18
$CH_3CH(OCH_3)CH_2CH_2OH$	—	—	85	67	18

are available, ΔS^* gets larger as the carbon chain gets more complex: presumably the more complex substrates do not penetrate the aqua-sheath so well in the initial state, therefore requiring a greater contraction in $Ce^{4+}\cdots HA$ to achieve the transition state for electron transfer, which results in a larger positive ΔS^* from the large ΔS^*_c.

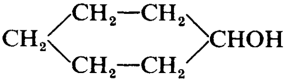
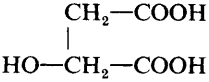
The oxidation of some substrates by Ce^{4+}_{aq} proceed by the alternative pathway

$$Ce^{4+}_{aq} + HA^{aq} \xrightarrow{\text{rapid}} H^+_{aq} + CeA^{3+}_{aq} \xrightarrow{\text{slow}} Ce^{3+} + \text{radical} \qquad (28)$$

involving the loss of a proton from HA in the initial state: values of ΔH_{pre} and ΔS_{pre} for the pre-equilibrium and of ΔH^* and ΔS^* for the redox step are given in table 7. Now ΔS_p for proton release contributes to ΔS_{pre}, which is large and negative for the carboxylic acids: presumably the counterbalancing positive ΔS_c is only small arising from the diffuse negative charge on $—COO^-$, producing little penetration of the aqua-sheath of Ce^{4+} in an ion-pair type complex $Ce^{4+}_{aq}A^-_{aq}$. However, large positive values of ΔS^* are found for these substrates in table 7, owing to the considerable contraction in the $Ce^{4+}\cdots A^-$ distance needed in the transition state to facilitate the electron transfer producing a large positive ΔS^*_c from the attendant release of oriented water. However, with the proton released with the electron in the oxidation of the C—H bond in A^- merely transferring to the $—COO^-$ group, resulting in little or no influence from ΔS^*_p, $|\Delta S_{pre}| < |\Delta S^*|$, leaving the overall entropy of activation, $\Delta S^*_{ov} = \Delta S_{pre} + \Delta S^*$, lying in the range 23–44 J K^{-1} mol^{-1}. The alcohols, with their more concentrated charge on $—O^-$, penetrate farther into the aqua-sheath of Ce^{4+}_{aq} and produce a large positive ΔS_{pre}, with a large positive ΔS_c counterbalancing the negative ΔS_p: because of the large penetration in the initial state, only a small contraction in $Ce^{4+}\cdots A^-$ is needed to produce the transition state for electron transfer and the low values of ΔS^*_c result in smaller values of ΔS^* than found with the carboxylate anions. The energetics for the oxidation of the $>$C—H bonds are relatively uninfluenced by these considerations as the values of ΔH^* lie in a close range over the whole series of carboxylic acids and alcohols.

Table 5 shows for the oxidation of undissociated hmpa a close parallel for Ag^{2+}hmpa and Mn^{3+}hmpa. The complete kinetic analysis for the latter[5] shows that the high oxidation rate of hmpa and pinacol by Mn^{3+}_{aq} compared with those for simple

Table 7. Comparison of values of ΔH_{pre}, ΔS_{pre}, ΔH^* and ΔS^* for the oxidation of HA by $\text{Ce}_{\text{aq}}^{4+}$ *via* reaction (28)

substrate, HA	ΔH_{pre} /kJ mol^{-1}	ΔS_{pre} /J K^{-1} mol^{-1}	ΔH^* /kJ mol^{-1}	ΔS^* /J K^{-1} mol^{-1}	ref.
$CH_2OHCOOH$	−40	−107	121	151	6
$CH_3CHOHCOOH$	−32	−76	105	113	6
$(CH_3)_2COHCOOH$	−54	−149	119	172	6
PhCHOHCOOH	−40	−96	98	121	6
$(CH_3)_2COH(CH_3)_2COH$	—	—	87	41	17
$(CH_3)_2CHOH$	—	—	112	75	15
$CH_3CHOHCH_2CH_3$	32	131	122	111	16
	81	307	98	35	16
 $HO{-}CH_2(CH_2{-}COOH){-}COOH$	—	—	86	40	19

alcohols and carboxylic acids oxidized by $\text{Mn}_{\text{aq}}^{3+}$ arises from the high positive ΔS_{c} produced by the chelation process in the pre-equilibrium: it is likely that a similar explanation holds for the positive ΔS_{ov}^* for Ag^{2+}hmpa and Ag^{2+}pin (where pin = pinacol). The positive ΔS_{ov}^* found for Ag(bipy)^{2+}pin and Ag(bipy)^{2+} $\text{Pr}^{\text{i}}\text{OH}$ may also arise in the same way, with the high positive ΔS_{c} arising from the close approach of the substrate to Ag^{2+} in the initial state allowed by the removal of one bipyridine from Ag(bipy)_2^{2+}. It is notable that VO_2^+hmpa and V(OH)_2^{3+}hmpa have negative values of ΔS_{ov}^*, although the values of ΔH_{ov}^* are close to those found for other aqua-cations. This could arise in two ways: the hydrolysed forms of the cation may prevent hmpa approaching as close to the V atom as it is able to do in the intermediate complexes involving the other cations, resulting in a much smaller positive ΔS_{c} to compensate for the large negative ΔS_{p}^*, or the system may be more rigid in the transition state, resulting in a lower entropy. ΔS_{ov}^* for the two complexes in table 5 involving the anionic ligand hmpa^- differ considerably, despite close agreement for their values of ΔH_{ov}^*. However, for $\text{Ce}^{4+}\text{hmpa}^-$, ΔS_{ov}^* lies at the bottom end of the range $\Delta S_{\text{ov}}^* = 23$–$44$ J K^{-1} mol^{-1} found in table 6 for the anions of other hydroxycarboxylic acids and it seems reasonable that this complex conforms to the explanations given above for these anions with $\text{Ce}_{\text{aq}}^{4+}$. On the other hand, the negative ΔS_{ov}^* for $\text{Ag(bipy)}^{2+}\text{hmpa}^-$ matches those values found for the complexes of V^{V} with the undissociated acid. It is difficult to visualise some specially rigid requirement for the transition state with this complex, and it is more likely that ΔS_{c} and ΔS_{c}^* are both very small with the bipyridine ligand restricting the close approach of the chelating hmpa^- to the Ag^{2+} atom, *i.e.* more like an ion pair, allowing the contribution of the negative ΔS_{p} to the initial state to dominate in ΔS_{ov}^*. This then raises the question of whether the alternative pathway involving Ag(bipy)_2^{2+}hmpa is operating, with both bipyridine ligands keeping Ag^{2+} and hmpa apart. However, this possibility is rejected on the grounds that the redox potential of Ag(bipy)^{2+} is higher[1-3] than that for Ag(bipy)_2^{2+} and the definitive observation of Ag^{2+}hmpa as a pathway indicates that the oxidation prefers Ag^{2+} in a high redox state.

[1] M. P. Heyward and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1981, 431.
[2] M. P. Heyward and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1981, 1863.
[3] M. P. Heyward and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1982, 2185.
[4] M. P. Heyward and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2155.
[5] C. F. Wells and C. Barnes, *Trans. Faraday Soc.*, 1971, **67**, 3297.
[6] Z. Amjad, A. McAuley and U. Gomwalk, *J. Chem. Soc., Dalton Trans.*, 1977, 82.
[7] A. F. M. Nazer and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1980, 2143.
[8] C. Baiocchi, G. Bovio and E. Mentasti, *Int. J. Chem. Kinet.*, 1982, **14**, 1017.
[9] C. F. Wells, *Tetrahedron*, 1966, **22**, 2685.
[10] A. F. M. Nazer and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1980, 2143.
[11] I. M. Heilbron and H. N. Bunbury, *Dictionary of Organic Compounds* (Eyre & Spottiswoode, London, 4th edn, 1965), vol. 3, p. 1741.
[12] C. F. Wells and D. Fox, *J. Chem. Soc., Dalton Trans.*, 1977, 1502.
[13] J. K. Brown, D. Fox, M. P. Heyward and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1979, 735.
[14] C. F. Wells and D. Fox, *J. Chem. Soc., Dalton Trans.*, 1977, 1498.
[15] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1970, **66**, 679.
[16] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1970, **66**, 2855.
[17] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1971, **67**, 1086.
[18] A. Prakash, R. N. Mehrotra and R. C. Kapoor, *J. Chem. Soc., Dalton Trans.*, 1979, 205.
[19] Z. Amjad and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 1974, 2521.

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