# Kinetics of the Oxidation of Hydrogen Peroxide by Bis(2,2′-bipyridine)silver(II) Ions

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The kinetics of the oxidation of hydrogen peroxide by $[Ag(bipy)_2]^{2+}$ have been investigated in aqueous nitric acid. It is found that the principal reactive species of $Ag^{II}$ is $[Ag(bipy)]^{2+}$ which has been shown to exist in equilibrium with $[Ag(bipy)_2]^{2+}$. There is no direct evidence that the reaction involves intermediate ternary complexes $Ag^{II}$-(bipy)$(H_2O_2)$. The mechanism and the transition-state parameters are contrasted with those for the oxidation of $H_2O_2$ by aqua-cations and compared with those for the oxidation of $H_2O_2$ by other cations complexed by nitrogen-containing ligands, including some of biological significance.

THE kinetics of the oxidation of hydrogen peroxide by the highly oxidizing aqua-cations $Fe^{III}$, $Co^{III}$, $Mn^{III}$, $Ce^{IV}$, and $Ag^{II}$ in aqueous perchlorate media show [1] that the general mechanism involves the rapid formation of intermediate complexes between the aqua-cation $M^{n+}$ and $H_2O_2$ which then decompose slowly *via* $M^{n+}(H_2O_2)$ and $M^{n+}(HO_2^-)$ to give oxygen. It has been confirmed [2] that the oxidation [3] of hydrogen peroxide by $Mn^{III}$ complexed with the 1,2-diaminocyclohexanetetra-acetate ion also proceeds through the rapid formation of an intermediate complex of the transition-metal complex with $H_2O_2$ followed by its slow decomposition and it is suggested [4] that the oxidation of hydrogen peroxide by bis(2,9-dimethyl-1,10-phenanthroline)copper(II) follows a similar course. In general,[5-8] for the oxidation of $H_2O_2$ at higher pH by $Cu^{II}$ complexed to nitrogen-containing ligands it is assumed that ternary complexes $Cu^{II}$(nitrogen ligand)$(H_2O_2)$ are formed in rapid pre-equilibria and that these subsequently decompose slowly giving molecular oxygen. Kinetic evidence exists for two such complexes of $H_2O_2$ with $[Cu(bipy)]^{2+}$ [6] and haemocyanin [7] as orders higher than one in $[H_2O_2]$ are found and in the absence of such ternary complexes would require the unlikely event of a higher-order collision of two $H_2O_2$ molecules with metal atoms; also, intermediate yellow colours observed for complexes of $Cu^{II}$ with 1,10-phenanthroline, ethylenediamine, or 2,2′ : 6′,2″-terpyridine when $H_2O_2$ is added have been ascribed to the formation of intermediate ternary complexes.[8] Similarly, intermediate ternary complexes are also suggested for the oxidation of $H_2O_2$ at higher pH by the cobalt(III) haematoporphyrin complex.[9] Although it has been suggested that the rate-controlling step in the oxidation of hydrogen peroxide by diammineaquacobalt(III) ions [10] and by tetra-aqua(ethylenediamine)cobalt(III) [11] is the substitution of $H_2O_2$ into the inner sphere of $Co^{III}$, the oxidation of $H_2O_2$ by $Ni^{III}$ complexed through nitrogen atoms by 2,2′-bipyridine [12] or by macrocyclic ligands [13] proceeds rapidly without substitution of $H_2O_2$ into the inner sphere of $Ni^{III}$. Alternative mechanisms for the oxidation of $H_2O_2$ by $[Co(NH_3)_2(OH_2)_4]^{3+}$ and $[Co(en)(OH_2)_4]^{3+}$ have been discussed.[12]

Some kinetic observations have been made on the oxidation of $H_2O_2$ by bis(2,2′-bipyridine)silver(II) ions but only in the acidity range $4 \times 10^{-5}$—$2 \times 10^{-2}$ mol dm$^{-3}$ which is generally much lower than the ranges used in the above work except for the copper(II) complexes and the cobalt(III) haematoporphyrin complex. Po and Chen [14] found that the reaction was first order in both $[Ag^{II}]$ and $[H_2O_2]$ and that the second-order rate constant varied in a sigmoid fashion with pH. The conclusion of Banerjee and Basu [15] and Thorpe and Kochi [16] from an examination of the visible and e.s.r. spectra of this silver(II) complex that the four nitrogen atoms form a square-planar configuration around the $Ag^{II}$ without any $H_2O$ molecules at the remaining apices of the octahedron is supported by the *X*-ray crystallographic examination of Atwood *et al.* [17] and by the spectrophotometric examination in aqueous nitric acid [18] where the observations can be explained by the existence of only equilibrium (1) without interference from hydrolytic equilibria. This also agrees with the conclusion of Halpern *et al.* [19]

$$[Ag(bipy)_2]^{2+} + H^+ \overset{K_h}{\rightleftharpoons} [Ag(bipy)]^{2+} + Hbipy^+ \quad (1)$$

from their e.s.r. spectra at 77 K that only two nitrogen atoms are attached in a concentrated nitric acid medium. Our investigation [18] of equilibrium (1) also showed that 2,2′-bipyridine needs to be present in excess of the stoicheiometric concentration to ensure that all the $Ag^{II}$ is fully complexed at low acidities, a precaution not adopted by Po and Chen [14] in their oxidation studies.

A kinetic investigation of the oxidation of $H_2O_2$ by $Ag^{II}$ complexed with 2,2′-bipyridine is reported here for an acidity range of 0.1—1.0 mol dm$^{-3}$, much higher than that used by Po and Chen,[14] and comparable with that used for the oxidation by aqua-cations [1] and by $Ni^{III}$ complexed with 2,2′-bipyridine.[12] Sufficient excess of 2,2′-bipyridine was always present to ensure that only equilibrium (1) operates.

## EXPERIMENTAL

*Materials.*—AnalaR sodium nitrate, nitric acid, and 2,2′-bipyridine were used; $Ag_2[CO_3]$ and $Ag[NO_3]$ were reagent grade. Water was distilled once from an all-glass still. Solutions of hydrogen peroxide were prepared by diluting Laporte 85% stabiliser-free $H_2O_2$ and were standardised by titration against standard $Ce^{IV}$. $[Ag(bipy)_2]^{2+}$ was prepared by anodic oxidation under nitrogen of a solution containing $2.0 \times 10^{-3}$ mol dm$^{-3}$ $Ag_2[CO_3]$ and $8.0 \times 10^{-3}$ mol dm$^{-3}$ 2,2′-bipyridine in 1.0 mol dm$^{-3}$ nitric acid.[18]

*Procedure.*—Freshly prepared solutions of $[Ag(bipy)_2]^{2+}$ in 1.0 mol dm$^{-3}$ nitric acid were diluted ten-fold to give final $[H^+]$ in the range 0.1—1.0 mol dm$^{-3}$ with the ionic strength $I = 1.00$ mol dm$^{-3}$ adjusted by $Na[NO_3]$ and with the excess $[Hbipy^+]$ over that required for the stoicheiometric formation of $[Ag(bipy)_2]^{2+}$ equal to $4.0 \times 10^{-3}$ mol dm$^{-3}$. For the investigation of the effect of $Ag^I$ ions on the rate of reaction, some $Na[NO_3]$ was replaced by $Ag[NO_3]$ to maintain $I = 1.00$ mol dm$^{-3}$. It has been found [18] that the excess 2,2′-bipyridine ensures that all the $Ag^{II}$ is present as the complex $[Ag(bipy)_2]^{2+}$ at low acidities; the absorption coefficients of the $Ag^{II}$(2,2′-bipyridine) complexes are independent of $[Hbipy^+]$ with this excess present. Without this latter precaution much faster rates were observed.

The kinetics of the oxidation were followed at 450 nm using a Durrum-Gibson stopped-flow spectrophotometer with a path length of 2 cm. Concentrations of nitric acid, sodium nitrate [and silver(I) nitrate where applicable], and bipyridine were always the same in each drive syringe for any particular experiment. The temperature was controlled to ±0.1 °C or better in the bath surrounding the drive syringes by the circulation of water from a thermostat, cooled by the circulation of a water–ethanediol mixture from a cryostat for the lower temperatures. The reaction traces were photographed on the storage screen of a Tektronix oscilloscope; decay curves were only considered acceptable if three successive runs gave coincident traces on the screen. All data except $\log_{10}$ (optical density) *versus* time plots were analysed by a least-squares procedure, where appropriate.

## RESULTS AND DISCUSSION

*Stoicheiometry.*—A solution containing hydrogen peroxide was allowed to react with an excess of $Ag^{II}$ ions. A ' blank ' containing no $H_2O_2$ but identical $[Hbipy^+]$, $[H^+]$, $[Ag^{II}]$, and ionic strength was prepared at the same time as the reaction mixture and $[Ag^{II}]$ was determined spectrophotometrically at 450 nm in both mixtures after the reaction was over; the values for the absorption coefficient determined previously [18] were used at each acidity. This use of a blank allowed the reaction of $Ag^{II}$ with water (which is estimated to be less than 1% of the total reaction) to be eliminated completely. Values for $\Delta[Ag^{II}]/\Delta[H_2O_2]$ are given in Table 1 for initial $[Ag^{II}]$ *ca.* $2.2 \times 10^{-4}$ mol dm$^{-3}$ with $[H_2O_2] = 3.6 \times 10^{-5}$—$7.2 \times 10^{-5}$ mol dm$^{-3}$. The mean value of $1.94 \pm 0.15$ shows that the reaction obeys the expected overall stoicheiometry shown in equation (2).

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

TABLE 1

Values of $|\Delta[Ag^{II}]|/|\Delta[H_2O_2]|$ for excess $[Hbipy^+] = 4.0 \times 10^{-3}$ mol dm$^{-3}$ at $I = 1.00$ mol dm$^{-3}$ and 25.0 °C

| $[H^+]_T$/mol dm$^{-3}$ | $\dfrac{\lvert\Delta[Ag^{II}]\rvert}{\lvert\Delta[H_2O_2]\rvert}$ |
|---|---|
| 0.10 | 1.79 |
| 0.10 | 1.86 |
| 0.10 | 1.90 |
| 0.50 | 1.89 |
| 0.50 | 2.04 |
| 1.00 | 2.04 |
| 1.00 | 2.08 |

mean 1.94 ± 0.15

*Kinetics of the Oxidation.*—Although some oscilloscope traces showed a very small initial increase in optical density, this was too erratic and of too short a duration for any significance to be ascribed to it. The excess bipyridine found necessary [18] for the absorption coefficient to be independent of $[Hbipy^+]$ was always used; in the absence of this excess the oxidation was completed 10 ms after mixing.

In all cases, $[H_2O_2]$ was in sufficient excess over $[Ag^{II}]$ to ensure pseudo-first-order conditions, and plots of $\log_{10}$ (optical density) against time were always linear for at least 80—90% reaction. With $I = 1.00$ mol dm$^{-3}$ for a constant $[H_2O_2] = 1.28 \times 10^{-3}$ mol dm$^{-3}$ in 0.30 mol dm$^{-3}$ $HNO_3$ at 10.5 °C, the pseudo-first-order rate constant $k_0 = 40 \pm 2$ s$^{-1}$ for $[Ag^{II}]$ in the range $0.56 \times 10^{-4}$—$5.10 \times 10^{-4}$ mol dm$^{-3}$. It is therefore concluded that the reaction is first order in $[Ag^{II}]$. Table 2 shows that, for constant $[H_2O_2] = 7.16 \times 10^{-4}$ mol dm$^{-3}$ and constant $[H^+] = 0.100$ mol dm$^{-3}$ at 25.0 °C, replacement of $Na^I$ ions by $Ag^I$ ions has no effect on $k_0$. Values of $k_0$ for varying $[H_2O_2]$ and $[H^+]$ for a range of temperatures are collected in Table 3. Plots of $k_0$ against $[H_2O_2]$ at constant acidity and temperature are always linear passing through the origin, as illustrated in Figure 1. The reaction is therefore also first order in $[H_2O_2]$ and values for the second-order rate constant $k$, together with their standard errors as determined by the application of the least-squares procedure, are given in Table 4.

TABLE 2

The effect of change in $[Ag^I]$ on the pseudo-first-order rate constant with initial $[Ag^{II}]$ *ca.* $1 \times 10^{-4}$ mol dm$^{-3}$, $[H_2O_2] = 7.16 \times 10^{-4}$ mol dm$^{-3}$, $[H^+]_T = 0.10$ mol dm$^{-3}$, and excess $[Hbipy^+] = 4.0 \times 10^{-3}$ mol dm$^{-3}$ at $I = 1.00$ mol dm$^{-3}$ and 25.0 °C

| $[Ag^I]$/mol dm$^{-3}$ | $k_0$/s$^{-1}$ |
|---|---|
| | 25.5 |
| 0.050 | 25.8 |
| 0.100 | 22.2 |
| 0.200 | 27.3 |
| 0.300 | 25.0 |

As there is no evidence from the stopped-flow traces and from the variation of $k_0$ with $[H_2O_2]$ at constant acidity and constant temperature for the involvement of intermediate $Ag^{II}$–$H_2O_2$ complexes, it is assumed that this oxidation proceeds in the outer sphere of $Ag^{II}$. It has been shown [18] that pre-equilibrium (1) is established rapidly and therefore equations (3) and (4) are two possible rate-determining steps; these will be followed by the rapid removal of $HO_2^{\bullet}$ radicals by more $Ag^{II}$, as in equation (5). The protonation of 2,2′-bipyridine released from the co-ordination sphere of the silver ions

$$[Ag(bipy)_2]^{2+} + H_2O_2 \xrightarrow[(+\,H^+)]{k_1} Ag^{I} + HO_2^{\bullet} + 2Hbipy^+ \qquad (3)$$

TABLE 3

Values of the pseudo-first-order rate constant for various $[H_2O_2]$, $[H^+]_T$, and temperatures with initial $[Ag^{II}]$ *ca.* $1 \times 10^{-4}$ mol dm$^{-3}$ and excess $[Hbipy^+] = 4.0 \times 10^{-3}$ mol dm$^{-3}$ at $I = 1.00$ mol dm$^{-3}$

| Temp./°C | $[H^+]_T$/ mol dm$^{-3}$ | $10^3[H_2O_2]$/ mol dm$^{-3}$ | $k_0$/s$^{-1}$ |
|---|---|---|---|
| 25.0 | 0.100 | 0.72 | 25.5 |
| 25.0 | 0.100 | 1.43 | 44.0 |
| 25.0 | 0.100 | 2.86 | 87 |
| 25.0 | 0.100 | 5.72 | 157 |
| 25.0 | 0.200 | 0.72 | 33.0 |
| 25.0 | 0.200 | 1.43 | 80 |
| 25.0 | 0.200 | 2.86 | 157 |
| 25.0 | 0.200 | 5.72 | 310 |
| 25.0 | 0.500 | 0.72 | 93 |
| 25.0 | 0.500 | 1.43 | 181 |
| 25.0 | 0.500 | 2.15 | 238 |
| 25.0 | 0.500 | 2.86 | 317 |
| 25.0 | 0.700 | 0.63 | 112 |
| 25.0 | 0.700 | 1.25 | 215 |
| 25.0 | 0.700 | 2.00 | 274 |
| 25.0 | 0.700 | 2.50 | 343 |
| 25.0 | 1.000 | 0.72 | 135 |
| 25.0 | 1.000 | 1.43 | 282 |
| 25.0 | 1.000 | 2.15 | 382 |
| 25.0 | 1.000 | 2.86 | 520 |
| 16.8 | 0.100 | 0.64 | 14.0 |
| 16.8 | 0.100 | 1.28 | 27.2 |
| 16.8 | 0.100 | 2.20 | 46.0 |
| 16.8 | 0.100 | 2.55 | 52 |
| 16.8 | 0.100 | 4.40 | 90 |
| 16.8 | 0.300 | 0.64 | 37.0 |
| 16.8 | 0.300 | 1.28 | 66 |
| 16.8 | 0.300 | 1.36 | 87 |
| 16.8 | 0.300 | 2.71 | 168 |
| 16.8 | 0.500 | 0.64 | 55 |
| 16.8 | 0.500 | 1.10 | 98 |
| 16.8 | 0.500 | 1.48 | 126 |
| 16.8 | 0.500 | 2.20 | 180 |
| 16.8 | 0.700 | 0.63 | 74 |
| 16.8 | 0.700 | 1.25 | 127 |
| 16.8 | 0.700 | 2.20 | 240 |
| 16.8 | 0.700 | 2.50 | 270 |
| 16.8 | 1.000 | 0.64 | 94 |
| 16.8 | 1.000 | 1.10 | 147 |
| 16.8 | 1.000 | 1.28 | 156 |
| 16.8 | 1.000 | 2.20 | 302 |
| 10.5 | 0.100 | 0.72 | 8.1 |
| 10.5 | 0.100 | 2.86 | 33.0 |
| 10.5 | 0.100 | 5.72 | 61 |
| 10.5 | 0.100 | 8.59 | 86 |
| 10.5 | 0.300 | 0.72 | 25.5 |
| 10.5 | 0.300 | 1.43 | 48.0 |
| 10.5 | 0.300 | 2.86 | 101 |
| 10.5 | 0.300 | 5.72 | 187 |
| 10.5 | 0.500 | 0.72 | 39.0 |
| 10.5 | 0.500 | 1.43 | 81 |
| 10.5 | 0.500 | 2.15 | 110 |
| 10.5 | 0.500 | 2.86 | 177 |
| 10.5 | 0.700 | 0.72 | 51 |
| 10.5 | 0.700 | 1.28 | 85 |
| 10.5 | 0.700 | 2.15 | 147 |
| 10.5 | 0.700 | 2.86 | 192 |
| 10.5 | 1.000 | 0.64 | 50 |
| 10.5 | 1.000 | 1.43 | 131 |
| 10.5 | 1.000 | 1.92 | 177 |
| 10.5 | 1.000 | 2.56 | 242 |
| 4.8 | 0.100 | 0.63 | 5.5 |
| 4.8 | 0.100 | 1.25 | 12.2 |
| 4.8 | 0.100 | 2.50 | 24.0 |
| 4.8 | 0.100 | 3.65 | 35.0 |
| 4.8 | 0.100 | 4.80 | 44.0 |
| 4.8 | 0.300 | 0.63 | 13.7 |
| 4.8 | 0.300 | 1.25 | 34.0 |
| 4.8 | 0.300 | 3.65 | 91 |
| 4.8 | 0.300 | 7.30 | 173 |
| 4.8 | 0.500 | 0.63 | 24.0 |
| 4.8 | 0.500 | 1.25 | 59 |
| 4.8 | 0.500 | 2.74 | 105 |
| 4.8 | 0.500 | 3.65 | 151 |
| 4.8 | 0.700 | 0.71 | 46.0 |
| 4.8 | 0.700 | 1.41 | 84 |
| 4.8 | 0.700 | 2.12 | 129 |
| 4.8 | 0.700 | 2.83 | 170 |
| 4.8 | 1.000 | 0.71 | 50 |
| 4.8 | 1.000 | 1.41 | 108 |
| 4.8 | 1.000 | 2.12 | 144 |
| 4.8 | 1.000 | 2.83 | 210 |

$$[Ag(bipy)]^{2+} + H_2O_2 \xrightarrow{k_2} Ag^I + HO_2^{\bullet} + Hbipy^+ \qquad (4)$$

$$Ag^{II} + HO_2^{\bullet} \xrightarrow{\text{fast}} Ag^I + O_2 + H^+ \qquad (5)$$

will be very rapid. The rate of disappearance of $Ag^{II}$ for steps (1) and (3)—(5) will be given by equation (6),

$$-\frac{d[Ag^{II}]}{dt} = \frac{2(k_1 + k_2K_h'h)[Ag^{II}]_T[H_2O_2]_T}{(1 + K_h'h)} \qquad (6)$$

where subscript T indicates the total concentration of all species, $h = [H^+]$, and $K_h' = K_h[Hbipy^+]^{-1}$ with

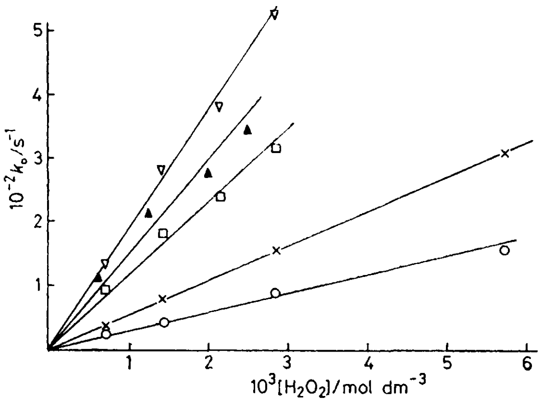

FIGURE 1 Plots of the pseudo-first-order rate constant against $[H_2O_2]$ with excess $[Hbipy^+] = 4.0 \times 10^{-3}$ mol dm$^{-3}$ at $I = 1.00$ mol dm$^{-3}$ and 25.0 °C for various acidities 0.100 (○), 0.200 (×), 0.500 (□), 0.700 (▲), 1.000 mol dm$^{-3}$ (▽)

$[Hbipy^+]$ maintained in effective constant excess at $4.0 \times 10^{-3}$ mol dm$^{-3}$.[18] The observed second-order rate constant $k$ will be given by equation (7). Equation (7)

$$k(1 + K_h'h) = 2(k_1 + k_2K_h'h) \qquad (7)$$

can be tested by plotting $k(1 + K_h'h)$ against $h$ using the values of $K_h'$ determined previously[18] in conjunction with the values of $k$ in Table 4. Figure 2 shows that linear plots are obtained for all temperatures in the range used (4.8—25.0 °C). These plots show that $k_1 \ll k_2$, and it is assumed that reaction (3) plays little part in the mechanism. Values for $10^{-4}\ k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$) determined from the slopes of Figure 2 are as follows: at 4.8 °C, 6.1; 10.5 °C, 8.4; 16.8 °C, 11.6; 25.0 °C, 14.4. A plot of log $k_2$ against reciprocal of absolute temperature is linear and, from the slope and intercept using the least-squares procedure, the enthalpy of activation $\Delta H^{\ddagger} =$

TABLE 4

Values of the second-order rate constant for the reaction of $[Ag(bipy)]^{2+}$ with $H_2O_2$ with excess $[Hbipy^+] = 4.0 \times 10^{-3}$ mol dm$^{-3}$ and at $I = 1.00$ mol dm$^{-3}$

| Temp./ °C | $[H^+]_T$/ mol dm$^{-3}$ | $10^{-3}k$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^{-4}k_2$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 4.8 | 0.100 | 9.3 ± 0.5 | |
| 4.8 | 0.300 | 23.3 ± 1.9 | |
| 4.8 | 0.500 | 39.9 ± 3.1 | |
| 4.8 | 0.700 | 59 ± 1 | |
| 4.8 | 1.000 | 73 ± 6 | 6.1 |
| 10.5 | 0.100 | 10.0 ± 0.7 | |
| 10.5 | 0.300 | 32.4 ± 1.0 | |
| 10.5 | 0.500 | 62 ± 8 | |
| 10.5 | 0.700 | 67 ± 1 | |
| 10.5 | 1.000 | 100 ± 1 | 8.4 |
| 16.8 | 0.100 | 20.2 ± 0.2 | |
| 16.8 | 0.300 | 64 ± 6 | |
| 16.8 | 0.500 | 79 ± 3 | |
| 16.8 | 0.700 | 110 ± 5 | |
| 16.8 | 1.000 | 135 ± 12 | 11.6 |
| 25.0 | 0.100 | 26.4 ± 1.1 | |
| 25.0 | 0.200 | 54 ± 3 | |
| 25.0 | 0.500 | 102 ± 6 | |
| 25.0 | 0.700 | 118 ± 12 | |
| 25.0 | 1.000 | 175 ± 9 | 14.4 |

30 ± 8 kJ mol$^{-1}$ and the entropy of activation $\Delta S^\ddagger = -62 \pm 26$ J K$^{-1}$ mol$^{-1}$ at 25 °C.

All the available evidence suggests that $Ag^{II}$ exists in a square-planar arrangement with the four nitrogen atoms of the two bipyridine ligands. Although this does not entirely exclude its existence as a considerably distorted octahedron for a $d^9$ ion with a severe Jahn-Teller distortion, the observation [18] that the variation of the absorption coefficient with acidity can be explained entirely by equilibrium (1) without any interference from the formation of hydroxo-complexes strongly supports the square-planar structure with $H_2O$ molecules excluded from the inner-sphere. It might therefore be supposed that our observation of the reactivity of $[Ag(bipy)]^{2+}$ being so much greater than that of $[Ag(bipy)_2]^{2+}$ towards $H_2O_2$ is in line with the conclusion of Sigel and co-workers [5,6,9] in their discussion of the biological activity of $Cu^{II}$ and $Co^{III}$ complexed with nitrogen ligands that the metal ion is unreactive toward $H_2O_2$ when it is completely complexed with N atoms. They found, for example, that $[Cu(bipy)]^{2+}$ is much more reactive than $[Cu(bipy)_2]^{2+}$, and they suggested that $Cu^{II}$ complexed with nitrogen ligands reacts with $H_2O_2$ only *via* ternary $Cu^{II}(ligand)(H_2O_2)$ complexes. However, although their assumption that the maximum co-ordination number towards N of $Co^{III}$ is six is probably correct, thus accounting for the high reactivity of $Co^{III}$ complexed with four N atoms toward $H_2O_2$ *via* ternary complexes,[9] their assumption [5,6] that the maximum co-ordination number to N of $Cu^{II}$ is four is probably incorrect. Irving and Mellor [20] have shown that the maximum co-ordination number of $Cu^{II}$ for N using 2,2′-bipyridine, 1,10-phenanthroline, and 5-methyl-1,10-phenanthroline is six, although, arising from steric hindrance, it is probably restricted to four for 2-methyl- and 2,9-dimethyl-1,10-phenanthroline. Moreover, although aqua-complexes seem to require the $H_2O_2$ in the inner sphere adjacent to the metal atom for oxidation to occur,[1] $H_2O_2$ certainly does not need to replace a 2,2′-bipyridine ligand from $Ni^{III}$ before the redox step occurs.[12] Although there is no evidence here for the participation of intermediate $Ag^{II}(bipy)(H_2O_2)$ complexes, they cannot be finally excluded. However, the much higher redox reactivity of $[Ag(bipy)]^{2+}$ with $H_2O_2$ compared with that of $[Ag(bipy)_2]^{2+}$ may be merely a reflection of the order in $E_0$ values (1.4 and 1.05 V respectively) [18] rather than the freeing of co-ordination sites. The importance of the relative redox potentials of the various complexes of $Cu^{II}$ with N ligands in controlling their reactivity towards $H_2O_2$ in chemical and biological situations has been emphasised by Sharma and Schubert.[7]

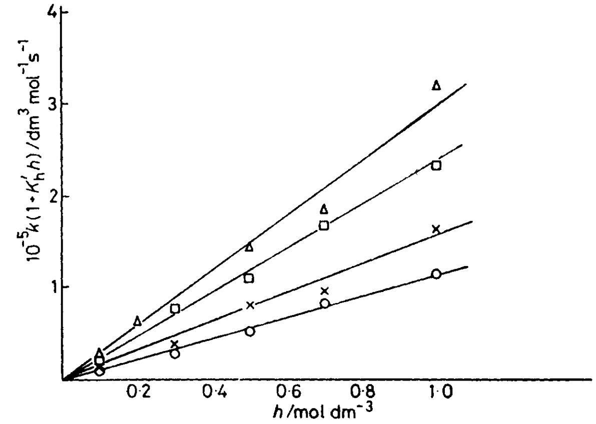

FIGURE 2 Plots of $k(1 + K_h'h)$ against $h$ with excess $[Hbipy^+] = 4.0 \times 10^{-3}$ mol dm$^{-3}$ at $I = 1.00$ mol dm$^{-3}$ for a range of temperatures: 4.8 (○), 10.5 (×), 16.8 (□), 25.0 °C (△)

For the aqua-cations reacting with $H_2O_2$, where *overall* values for the entropies of activation are available they are all positive, whereas $\Delta S^*$ for $[Ni(bipy)_3]^{3+} + H_2O_2$ has a large negative value.[12] This has been interpreted as showing a different balance between the positive $\Delta S^\ddagger$ arising from the loss of restriction of solvent water molecules in the transition state due to the loss of charge on the cation and the negative $\Delta S^\ddagger_{prot.}$ arising from the restriction imposed on water molecules in the transition state by the oxidative loss of the proton from $H_2O_2$ or $HO_2^-$. $\Delta S^\ddagger_{elec.}$ for $[Ni(bipy)_3]^{3+}$ will be smaller than that for an aqua-cation with $H_2O_2$ adjacent to the metal due to the relative remoteness of the charge from the solvent molecules or to the diffuseness of the charge in $[Ni(bipy)_3]^{3+}$. The negative $\Delta S^\ddagger$ values found for $[Ag(bipy)]^{2+}$ and for bis(2,9-dimethyl-1,10-phenanthroline)-copper(II) [4] in their reactions with $H_2O_2$ suggest therefore that the charge change here is also somewhat remote or diffuse in relation to solvent water molecules, whereas for *cis*-diammineaquacobalt(III) ions reacting with $H_2O_2$ [10] the smaller size of the complex and the accessibility of $H_2O$ molecules to the metal atom produce a positive value of $\Delta S^\ddagger$.

A detailed comparison of our results with those of Po and Chen is not feasible as, apart from the different ranges of acidities, these latter authors did not employ an excess of Hbipy$^+$.

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