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Kinetics of the Oxidation of 2,3-Dimethylbutane-2,3-diol by Bis(2,2′-bipyridine)silver(II) Ions in Aqueous Nitrate Media

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The stoichiometry and the kinetics of the oxidation of 2,3-dimethylbutane-2,3-diol (pinacol) by $[Ag(bipy)_2]^{2+}$ ions have been investigated. It is shown that the oxidation proceeds through intermediate complexes involving Ag^{II} and pinacol. Although $[Ag(bipy)_2]^{2+}$ itself is eliminated as a participant in these oxidatively active complexes, $[Ag(bipy)(pinacol)]^{2+}$ remains as a possible intermediate. The kinetics show that one of the principal pathways involves Ag^{2+}_{aq} complexed with un-ionised pinacol, but they do not distinguish between the involvement of $[Ag(bipy)(pinacol)]^{2+}$ and $[Ag^{2+}(CH_3)_2COH\cdot(CH_3)_2CO^-]$ in the other principal path: the linear Arrhenius plots suggest that the latter two are alternatives and not parallel courses. Values for the enthalpies and entropies of activation are determined. This oxidation is compared with the oxidation of other substrates by $[Ag(bipy)_2]^{2+}$; the pathway involving oxidation by Ag^{2+} with all the bipyridine removed is compared with the oxidation of other substrates by Ag^{2+}_{aq} and the oxidation of pinacol and other substrates by other aquacations.

Following our spectrophotometric investigations of the equilibria existing between Ag^{2+} ions and 2,2′-bipyridine in aqueous nitrate media[1] and the kinetic investigation of the oxidation of hydrogen peroxide [2] and isopropylalcohol[3] by bis(2,2′-bipyridine) silver(II) ions, we now report the results of our kinetic investigation of the oxidation of 2,3-dimethylbutane-2,3-diol (pinacol) by $[Ag(bipy)_2]^{2+}$. We wish to compare this kinetic study with that for the oxidation of isopropyl alcohol by $[Ag(bipy)_2]^{2+}$,[3] as has been done for the aquacations Mn^{III}_{aq} [4,5] and Ce^{IV}_{aq}.[6,7] Some kinetic work with $[Ag(bipy)_2]^{2+}$ has also been reported[8] with iminodiacetic acid and *N*-methyliminodiacetic acid as substrates.

Special attention has to be given to the variation of rate with $[Ag^I]$ in the reactions of Ag^{II}. This variation was found[9] to be quite considerable for the oxidation of isopropyl alcohol by Ag^{II}_{aq}, where it was shown that Ag^{III}_{aq} formed *via* equilibrium (1)[10] is not involved,

$$Ag^{II}+Ag^{II}\rightleftharpoons Ag^{III}+Ag^{I} \qquad (1)$$

and the backward step in reaction (2) was proposed:

$$Ag^{II}_{aq}+(CH_3)_2CHOH\rightleftharpoons\{Ag^{I}(CH_3)_2\dot{C}OH,H^+_{aq}\}_{cage} \qquad (2)$$

involving Ag^I ions in the cage wall before $\{Ag^I\cdot(CH_3)_2\dot{C}OH,H^+_{aq}\}$ can separate into the initial products. A detailed kinetic analysis[9] of the variation of rate with $[Ag^I]$ showed that individual rate constants could be derived. A similar effect was found in the kinetics of the oxidation of isopropyl alcohol by $[Ag(bipy)_2]^{2+}$,[3] but only in the presence of very high $[Ag^I]$, allowing the derivation of individual rate constants at low $[Ag^I]$. A similar effect of Ag^{I}_{aq} ions, without the involvement of Ag^{III}_{aq}, was not unexpectedly found[11] for the kinetics of the oxidation of other simple alcohols by Ag^{II}_{aq} and as no detailed study of the variation of rate with $[Ag^{I}_{aq}]$ was conducted for each substrate,[11] the 'individual' rate constants quoted in this study at a fixed $[Ag^{I}]$ are complex quantities in which $[Ag^{I}_{aq}]$ is also incorporated.[9] No test for the dependence of rate on $[Ag^{I}_{aq}]$ was performed in the kinetic study[12] of the oxidation of cyclohexanol, cyclopentanol, pentan-2-ol and benzyl alcohol by Ag^{II}_{aq}, so the reported rate constants[12] may well be complex quantities involving $[Ag^{I}_{aq}]$ here also. This certainly applies to the kinetic investigation[13] of the oxidation of aliphatic carboxylic acids by Ag^{II}_{aq}, where an effect of added $[Ag^{I}_{aq}]$ was noticed. However, no kinetic effect of $[Ag^{I}_{aq}]$ was observed in the oxidation of formic acid[14] and aliphatic aldehydes[15] by Ag^{II}_{aq}.

Unfortunately, no comparison can be made of our results on $[Ag(bipy)_2]^{2+}$ with isopropyl alcohol and pinacol as substrates with their oxidation by $[Ni(bipy)_3]^{3+}$,[16] since the latter reactions are too fast to study using the stopped-flow technique.

EXPERIMENTAL

MATERIALS

$[Ag(bipy)_2]^{2+}(NO_3)_2$ was prepared in solution by anodic oxidation under nitrogen of $AgNO_3$ in aqueous nitric acid in the presence of sufficient 2,2′-bipyridine to maintain an excess of 4.0×10^{-3} mol dm^{-3} after the conversion of Ag^{I} to Ag^{II}. Pinacol was recrystallized as the hexahydrate from boiling water and solutions were standardized using periodic acid: the latter reagent, prepared by dissolving 2.5 g of HIO_4 in 100 cm^3 of water with the addition of 400 cm^3 of AnalaR glacial acetic acid, was stored in a dark, stoppered bottle. All other materials were as described previously.[1-3, 17]

PROCEDURES

Concentrations of $[Ag(bipy)_2]^{2+}$ were determined spectrophotometrically at 450 nm using the recorded variation of extinction coefficient with acidity.[1] Acetone was removed from the reaction mixture (first neutralised with KOH) by high-vacuum distillation in a closed system[4-7] and then estimated spectrophotometrically as the anion of the 2,4-dinitrophenylhydrazone.[17]

Rates of decay of $[Ag^{II}]$ were followed spectrophotometrically at 450 nm using the thermostatted cell compartment of a Unicam SP500, a Unicam SP6-500 or a Unicam SP800 spectrophotometer, the latter coupled with a Honeywell chart recorder, or a Durrum–Gibson stopped-flow spectrophotometer coupled with a Tektronix oscilloscope with a storage screen. Precautions[7] were taken against the possible preoxidation of pinacol by nitric acid. As in the previous work with the $[Ag(bipy)_2]^{2+}$ ion,[1-3] excess [bipy] = 4.0×10^{-3} mol dm^{-3} was always present in the reaction mixtures.

RESULTS AND DISCUSSION

STOICHIOMETRY

Owing to the low rate of reaction when $[Ag^{II}]_{initial}/[pinacol]_{initial} > 1$, becoming comparable with the rate of oxidation of water by $[Ag(bipy)_2]^{2+}$, it was not possible to determine the consumption rates $\Delta[pinacol]/\Delta[Ag^{II}]$. However, with an excess of pinacol over Ag^{II}, an accurate estimation of the acetone produced can be made after neutralising the nitric acid with KOH and distilling off the acetone under high vacuum, as done in the oxidation of isopropyl alcohol by $[Ag(bipy)_2]^{2+}$.[3] The concentration of acetone in the distillate was determined spectrophotometrically using 2,4-dinitrophenylhydrazine in alkaline conditions.[17] The values for $|\Delta[Ag^{II}]|/|\Delta[acetone]|$ in table 1 show that the overall reaction can be represented by step (3) with or without oxygen present:

$$2Ag^{II} + \{(CH_3)_2COH\}_2 \rightarrow 2Ag^{I} + 2(CH_3)_2CO + 2H^{+}. \qquad (3)$$

Table 1. Values for $|[\Delta[Ag^{II}]|/|\Delta[acetone]|$ for excess $[bipyH^+] = 4.0 \times 10^{-3}$ mol dm^{-3} at ionic strength 1.00 mol dm^{-3} and 20 °C

$[H^+]$/ mol dm^{-3}	[pinacol] /10^{-2} mol dm^{-3}	$\frac{\lvert\Delta[Ag^{II}]\rvert}{\lvert\Delta[acetone]\rvert}$
0.100	3.40	0.94
0.100	1.70	0.98
0.100	1.70	1.03[a]
1.00	3.40	0.98
1.00	1.70	1.04
1.00	1.70	0.98[a]

[a] Under nitrogen.

RATES OF OXIDATION AT 25.0 °C

Rates were measured with [pinacol] > $[Ag^{II}]$, the excess $[bipy] = 4.0 \times 10^{-3}$ mol dm^{-3} over that required to complex $[Ag^{II}]$ and the ionic strength maintained at $I = 1.00$ mol dm^{-3} by the addition of $NaNO_3$ to the aqueous nitric acid. With initial $[Ag^{II}] \approx 2 \times 10^{-4}$ mol dm^{-2} and [pinacol] $\approx (4\text{–}40) \times 10^{-2}$ mol dm^{-3}, plots of log (optical density) against time were always linear with $[HNO_3]$ in the range 0.1–1.0 mol dm^{-3}. The values for the pseudo-first-order rate constant k_0 derived from the slopes of these plots are given in table 2. Fig. 1 shows that plots of k_0^{-1} against $[pinacol]^{-1}$ at constant acid concentration give straight lines with an intercept on the k_0^{-1} axis. Values for the slopes and intercepts of these linear plots together with their standard deviations, determined using the least-squares procedure, are given in table 3.

The results in table 2 show that the presence of molecular oxygen does not affect the kinetics. Table 2 also shows that variations in rate arising from specific ion effects when H^+ is replaced by Na^+ to maintain the ionic strength at 1.00 mol dm^{-3} whilst varying $[H^+]$ do not occur as the rate remains unchanged when $LiNO_3$ is used for this purpose instead of $NaNO_3$. Specific ion effects due to the production of Ag^I, such as were found in the oxidation of isopropyl alcohol by Ag^{2+}_{aq}[9] and (at high $[Ag^I]$) by $[Ag(bipy)_2]^{2+}$,[3] and in the oxidation of other alcohols by Ag^{2+}_{aq},[11] do not occur in the oxidation of pinacol by $[Ag(bipy)_2]^{2+}$, as the rate is not influenced (table 2) by replacement of $NaNO_3$ by $AgNO_3$ in the reaction mixture.

VARIATION OF RATE AND TEMPERATURE

Linear plots of log(optical density) against time were also found for the decay of $[Ag(bipy)_2^{2+}]$ in the presence of excess pinacol at 19.5, 30.0 and 35.0 °C at constant $[H^+]$ over a range of added concentrations of HNO_3 with the ionic strength always maintained at $I = 1.00$ mol dm^{-3} with the addition of $NaNO_3$. The values of k_0 are collected in table 2. At constant $[H^+]$ and temperature, plots of k_0^{-1} against $[pinacol]^{-1}$ are linear and the values of the slopes and intercepts with their standard deviations are included in table 3. Some of the rates at 35.0 °C were too high to be determined using conventional spectrophotometry, and the stopped-flow technique was used in these cases: the upper limit on the concentration of pinacol used at 35.0 °C was imposed by its solubility.

Table 2. Values for the pseudo-first-order rate constant for various [pinacol], $[H^+]$ and temperatures with initial $[Ag^{II}] = 2 \times 10^{-4}$ mol dm^{-3} and excess $[bipyH^+] = 4.0 \times 10^{-3}$ mol dm^{-3}

$[H^+]_T$ /mol dm^{-3}	[pinacol] /10^{-3} mol dm^{-3}	$k_0/10^{-4}$ s^{-1}	$[H^+]_T$ /mol dm^{-3}	[pinacol] /10^{-3} mol dm^{-3}	$k_0/10^{-4}$ s^{-1}
		$T = 25.0$ °C			
0.100	4.00	0.97	0.500	10.0	21.8^e
0.100	5.00	1.37	0.500	10.0	22.0^f
0.100	10.0	2.90	0.500	13.6	28.3
0.100	20.0	4.50	0.500	13.6	28.2^a
0.100	30.0	4.90	0.500	15.0	33.3
0.100	30.0	4.90^b	0.500	15.0	35.5
0.100	40.0	6.6	0.500	15.0	32.8^b
0.300	5.00	6.3	0.500	20.0	43.0
0.300	10.0	12.5	0.500	20.4	44.0
0.300	15.0	16.8	0.500	20.4	44.0^a
0.300	20.0	21.2	0.500	25.0	51
0.300	30.0	31.8	0.500	30.0	58
0.300	40.0	38.3	0.800	5.00	21.7
0.500	5.00	12.1	0.800	10.0	37.2
0.500	5.00	11.4^b	0.800	15.0	51
0.500	5.00	12.0^a	0.800	20.0	67
0.500	6.8	14.3^a	0.800	30.0	98
0.500	6.8	14.4	1.00	5.00	22.8
0.500	10.0	22.7	1.00	10.0	44
0.500	10.0	22.3^b	1.00	15.0	63
0.500	10.0	22.1^a	1.00	20.0	79
0.500	10.0	20.0^d	1.00	25.0	97
		$T = 19.5$ °C			
0.100	10.0	1.02	0.500	10.0	11.5
0.100	20.0	1.87	0.500	20.0	18.5
0.100	30.0	2.63	0.500	40.0	37.2
0.100	40.0	3.30	0.800	5.00	9.3
0.300	5.00	2.70	0.800	6.00	10.9
0.300	6.00	3.50	0.800	10.0	16.7
0.300	6.00	3.50	0.800	20.0	31.0
0.300	10.00	5.6	0.800	30.0	42.0
0.300	20.0	11.7	1.00	5.00	11.3
0.300	30.0	14.9	1.00	6.00	11.9
0.300	40.0	22.5	1.00	10.0	20.9
0.500	5.00	6.3	1.00	20.0	41.0
0.500	6.00	7.4	1.00	30.0	52
		$T = 30.0$ °C			
0.100	5.00	3.13	0.500	15.0	56
0.100	10.0	6.0	0.500	20.0	82
0.100	20.0	10.3	0.500	30.0	108
0.100	30.0	13.6	0.800	5.00	35.8
0.100	40.0	18.5	0.800	6.00	42
0.300	5.00	11.9	0.800	10.0	74
0.300	6.00	15.2	0.800	15.0	113
0.300	10.0	19.5	0.800	20.0	158
0.300	20.0	45.0	1.00	5.00	52
0.300	30.0	59	1.00	6.00	56
0.300	40.0	69	1.00	10.0	107
0.500	5.00	22.5	1.00	12.0	109
0.500	10.0	39.0	1.00	15.0	153

Table 2. (*cont.*)

$[H^+]_T$ /mol dm^{-3}	[pinacol] /10^{-3} mol dm^{-3}	$k_0/10^{-4}$ s^{-1}	$[H^+]_T$ /mol dm^{-3}	[pinacol] /10^{-3} mol dm^{-3}	$k_0/10^{-4}$ s^{-1}
		$T = 35.0$ °C			
0.100	2.00	2.67	0.500	85.0	550^c
0.100	5.00	5.2	0.800	2.00	33.7
0.100	10.0	8.4	0.800	3.00	44.0
0.100	20.0	16.7	0.800	5.00	77
0.100	30.0	24.5	0.800	6.00	90
0.300	2.00	10.7	0.800	10.0	148
0.300	3.00	17.8	1.00	2.00	47
0.300	5.00	26.2	1.00	2.00	49
0.300	10.0	50	1.00	3.00	71
0.300	30.0	119	1.00	3.00	68
0.500	2.00	23.8			
0.500	2.00	22.2	1.00	3.00	70
0.500	3.00	30.8	1.00	4.00	89
0.500	5.00	49	1.00	5.00	113
0.500	10.0	91	1.00	6.00	123
0.500	20.0	188	1.00	34.0	570^c
0.500	34.0	265^c	1.00	51.0	870^c
0.500	51.0	350^c	1.00	85.0	1270^c

[a] Ionic strength adjusted with LiNo$_3$. [b] Under nitrogen. [c] Using the stopped-flow technique. [d] $[Ag^I] = 2.50 \times 10^{-2}$ mol dm^{-3}. [e] $[Ag^I] = 5.00 \times 10^{-2}$ mol dm^{-3}. [f] $[Ag^I] = 7.50 \times 10^{-2}$ mol dm^{-3}.

MECHANISM OF THE OXIDATION

First we have equilibria (4) and (5) involving the oxidant and reductant:

$$[Ag(bipy)_2]^{2+} + H^+ \xrightarrow{K_h} [Ag(bipy)]^{2+} + bipy\,H^+ \qquad (4)$$

$$pin + H^+ \xrightarrow{K_c} pin\,H^+ \qquad (5)$$

both of which have already been investigated[1, 5] [pin is the ligand $(CH_3)_2COH \cdot (CH_3)_2COH$]. Then we must consider all the possible pre-equilibria involving the Ag^{II} complexes and the ligand substrate:

$$[Ag(bipy)]^{2+} + pin \xrightleftharpoons{\beta} [Ag(bipy)pin]^{2+} \qquad (6)$$

$$[Ag(bipy)_2]^{2+} + pin \xrightleftharpoons{\beta'} [Ag(bipy)_2pin]^{2+} \qquad (7)$$

$$[Ag(bipy)pin]^{2+} \xrightleftharpoons{K_1} [Ag(bipy)(pin^-)]^+ + H^+ \qquad (8)$$

$$[Ag(bipy)pin]^{2+} + H^+ \xrightleftharpoons{K_2} [Agpin]^{2+} + bipyH^+ \qquad (9)$$

$$[Agpin]^{2+} \xrightleftharpoons{K_3} [Agpin^-]^+ + H^+ \qquad (10)$$

$$[Ag(bipy)_2pin]^{2+} \xrightleftharpoons{K_1'} [Ag(bipy)_2(pin^-)]^+ + H^+ \qquad (11)$$

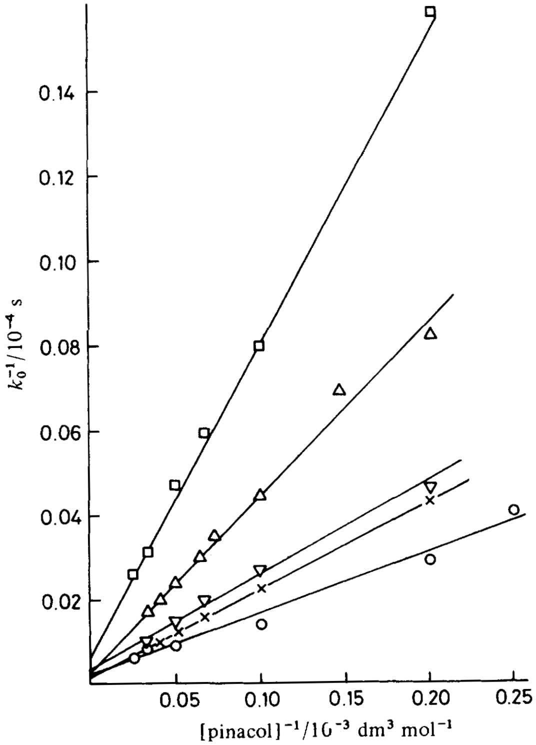

Fig. 1. Plots of Ak_0^{-1} against $[\text{pinacol}]^{-1}$ for varying $[\text{H}^+]$ with excess $[\text{bipyH}^+] = 4.0 \times 10^{-3}$ mol dm^{-3}, $I = 1.00$ mol dm^{-3} and 25.0 °C: ○, $[\text{H}^+]_\text{T} = 0.100$ mol dm^{-3}, $A = 0.04$; □, $[\text{H}^+]_\text{T} = 0.300$ mol dm^{-3}, $A = 1.00$; △, $[\text{H}^+]_\text{T} = 0.500$, $A = 1.00$; ▽, $[\text{H}^+]_\text{T} = 0.800$, $A = 1.00$; ×, $[\text{H}^+]_\text{T} = 1.00$, $A = 1.00$.

$$[\text{Ag(bipy)}_2\text{pin}] + \text{H}^+ \overset{K_2'}{\rightleftharpoons} [\text{Ag(bipy)(pin}^-)]^+ + \text{bipyH}^+ \qquad (12)$$

where pin$^-$ is the ligand $(\text{CH}_3)_2\text{COH}\cdot(\text{CH}_3)_2\text{CO}^-$.

All these equilibria will be established very quickly compared with the possible rate-determining steps in the oxidation:

$$[\text{Ag(bipy)pin}]^{2+} \xrightarrow{k_1} \text{Ag}^\text{I} + (\text{CH}_3)_2\dot{\text{C}}\text{OH} + (\text{CH}_3)_2\text{CO} + \text{H}^+ \qquad (13)$$

$$[\text{Ag(bipy)(pin}^-)]^+ \xrightarrow{k_2} \text{Ag}^\text{I} + (\text{CH}_3)_2\dot{\text{C}}\text{OH} + (\text{CH}_3)_2\text{CO} \qquad (14)$$

$$[\text{Ag(bipy)}_2\text{pin}]^{2+} \xrightarrow{k_1'} \text{Ag}^\text{I} + (\text{CH}_3)_2\dot{\text{C}}\text{OH} + (\text{CH}_3)_2\text{CO} + \text{H}^+ \qquad (15)$$

$$[\text{Ag(bipy)}_2\text{(pin}^-)]^+ \xrightarrow{k_2'} \text{Ag}^\text{I} + (\text{CH}_3)_2\dot{\text{C}}\text{OH} + (\text{CH}_3)_2\text{CO} \qquad (16)$$

$$[\text{Ag(pin)}]^{2+} \xrightarrow{k_3} \text{Ag}^\text{I} + (\text{CH}_3)_2\dot{\text{C}}\text{OH} + (\text{CH}_3)_2\text{CO} + \text{H}^+ \qquad (17)$$

$$[\text{Ag(pin}^-)]^+ \xrightarrow{k_4} \text{Ag}^\text{I} + (\text{CH}_3)_2\dot{\text{C}}\text{OH} + (\text{CH}_3)_2\text{CO}. \qquad (18)$$

Table 3. Values for the slopes and intercepts for the plots of k_0^{-1} against [pinacol]$^{-1}$ for varying $[H^+]_T$ and temperature at ionic strength 1.00 mol dm^{-3}

T/°C	$[H^+]_T$ /mol dm^{-3}	slope /mol dm^{-3} s^{-1}	intercept /s
19.5	0.100	91 ± 2	790 ± 100
19.5	0.300	17.9 ± 0.2	0 ± 176
19.5	0.500	7.4 ± 0.5	124 ± 23
19.5	0.800	5.0 ± 0.1	78 ± 14
19.5	1.00	4.44 ± 0.36	38 ± 46
25.0	0.100	33 ± 6	1350 ± 770
25.0	0.300	7.5 ± 0.1	77 ± 15
25.0	0.500	4.21 ± 0.39	30 ± 14
25.0	0.800	2.10 ± 0.14	46 ± 15
25.0	1.00	2.10 ± 0.19	20 ± 11
30.0	0.100	14.9 ± 0.2	205 ± 19
30.0	0.300	3.90 ± 0.30	50 ± 41
30.0	0.500	2.10 ± 0.15	28 ± 17
30.0	0.800	1.44 ± 0.08	9 ± 11
30.0	1.00	1.02 ± 0.05	2.3 ± 6.6
35.0	0.100	7.0 ± 0.04	344 ± 16
35.0	0.300	1.80 ± 0.06	18 ± 17
35.0	0.500	0.85 ± 0.98	17 ± 7
35.0	0.800	0.59 ± 0.03	14 ± 0.2
35.0	1.00	0.46 ± 0.04	14 ± 9

In reactions (13)–(16) some rearrangement of the disposition of the 2,2′-bipyridine probably follows the oxidation step and is omitted for simplicity. The redox steps are then followed by a very rapid redox step involving the free radical produced above:

$$\mathrm{Ag^{II}} + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} \xrightarrow{\text{fast}} (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{H^+} \qquad (19)$$

corresponding to the observed value for $|\Delta[\mathrm{Ag^{II}}]|/|\Delta[\text{acetone}]|$.

For the overall rate of disappearance of all species of Ag^{II} involving pre-equilibria (4)–(12) and reactions (13)–(18) followed by (19), the pseudo-first-order rate constant with a large excess of pinacol is as in eqn (20):

$$k_0 = \frac{2\{\beta(k_1 K'_h h + k_2 K_1 K'_h + k_3 K'_2 K_h h^2 + k_4 K_3 K'_2 K'_h h) + \beta'(k'_1 + k'_2 K'_1 h^{-1})\}\,[\mathrm{pin}]_T}{(1 + K'_h h)(1 + K_c h) + [\mathrm{pin}]_T\,\{\beta(K'_h h + K_1 K'_h + K'_2 K'_h h^2 + K'_2 K_3 K'_h h) + \beta'(1 + K'_1 h^{-1})} \qquad (20)$$

where $[\mathrm{pin}]_T$ is the total amount of pinacol present in all species in solution, $h = [H^+]_T$, $K'_h = K_h/[\mathrm{bipyH^+}]$ and $K'_2 = K_2/[\mathrm{bipyH^+}]$. Inverting and rearranging eqn (20) gives eqn (21):

$$k_0^{-1} = \frac{(1 + K'_h h)(1 + K_c h)}{2\{\beta(k_1 K'_h h + k_2 K_1 K'_h + k_3 K'_2 K'_h h^2 + k_3 K_3 K'_2 K'_h h) + \beta'(k'_1 + k'_2 K'_1 h^{-1})\}\,[\mathrm{pin}]_T}$$
$$+ \frac{\beta(K'_h h + K_1 K'_h + K'_h K'_2 h^2 + K'_h K'_2 K_3 h) + \beta'(1 + K_1 h^{-1})}{2\{\beta(k_1 K'_h h + k_2 K_1 K'_h + k_3 K'_2 K'_h h^2 + k_4 K_3 K'_2 K'_h h) + \beta'(k'_1 + k'_2 K'_1 h^{-1})\}} \qquad (21)$$

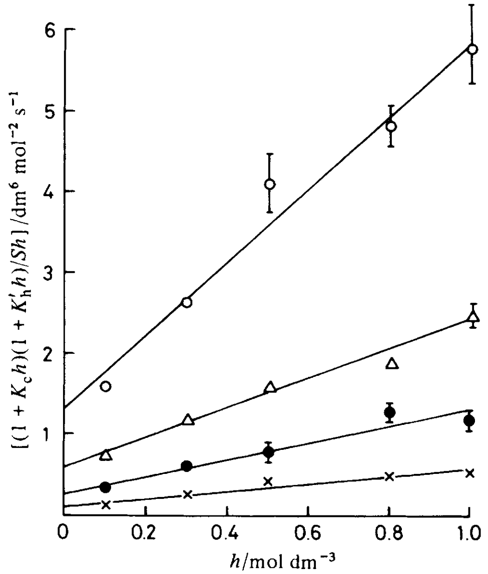

Fig. 2. Plots of $(1+K_c h)\,(1+K'_h h)\,(Sh)^{-1}$ against h for varying temperature with excess [bipyH$^+$] = 4.0×10^{-3} and I = 1.00 mol dm^{-3}: ×, 19.5; ●, 25.0; △, 30.0; ○, 35.0 °C.

Table 4. Values for $k_3\beta K'_2$ and $\beta(k_1+k_4K'_2K_3)$ for varying temperature with excess [bipyH$^+$] = 4.0×10^{-3} mol dm^{-3} and ionic strength 1.00 mol dm^{-3}

T/°C	$k_3\beta K'_2$ /dm^6 mol^{-2} s^{-1}	$\beta(k_1+k_4K'_2K_3)$ /dm^3 mol^{-1} s^{-1}
19.5	0.31 ± 0.06	0.08 ± 0.04
25.0	0.65 ± 0.11	0.17 ± 0.67
30.0	1.04 ± 0.10	0.35 ± 0.06
35.0	2.31 ± 0.22	0.68 ± 0.14

which predicts linear plots of k_0^{-1} against $[\mathrm{pin}]_T^{-1}$ with intercepts on the ordinate for constant acidity and temperature, as observed.

From eqn (21) the slopes S of such linear plots should fit eqn (22):

$$(1+K'_h h)(1+K_c h)S^{-1} = 2\beta K'_h\,(k_1h+k_2K_1+k_3K'_2h^2+k_4K_3K'_2h)+2\beta'(k'_1+k'_2K'_1h^{-1}). \quad (22)$$

The left-hand side of eqn (22) does not give a straight line when plotted against h. but fig. 2 shows that plots of $(1+K_h h)(1+K_c h)h^{-1}S^{-1}$ against h give linear plots for each temperature with an intercept on the ordinate. Dividing each side of eqn (22) by h gives

$$(1+K'_h h)(1+K_c h)h^{-1}S^{-1} = 2\beta K'_h(k_1+k_2K_1h^{-1}+k_3K'_2h+k_4K_3K'_2)+2\beta'(k'_1h^{-1}+k'_2K'_1h^{-2}). \quad (23)$$

Fig. 2 shows that terms on the right-hand side of eqn (23) containing inverse powers of h can be neglected. From eqn (23) the slopes of fig. 2 give $2k_3\beta K'_h K'_2$ and the

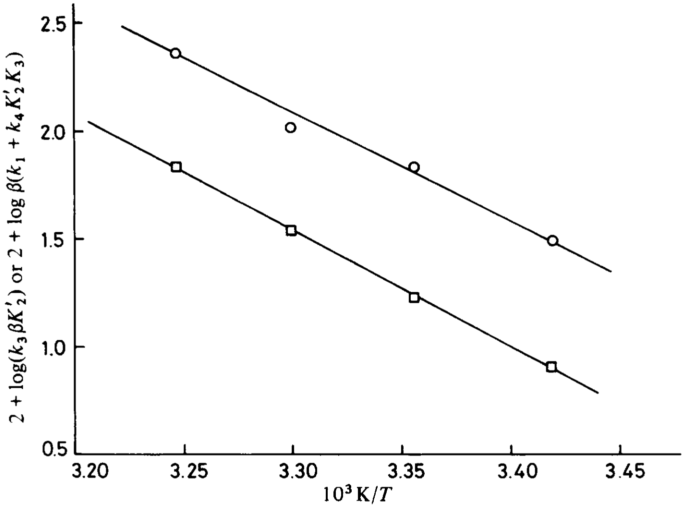

Fig. 3. Plots of log $(k_3 \beta K_2')$ (○) and log $\beta(k_1 + k_4 K_2' K_3)$ (□) against reciprocal of absolute temperature for excess [bipyH$^+$] = 4×10^{-3} mol dm^{-3} and $I = 1.00$ mol dm^{-3}.

intercepts $2(k_1 + k_4 K_3 K_2') \beta K_h'$. The values for the slopes and intercepts together with their standard deviations were calculated using the least-squares procedure and the values for $k_3 \beta K_2'$ and $\beta(k_1 + k_4 K_2' K_3)$ calculated from these using the known values[1] of K_h' are collected in table 4. The deviations in the intercepts from fig. 1 are too great for them to be used in a test of the mechanism.

TRANSITION-STATE PARAMETERS FOR THE OXIDATION OF PINACOL BY $[Ag(bipy)_2]^{2+}$

Fig. 3 shows that plots of the logarithm of both these functions against reciprocal of the absolute temperature are linear, which suggests that in the case of $\beta(k_1 + k_4 K_2' K_3)$ one part dominates. The least-squares procedure has been applied to these data to derive overall values for the enthalpy ΔH^* and entropy ΔS^* of activation. If βk_1 dominates the latter function, the overall ΔS^* is 81 ± 5 J K^{-1} mol^{-1}; however, if $\beta k_4 K_2 K_3$ dominates, the overall ΔS^* is 35 ± 5 J K^{-1} mol^{-1} (allowing for the change from K_2' to K_2): in either case, the overall ΔH^* is 49.5 ± 0.7 kJ mol^{-1}. For $k_3 \beta K_2$, the overall ΔH^* is 45.3 ± 3.3 kJ mol^{-1}, with the overall $\Delta S^* = 18 \pm 12$ J K^{-1} mol^{-1}, allowing for the change from K_2' to K_2.

There is no sure way of differentiating between reactions (13) and (18) as possibilities. It could be argued that, as reaction (17) is known to constitute the other pathway, reaction (18) is the more likely, involving complete removal of 2,2′-bipyridine from the Ag^{II} as is involved in reaction (17). On the other hand, as a Ag^{II}-bipyridine complex is involved[18] as an active entity in one pathway in the oxidation of 2-hydroxy-2-methylpropanoic acid by $[Ag(bipy)_2]^{2+}$, in addition to a pathway analogous to reaction (17), reaction (13) is perhaps more likely with pinacol.

COMPARISON WITH THE OXIDATION OF OTHER SUBSTRATES BY $[Ag(bipy)_2]^{2+}$

The one unambiguous pathway for the oxidation of pinacol by $[Ag(bipy)_2]^{2+}$ involves the complete removal of both bipyridine molecules before the redox step occurs, contrasting with both isopropyl alcohol and hydrogen peroxide as substrates where only one bipyridine is removed before the redox step. The oxidations of both pinacol and isopropyl alcohol by $[Ag(bipy)_2]^{2+}$ involve intermediate complexes and, as the values of the overall ΔS^* ($J\ K^{-1}\ mol^{-1}$) for these two substrates [isopropyl alcohol, 13; pinacol by reaction (17), 18] are close, the higher reactivity of pinacol *via* reaction (17) derives from a lower overall ΔH^* ($kJ\ mol^{-1}$), 45.3 compared with 88 for isopropyl alcohol. This latter relative invariance in ΔS^* suggests that the removal of all the bipyridines before reaction (17) occurs does not arise from some necessary steric requirement involved in the chelation of pinacol, as this is likely to be reflected in the overall ΔS^*. Thus the lower overall ΔH^* with reaction (17) probably reflects the higher redox potential E° of 2.0 V for Ag^{II}_{aq} compared with 1.4 V for $[Ag(bipy)]^{2+}$, pinacol proceeding through $[Ag\ pinacol]^{2+}$ and isopropyl alcohol through $[Ag(bipy)isoPrOH]^{2+}$. The absence of any redox activity of $[Ag(bipy)_2]^{2+}$ towards pinacol, isopropyl alcohol or hydrogen peroxide presumably lies in its low E° (1.05 V). The oxidation of hydrogen peroxide by $[Ag(bipy)]^{2+}$, which involves no intermediate complexes, has a value for ΔS^* ($-62\ J\ K\ mol^{-1}$) quite different from those found for the organic substrates.

COMPARISON WITH THE OXIDATION OF ORGANIC SUBSTRATES BY AQUA-CATIONS

As the rate-determining step in the specified pathway for the oxidation of pinacol by $[Ag(bipy)_2]^{2+}$ involves an oxidation by Ag^{2+}_{aq}, this can be compared with oxidations by Ag^{2+}_{aq} and by other aqua-cations. Although this latter reaction involves an intermediate complex, no such complexes were detected in the oxidation of isopropyl alcohol by aquasilver(II) ions.[9] In this, Ag^{II}_{aq} can be compared with the oxidation of isopropyl alcohol[4] and pinacol[5] by aquamanganese(III) ions, where only the latter involves intermediate complexes. In the latter case the much higher reactivity of pinacol arises principally from the overall positive value of ΔS^* for pinacol compared with that for isopropyl alcohol, ascribed to the larger amount of restricted water released from the neighbourhood of Mn^{3+}_{aq} when pinacol is chelated in the intermediate: the Mn^{3+}—substrate distance in the transition state for isopropyl alcohol must be much greater than that for pinacol. The oxidation of both isopropyl alcohol[6] and pinacol[7] by aquacerium(IV) ions proceeds through intermediate complexes, $Ce^{4+}ROH_{aq}$ and $Ce^{4+}RO^-_{aq}$ (as found also for Mn^{3+}_{aq} + pinacol). Only the $Ce^{4+}ROH_{aq}$ pathway is comparable with the $Ag^{2+}ROH_{aq}$ pathway found for pinacol and $[Ag(bipy)_2]^{2+}$, and the overall $\Delta S^*/J\ K\ mol^{-1}$ is about the same for Ce^{4+} with isopropyl alcohol (235) and pinacol (223). However, the entropy of formation of the intermediate complex is greater for isopropyl alcohol ($242\ kJ\ mol^{-1}$) than for pinacol ($156\ kJ\ mol^{-1}$), and this has been ascribed to the greater ability of the smaller isopropyl alcohol to penetrate the aquasheath of Ce^{4+}_{aq} than that for the larger pinacol, releasing more restricted water from around Ce^{4+}_{aq} in the former case. This is then compensated by a higher positive ΔS^* for the rate-determining step in the oxidation in the complex $Ce^{4+}ROH_{aq}$ for pinacol (67) compared with that for isopropyl alcohol (−7.5), as more restricted water has to be swept out of the neighbourhood of Ce^{4+}_{aq} in the change initial → transition state to bring pinacol close enough for the electron to be transferred. Ce^{4+}_{aq} appears to contrast with both Mn^{3+}_{aq} and Ag^{2+}_{aq} in this, as the latter do not complex with isopropyl alcohol. This absence of complexation in the latter cases probably arises from the tighter fit of the smaller number of water molecules around Mn^{3+}_{aq} and Ag^{2+}_{aq} compared with $Ce^{4+}(H_2O)_n$ where n probably exceeds six, the smaller size of the former two aqua-cations allowing the isopropyl alcohol to get close enough, with their values of E° higher than E° for Ce^{4+}_{aq} for the electron transfer to occur without involving complexation.

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