Kinetics of the Oxidation of Isopropyl Alcohol by Bis(2,2′-bipyridine)silver(II) Ions

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The oxidation of isopropyl alcohol by $[Ag(bipy)_2]^{2+}$ is first order in $[Ag(bipy)_2]^{2+}$ and the order in Pr^iOH is between zero and unity. The kinetics show that intermediate complexes are involved and from the variation of rate with acidity one formed between $[Ag(bipy)]^{2+}$ and Pr^iOH can be specified as the only one involved. At high added $[Ag^I]$ a back reaction is found and this is discussed in terms of the influence of Ag^I ions in the solvent wall of a cage before the Ag^I and radical formed in the oxidation can diffuse out. Values for ΔH^* and ΔS^* for the oxidation at low $[Ag^I]$ are compared with ΔH^* and ΔS^* for the oxidation of Pr^iOH and aqua-cations.

The kinetics of the oxidation of isopropyl alcohol in aqueous perchlorate media by oxidizing aqua-cations have been investigated for $Mn^{III}(aq)$,[1] $Ce^{IV}(aq)$,[2] $Co^{III}(aq)$,[3] $V^{V}(aq)$,[4] and $Ag^{II}(aq)$,[5] where hydrolytic equilibria of the cations are involved as well as inactivation[6] of the substrate involving solvation of the proton.[7] It would therefore be of interest to investigate the kinetics of the oxidation of this substrate by cations where no water molecules are present in the inner co-ordination sphere of the cation, eliminating the influence of the hydrolytic equilibria. Unfortunately, the rate of the reaction of the highly oxidizing[8] cation $[Ni(bipy)_3]^{3+}$ with Pr^iOH is comparable[9] with the rate of oxidation of water by $[Ni(bipy)_3]^{3+}$ and kinetic investigations of the oxidation of alcohols by this cation are restricted to the more easily oxidizable phenyl-substituted alcohols.[9] However, we found that $[Ag(bipy)_2]^{2+}$ reacts with Pr^iOH at a reasonable rate. This complex exists in a square-planar arrangement[10,11] and it seems unlikely that water molecules are in contact with the Ag^{2+} ion in aqueous nitric acid.[11,12]

Experimental

Materials.—The cation $[Ag(bipy)_2]^{2+}$ was prepared as described earlier[11,12] by the anodic oxidation under nitrogen of solutions of Ag^I in aqueous nitric acid with sufficient 2,2′-bipyridine (bipy) present to provide an excess concentration of 4.0×10^{-3} mol dm^{-3} after formation of the $[Ag(bipy)_2]^{2+}$. Isopropyl alcohol was purified by refluxing with 2,4-dinitrophenylhydrazine followed by fractional distillation.[7] All other materials were as used previously.[11,12]

Procedure.—Rates were followed in the thermostatted cell compartment of a Unicam SP 500, a Unicam SP 800, or a Unicam SP 6-500 spectrophotometer: the SP 800 was coupled with a scale expansion unit and a Honeywell chart recorder. A fixed wavelength of 450 nm was employed. The temperature in all three spectrophotometers was controlled with water circulated from a thermostat. Unless otherwise stated the ionic strength was maintained at $I = 1.00$ mol dm^{-3} by the addition of AnalaR sodium nitrate. Initial concentrations of $[Ag(bipy)_2]^{2+}$ were $\sim 2 \times 10^{-4}$ mol dm^{-3}. As in the oxidation of hydrogen peroxide by $[Ag(bipy)_2]^{2+}$,[12] rates were found to be very fast unless the excess concentration of 2,2′-bipyridine was maintained at 4×10^{-3} mol dm^{-3}, as found necessary to obtain reproducible results in the investigation[11] of equilibria involving $[Ag(bipy)_2]^{2+}$.

Acetone was determined by distillation in a closed system under high vacuum after neutralization of the nitric acid with KOH, followed by spectrophotometric estimation as the 2,4-dinitrophenylhydrazone anion[13] as used in all the oxidations by aqua-cations.[1–5] Concentrations of $[Ag(bipy)_2]^{2+}$ were determined spectrophotometrically using the absorption coefficients available at each acidity.[11]

Table 1. Values of $|\Delta[Ag^{II}]|/|\Delta[Me_2CO]|$ for excess $[Hbipy^+] = 4 \times 10^{-3}$ mol dm^{-3} at $I = 1.00$ mol dm^{-3} and 20 °C

$[H^+]$/ mol dm^{-3}	$[Pr^iOH]$/ mol dm^{-3}	$\frac{\lvert\Delta[Ag^{II}]\rvert}{\lvert\Delta[Me_2CO]\rvert}$
0.100	0.57	2.21
0.100	1.15	2.31
0.100	2.29	1.84
1.000	0.57	1.98 *
1.000	1.15	1.96
1.000	2.29	1.99

* Under nitrogen.

Results and Discussion

Stoicheiometry.—Although the reaction was too slow to determine $|\Delta[Pr^iOH]|/|\Delta[Ag^{II}]|$ using an excess of $[Ag(bipy)_2]^{2+}$ over the concentration of Pr^iOH, $|\Delta[Ag^{II}]|/|\Delta[Me_2CO]|$ could be determined using a large excess of Pr^iOH over the concentration of $[Ag(bipy)_2]^{2+}$ in aqueous nitric acid. The values for this latter ratio determined at $I = 1.00$ mol dm^{-3} are given in Table 1 for a range of acidities and varying $[Pr^iOH]$. It was found that nitric acid itself produced no oxidation during the period allowed for the reaction. The consumption of $[Ag(bipy)_2]^{2+}$ in its oxidation of water was found never to exceed 5% of the total decrease in $[Ag^{II}]$ at 0.1 mol dm^{-3} HNO_3 and was considerably less than 5% at the higher acidities. As a small correction has been applied to $[Ag^{II}]$ used in Table 1 to allow for this, the slightly high values found for $|\Delta[Ag^{II}]|/|\Delta[Me_2CO]|$ at 0.1 mol dm^{-3} HNO_3 with low values for $[Pr^iOH]$ may be due to secondary attack of $[Ag(bipy)_2]^{2+}$ on the acetone, although experimentally it was found that loss of $[Ag^{II}]$ due to attack on the acetone would account for much less than 5% of the total decrease in $[Ag^{II}]$. Table 1 shows that the ratio is unchanged when the reaction is performed under nitrogen. The mean value for the ratio $|\Delta[Ag^{II}]|/|\Delta[Me_2CO]| = 2.05 \pm 0.16$, and the overall reaction is as shown in equation (1), analogous to that found for the aqua-cations.[1–5]

$$2\,Ag^{II} + (CH_3)_2CHOH \longrightarrow 2\,Ag^{I} + (CH_3)_2CO + 2\,H^+(aq) \quad (1)$$

Table 2. Values for the pseudo-first-order rate constant for various [$\mathrm{Pr^iOH}$], $[\mathrm{H^+}]_\mathrm{T}$, and temperatures with initial [$\mathrm{Ag^{II}}$] = 2×10^{-4} mol dm^{-3} and excess [$\mathrm{Hbipy^+}$] = 4.0×10^{-3} mol dm^{-3} at I = 1.00 mol dm^{-3}

θ_c/°C	$[\mathrm{H^+}]_\mathrm{T}$/ mol dm^{-3}	[$\mathrm{Pr^iOH}$]/ mol dm^{-3}	$10^4 k_0$/s^{-1}
25.0	0.100	0.229	4.20
25.0	0.100	0.459	5.9
25.0	0.100	1.376	9.1
25.0	0.200	0.229	5.8
25.0	0.200	0.459	7.7
25.0	0.200	0.688	8.7
25.0	0.200	1.376	13.1
25.0	0.300	0.229	5.9
25.0	0.300	0.459	9.1
25.0	0.300	0.688	9.7
25.0	0.300	1.376	17.6
25.0	0.400	0.115	6.0
25.0	0.400	0.229	9.4
25.0	0.400	0.459	18.4
25.0	0.400	0.688	22.9
25.0	0.500	0.115	7.1
25.0	0.500	0.115	6.8 [b]
25.0	0.500	0.161	9.1 [a]
25.0	0.500	0.229	10.9
25.0	0.500	0.229	11.1 [b]
25.0	0.500	0.332	15.1
25.0	0.500	0.332	15.4 [a]
25.0	0.500	0.459	19.8
25.0	0.500	0.459	20.0 [b]
25.0	0.500	0.483	19.5 [a]
25.0	0.500	0.483	21.2
25.0	0.500	0.551	24.0
25.0	0.500	0.551	23.3 [a]
25.0	0.500	0.688	28.0
25.0	0.500	0.918	28.5
25.0	0.500	0.918	31.5 [b]
25.0	0.500	1.376	35.7
25.0	0.700	0.115	9.3
25.0	0.700	0.229	17.1
25.0	0.700	0.459	22.3
25.0	0.700	1.376	41.0
25.0	1.000	0.115	11.5
25.0	1.000	0.229	19.0
25.0	1.000	0.459	29.8
25.0	1.000	0.688	35.7
19.4	0.400	0.115	2.44
19.4	0.400	0.229	4.58
19.4	0.400	0.459	6.4
19.4	0.400	1.376	13.0
19.4	0.600	0.115	3.80
19.4	0.600	0.299	6.0
19.4	0.600	0.459	9.8
19.4	0.600	1.376	14.6
19.4	0.800	0.115	4.75
19.4	0.800	0.229	7.5
19.4	0.800	0.459	11.7
19.4	0.800	1.376	19.5
19.4	1.000	0.115	4.73
19.4	1.000	0.229	9.2
19.4	1.000	0.459	15.4
19.4	1.000	1.376	26.8
29.7	0.400	0.115	10.8
29.7	0.400	0.229	18.2
29.7	0.400	0.459	30.0
29.7	0.400	1.379	41.0
29.7	0.800	0.115	16.0
29.7	0.800	0.229	28.1
29.7	0.800	0.459	40.5
29.7	0.800	1.376	83
29.7	1.000	0.115	19.9
29.7	1.000	0.229	32.3
29.7	1.000	0.459	53
29.7	1.000	1.379	110
35.0	0.300	0.229	25.1
35.0	0.300	0.459	40.0
35.0	0.300	0.688	43.0
35.0	0.300	1.376	51
35.0	0.500	0.115	21.4
35.0	0.500	0.229	31.2
35.0	0.500	0.459	46.5
35.0	0.500	1.376	84
35.0	0.700	0.115	26.1
35.0	0.700	0.229	42.3
35.0	0.700	0.459	60
35.0	0.700	0.688	85
35.0	0.700	1.376	128
35.0	0.800	0.115	28.0
35.0	0.800	0.229	40.7
35.0	0.800	0.459	73
35.0	0.800	1.376	154
35.0	1.000	0.115	30.5
35.0	1.000	0.229	51
35.0	1.000	0.459	79
42.5	0.100	0.092	8.8
42.5	0.100	0.115	9.9
42.5	0.100	0.229	17.0
42.5	0.100	0.459	25.2
42.5	0.400	0.055	21.3
42.5	0.400	0.074	23.3
42.5	0.400	0.092	27.3
42.5	0.400	0.115	28.8
42.5	0.400	0.229	42.0
42.5	0.600	0.046	26.8
42.5	0.600	0.055	28.5
42.5	0.600	0.074	33.4
42.5	0.600	0.092	41.0
42.5	0.600	0.115	49.0
42.5	0.800	0.046	30.6
42.5	0.800	0.055	33.9
42.5	0.800	0.074	40.0
42.5	0.800	0.092	47.0
42.5	0.800	0.115	57
42.5	1.000	0.046	35.3
42.5	1.000	0.055	39.1
42.5	1.000	0.074	49.0
42.5	1.000	0.092	56
42.5	1.000	0.115	66

[a] Ionic strength adjusted with $\mathrm{LiNO_3}$. [b] Under nitrogen.

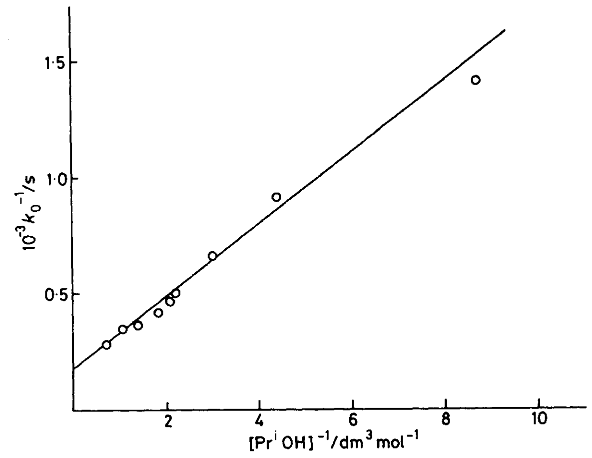

Figure 1. Plot of k_0^{-1} against $[\text{Pr}^i\text{OH}]^{-1}$ for excess $[\text{Hbipy}^+] = 4 \times 10^{-3}$ mol dm^{-3}, $[\text{H}^+]_\text{T} = 0.500$ mol dm^{-3}, 25 °C, and $I = 1.00$ mol dm^{-3}

Table 3. Values for the slopes and intercepts for the plots of k_0^{-1} against $[\text{Pr}^i\text{OH}]^{-1}$ for varying $[\text{H}^+]_\text{T}$ and temperatures at $I = 1.00$ mol dm^{-3}

θ_c/°C	$[\text{H}^+]_\text{T}$/ mol dm^{-3}	Slope/ mol dm^{-3} s	Intercept/ s
19.4	0.400	405 ± 15	528 ± 65
19.4	0.600	249 ± 7	578 ± 40
19.4	0.800	198 ± 8	410 ± 36
19.4	1.000	219 ± 4	195 ± 18
25.0	0.100	355 ± 30	900 ± 80
25.0	0.200	250 ± 29	670 ± 80
25.0	0.300	280 ± 12	470 ± 80
25.0	0.400	173 ± 9	207 ± 42
25.0	0.500	148 ± 9	186 ± 34
25.0	0.700	88 ± 22	239 ± 107
25.0	1.000	82 ± 5	162 ± 24
29.7	0.400	87 ± 2	172 ± 8
29.7	0.600	72 ± 1	125 ± 8
29.7	0.800	65 ± 5	85 ± 22
29.7	1.000	50 ± 5	73 ± 31
35.0	0.300	52 ± 3	154 ± 8
35.0	0.500	43 ± 2	110 ± 13
35.0	0.700	36 ± 2	73 ± 10
35.0	0.800	35 ± 2	62 ± 12
35.0	1.000	31 ± 2	64 ± 10
42.5	0.100	87 ± 7	215 ± 51
42.5	0.400	16.8 ± 2.0	184 ± 24
42.5	0.600	13.2 ± 1.6	106 ± 25
42.5	0.800	11.4 ± 0.8	84 ± 13
42.5	1.000	10.2 ± 1.4	65 ± 7

Table 4. Values of the pseudo-first-order rate constant (10^4k_0/s^{-1}) varying $[\text{H}^+]_\text{T}$ and $[\text{Ag}^\text{I}]$ with excess $[\text{Hbipy}^+] = 4 \times 10^{-3}$ mol dm^{-3}, $[\text{Pr}^i\text{OH}] = 0.459$ mol dm^{-3}, 25.0 °C, and $I = 1.00$ mol dm^{-3}

$10^2[\text{Ag}^\text{I}]$/ mol dm^{-3}	$[\text{H}^+]_\text{T}$/mol dm^{-3}			
	0.100	0.300	0.500	0.700
0	5.9	8.6	21.3	22.5
0.50	3.6		13.7	
1.00	1.74	4.60	9.6	14.8
2.50	0.55		6.0	7.2
5.00	0.38	1.70	3.8	4.5
10.00		1.08	2.08	2.62

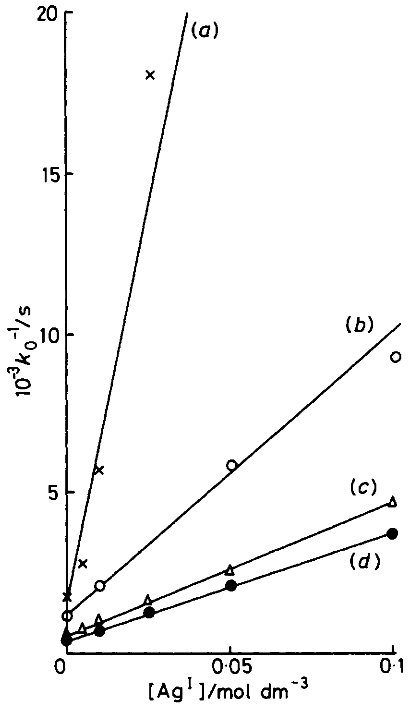

Figure 2. Plot of k_0^{-1} against $[\text{Ag}^\text{I}]$ for excess $[\text{Hbipy}^+] = 4 \times 10^{-3}$ mol dm^{-3}, $[\text{Pr}^i\text{OH}] = 0.459$ mol dm^{-3}, 25.0 °C, and $I = 1.00$ mol dm^{-3} with $[\text{H}^+]_\text{T}$ = (*a*) 0.100, (*b*) 0.300, (*c*) 0.500, and (*d*) 0.700 mol dm^{-3}

Rates of Oxidation with Low $[\text{Ag}^\text{I}]$.—Plots of log (optical density) against time for $[\text{Pr}^i\text{OH}] \gg [\text{Ag}^\text{II}]$ were always linear for an extent of reaction exceeding 80% at 19.4, 25.0, 29.7, 35.0, and 42.5 °C. Values for the pseudo-first-order rate constant k_0 obtained for a range of $[\text{Pr}^i\text{OH}]$ with a range of acidities at each temperature are given in Table 2: each value is the mean of two determinations and sometimes of three determinations. Ionic strength was normally adjusted to $I = 1.00$ mol dm^{-3} with the addition of sodium nitrate, but Table 2 shows that no change in rate occurs when sodium nitrate is replaced by lithium nitrate. Plots of k_0 against $[\text{Pr}^i\text{OH}]$ at constant acidity are curves but plots of k_0^{-1} against $[\text{Pr}^i\text{OH}]^{-1}$ are linear, and a typical example is shown in Figure 1. Table 2 also shows that removal of oxygen with nitrogen has no effect on the rate of oxidation. It is found that the slopes and intercepts of the plots of k_0^{-1} against $[\text{Pr}^i\text{OH}]^{-1}$ at constant acidity and constant temperature decrease as the acidity increases. Values for these slopes and intercepts derived using the least-squares procedure are given in Table 3.

Rates of Oxidation with High $[\text{Ag}^\text{I}]$ *at* 25 °C.—When sodium nitrate was replaced by silver nitrate the plots of log (optical density) against time remained linear but k_0 decreased with increasing $[\text{Ag}^\text{I}]$ at constant acidity (Table 4). Figure 2 shows that k_0^{-1} varies linearly with $[\text{Ag}^\text{I}]$ at constant acidity always having an intercept on the k_0^{-1} axis.

Mechanism of the Oxidation.—The linear plots of k_0^{-1} against $[\text{Pr}^i\text{OH}]^{-1}$ at constant acidity and temperature show that the oxidation proceeds through intermediate complexes involving an Ag$^\text{II}$–bipyridine species and Pr^{i}OH, although no spectral changes could be detected on mixing solutions of

$[\mathrm{Ag(bipy)_2}]^{2+}$ and $\mathrm{Pr^{i}OH}$. The retarding effect of added $\mathrm{Ag^{I}}$ cannot be interpreted by the influence of a disproportionation equilibrium [equation (2)] as this would require a kinetic order in $[\mathrm{Ag^{II}}]$ of two to be observed and the order in $[\mathrm{Ag^{II}}]$ remains as one at high $[\mathrm{Ag^{I}}]$. As the lack of any effect with $\mathrm{Li^{I}}$ suggests a specific effect of $\mathrm{Ag^{I}}$, we therefore have a similar situation to that found in the oxidation of $\mathrm{Pr^{i}OH}$ by aquasilver(II) ions [5] and in the oxidation of methanol by aquamanganese(III) ions.[14]

$$\mathrm{Ag^{II}} + \mathrm{Ag^{II}} \rightleftharpoons \mathrm{Ag^{I}} + \mathrm{Ag^{III}} \qquad (2)$$

The former case is exactly similar to that found here for oxidation by $\mathrm{Ag^{II}}$–bipyridine complexes, and in the latter case, too, the addition of high $[\mathrm{Mn^{II}(aq)}]$ retards the rate of oxidation without altering the kinetic orders in $[\mathrm{Mn^{III}(aq)}]$ and [MeOH]. We conclude that here also the redox step first occurs in a solvent cage and that $\mathrm{Ag^{I}}$ ions present in the walls of the cage when $[\mathrm{Ag^{I}}]$ is high induce a reverse reaction.

Including the equilibrium [11] involving $[\mathrm{Ag(bipy)_2}]^{2+}$ and $[\mathrm{Ag(bipy)}]^{2+}$ and the solvent sorting [7] around the proton, the following pre-equilibria will be involved [equations (3)—(8); β and β' are formation equilibrium constants].

$$[\mathrm{Ag(bipy)_2}]^{2+} + \mathrm{H^+} \overset{K_h}{\rightleftharpoons} [\mathrm{Ag(bipy)}]^{2+} + \mathrm{Hbipy^+} \qquad (3)$$

$$\mathrm{Pr^{i}OH} + \mathrm{H^+(aq)} \overset{K_c}{\rightleftharpoons} \mathrm{Pr^{i}OH_2{}^+(aq)} \qquad (4)$$

$$[\mathrm{Ag(bipy)}]^{2+} + \mathrm{Pr^{i}OH} \overset{\beta}{\rightleftharpoons} [\mathrm{Ag(bipy)(Pr^{i}OH)}]^{2+} \qquad (5)$$

$$[\mathrm{Ag(bipy)_2}]^{2+} + \mathrm{Pr^{i}OH} \overset{\beta'}{\rightleftharpoons} [\mathrm{Ag(bipy)_2(Pr^{i}OH)}]^{2+} \qquad (6)$$

$$[\mathrm{Ag(bipy)(Pr^{i}OH)}]^{2+} \overset{K}{\rightleftharpoons} [\mathrm{Ag(bipy)(Pr^{i}O)}]^{+} + \mathrm{H^+(aq)} \qquad (7)$$

$$[\mathrm{Ag(bipy)_2(Pr^{i}OH)}]^{2+} \overset{K'}{\rightleftharpoons} [\mathrm{Ag(bipy)_2(Pr^{i}O)}]^{+} + \mathrm{H^+(aq)} \qquad (8)$$

Assuming that each complex is involved in a redox step, each with its individual solvent cage, $(\mathrm{Ag^{I}}, \text{radical}) = (\text{cage})$, as the immediate product, the following rate-determining steps will be involved [equations (9)—(12)]. The free radical, $\mathrm{(CH_3)_2\dot{C}OH}$, produced by diffusion out of the cages will be converted rapidly by a further redox process on encounter with an $\mathrm{Ag^{II}}$ species into the product acetone as in equation (13), where the rate of reaction (13) is much faster than the steps in (9)—(12).

$$[\mathrm{Ag(bipy)(Pr^{i}OH)}]^{2+} \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} (\text{cage})^1 \xrightarrow{k_{1d}} \mathrm{Ag^{I}} + \text{radical} \qquad (9)$$

$$[\mathrm{Ag(bipy)_2(Pr^{i}OH)}]^{2+} \underset{k_{1b}}{\overset{k'_{1f}}{\rightleftharpoons}} (\text{cage})^2 \xrightarrow{k'_{1d}} \mathrm{Ag^{+}} + \text{radical} \qquad (10)$$

$$[\mathrm{Ag(bipy)(Pr^{i}O)}]^{+} \underset{k_{2b}}{\overset{k_{2f}}{\rightleftharpoons}} (\text{cage})^3 \xrightarrow{k_{2d}} \mathrm{Ag^{I}} + \text{radical} \qquad (11)$$

$$[\mathrm{Ag(bipy)_2(Pr^{i}O)}]^{+} \underset{k'_{2b}}{\overset{k'_{2f}}{\rightleftharpoons}} (\text{cage})^4 \xrightarrow{k'_{2d}} \mathrm{Ag^{I}} + \text{radical} \qquad (12)$$

$$\mathrm{Ag^{II}} + \text{radical} \longrightarrow \mathrm{Ag^{I}} + \text{acetone} + \mathrm{H^+(aq)} \qquad (13)$$

If the back reactions in (9)—(12) are all assumed to be first order in $[\mathrm{Ag^{I}}]$ present in the cage wall, as assumed in the $\mathrm{Ag^{II}(aq)} + \mathrm{Pr^{i}OH}$ reaction [5] and in the $\mathrm{Mn^{III}(aq)}$ + MeOH reaction,[14] and applying the stationary-state theory to each (cage)^1—(cage)^4, equation (14) follows, where $K'_h = K_h/[\mathrm{Hbipy^+}]$, $h = [\mathrm{H^+(aq)}]$, and subscript T indicates a total concentration.

$$k_0^{-1} = \frac{(1 + K'_h h)(1 + K_c h) + [\mathrm{Pr^{i}OH}]_T[\beta K'_h(h + K) + \beta'(1 + K'h^{-1})]}{2[\mathrm{Pr^{i}OH}]_T\left(\dfrac{k_{1d}k_{1f}\beta K'_h h}{k_{1b}[\mathrm{Ag^{I}}] + k_{1d}} + \dfrac{k'_{1d}k_{1f}\beta'}{k'_{1b}[\mathrm{Ag^{I}}] + k'_{1d}} + \dfrac{k_{2d}k_{2f}\beta K'_h K}{k_{2b}[\mathrm{Ag^{I}}] + k_{2d}} + \dfrac{k'_{2d}k'_{2f}\beta' K' h^{-1}}{k'_{2b}[\mathrm{Ag^{I}}] + k'_{2d}}\right)} \qquad (14)$$

If $k_{1d} = k'_{1d} = k_{2d} = k'_{2d}$ and $k_{1b} = k'_{1b} = k_{2b} = k'_{2b}$ (f = forward, b = back, d = dissociation), equation (14) reduces to the form equation (15) where a and b are constants at constant acidity and temperature, consistent with the experimental variation as illustrated in Figure 2.

$$k_0^{-1} = a + b[\mathrm{Ag^{I}}] \qquad (15)$$

Unfortunately, with the aqua-cations $\mathrm{Ag^{II}(aq)}$ [5] and $\mathrm{Mn^{III}(aq)}$, [14] the kinetics of the cation + alcohol redox reactions have to be investigated using high added concentrations of $\mathrm{Ag^{I}(aq)}$ or $\mathrm{Mn^{II}(aq)}$ to repress the formation of $\mathrm{Ag^{III}(aq)}$ or $\mathrm{Mn^{IV}(aq)}$ respectively, and therefore the derived rate constants for $\mathrm{Ag^{II}(aq)} + \mathrm{Pr^{i}OH}$ and $\mathrm{Mn^{III}(aq)}$ + MeOH are composite quantities only relevant when a complete analysis of the variation of rate with $[\mathrm{Ag^{I}(aq)}]$ or $[\mathrm{Mn^{II}(aq)}]$ has been carried out. With $\mathrm{Ag^{II}(aq)}$ as the oxidant, $\mathrm{Ag^{I}(aq)}$ affects [15] the rates of oxidation of all alcohols, and when such an analysis has not been carried out, the rate data are composite quantities including a term in $[\mathrm{Ag^{I}(aq)}]$: such composite rate data of Baiocchi and Mentasti [15] cannot therefore be used to assess the extent of the participation of equilibrium (4) in the mechanism. However, with $[\mathrm{Ag(bipy)_2}]^{2+}$ as the oxidant, such an analysis is not needed as rate constants can be determined at low $[\mathrm{Ag^{I}}]$ where they are insensitive to changes in $[\mathrm{Ag^{I}}]$.

When $[\mathrm{Ag^{I}}]$ is low, equation (14) becomes (16) which requires a linear variation of k_0^{-1} with $[\mathrm{Pr^{i}OH}]_T^{-1}$ at constant acidity and temperature producing an intercept on the k_0^{-1} axis, as observed.

$$k_0^{-1} = \frac{(1 + K'_h h)(1 + K_c h)}{2[\mathrm{Pr^{i}OH}]_T[\beta K'_h(k_{1f}h + k_{2f}K) + \beta'(k'_{1f} + k'_{2f}K'_h{}^{-1})]} + \frac{\beta K_h(h + K) + \beta'(1 + K'_h{}^{-1})}{2[\beta K'_h(k_{1f}h + k_{2f}K) + \beta'(k'_{1f} + k'_{2f}K'h^{-1})]} \qquad (16)$$

If S is the slope of these latter plots, then equation (17) follows. Figure 3 shows that plots of the left-hand side of equation (17), using the experimental values of S in Table 3 in conjunction with the values of K'_h [11] and K_c,[7] against h give linear plots intercepting at the origin for all temperatures.

$$S^{-1}(1 + K'_h h)(1 + K_c h) = 2\{\beta K'_h(k_{1f}h + k_{2f}K) + \beta'(k_{1f} + k_{2f}K'h^{-1})\} \qquad (17)$$

We conclude, therefore, from equation (17) that $k_{2f} \ll k_{1f}$ and $\beta'(k_{1f} + k_{2f}K'h^{-1}) \ll \beta K'_h k_{1f} h$ and that equation (17) reduces to (18), with only reaction (9) active as a rate-determining step and only species $[\mathrm{Ag(bipy)}]^{2+}$ really involved in the oxidation.

$$S^{-1}(1 + K'_h h)(1 + K_c h) = 2\beta K'_h k_{1f} h \qquad (18)$$

Values for $k_{1f}\beta$ determined from a least-squares analysis of the plots in Figure 3 are collected in Table 5. The plot of log $k_{1f}\beta$ against reciprocal of the absolute temperature is linear and from a least-squares analysis the enthalpy of activation $\Delta H^* = 88 \pm 5$ kJ mol^{-1} and the entropy of activation $\Delta S^* = 13 \pm 15$ J K^{-1} mol^{-1}.

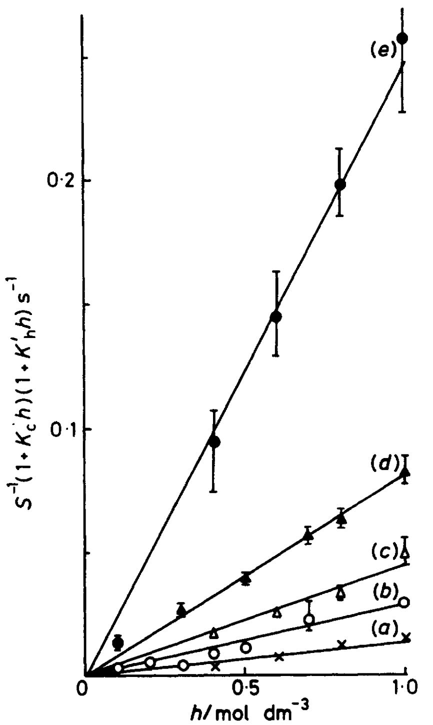

Figure 3. Plot of $S^{-1}(1 + K_c h)(1 + K'_h h)$ against h for excess [Hbipy$^+$] = 4 × 10^{-3} mol dm^{-3} and I = 1.00 mol dm^{-3} with temperature as follows: (*a*) 19.4, (*b*) 25.0, (*c*) 29.7, (*d*) 35.0, and (*e*) 42.5 °C

Table 5. Values of $k_{1f}\beta$ for varying temperature with excess [Hbipy$^+$] = 4 × 10^{-3} mol dm^{-3} and I = 1.00 mol dm^{-3}

θ_c/°C	$10^3 k_{1f}\beta$/ dm^3 mol^{-1} s^{-1}
19.4	7.9 ± 1.7
25.0	19.4 ± 3.4
29.7	29.8 ± 4.5
35.0	41.5 ± 2.0
42.5	127.5 ± 2.3

Table 6. Comparison of overall values for ΔH^*, ΔS^*, and ΔG^* for the oxidation of Pr^{i}OH with E^0 values for the oxidizing cation

Cation	ΔH^*/ kJ mol^{-1}	ΔS^*/ J K^{-1} mol^{-1}	ΔG^*/ kJ mol^{-1}	E^0/V
Ag^{II}(aq)	56	6	54	*ca.* 2.0
Co^{III}(aq)	98	80	74	1.95
Ce^{IV}(aq)	153	235	82	1.76
[Ag(bipy)]$^{2+}$	88	13	84	1.45
Mn^{III}(aq)	102	25	95	1.56
V^V(aq)	105	−43	117	1.00

Comparison with the Oxidation of Isopropyl Alcohol by Aqua-cations.—Table 6 shows a comparison of overall values of ΔG^*, ΔH^*, and ΔS^* and the redox potential E^0 of the oxidizing ion. The value of E^0 for [Ag(bipy)]$^{2+}$ has been calculated.[11] The cation [Ag(bipy)]$^{2+}$ fits in roughly with the earlier observation[4] that the increase in the free energy of activation ΔG^* parallels the decrease in E^0. However, the apportionment of this effect between the enthalpy and entropy changes remains specific to the particular oxidizing ion and the mechanism involved and will influence a detailed comparison of ΔG^* and E^0. For the simple direct attack involved with Ag^{II}(aq) and Mn^{III}(aq), ΔH^* is higher for the lower E^0 and the higher ΔS^* for Mn^{3+}(aq) is consistent with the greater solvent configurational changes pertaining to the reduction in ionic charge expected for the higher charge of Mn^{3+}(aq) compared with Ag^{2+}(aq). The relatively high ΔS^* for Co^{III}(aq), also involving direct attack, can be ascribed to the large solvent configurational changes accompanying a two-electron transfer with dimeric Co^{III}(aq).[3-5] Ce^{IV}(aq), with its intermediate complex,[2] requires a high overall ΔH^* to remove coordinated water to bring the Pr^{i}OH molecule close to the Ce atom and this release of water is accompanied by a large positive ΔS^*.[16] In contrast to the data for Ce^{IV}(aq), ΔH^* and ΔS^* for the oxidation by [Ag(bipy)]$^{2+}$, which also proceeds through an intermediate complex, appear to lie in their natural place in relation to the change in E^0; this suggests that the intermediate [Ag(bipy)]$^{2+}$–ROH complex might be outer sphere rather than inner sphere as with Ce^{IV}(aq). At first sight this may appear inconsistent with the much greater reactivity of [Ag(bipy)]$^{2+}$ in this oxidation compared with [Ag(bipy)$_2$]$^{2+}$, although no spectrophotometric evidence was found for an inner-sphere [Ag(bipy)]$^{2+}$–ROH complex. However, the same extreme difference in oxidative reactivity is also found with hydrogen peroxide as substrate[12] where no intermediate complex is detected. It was noted[12] that this naturally follows from E^0 = 1.45 V for [Ag(bipy)]$^{2+}$ being greater than E^0 = 1.05 V for [Ag(bipy)$_2$]$^{2+}$.[11]

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