Spectrophotometric Investigations in Aqueous Solution at Elevated Temperatures

Kinetics of the Reduction of Copper(I) to Copper(I) at 473 K in Aqueous Solution in the Presence of 2,2'-Bipyridyl

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The kinetics of reduction of the aqueous bis(2,2'-bipyridyl) copper(II) cation by water to the corresponding copper(I) cation have been investigated spectrophotometrically at 473 K in the concentration ranges $(0.2-2.5) \times 10^{-3}$ mol dm^{-3} copper perchlorate, $(0.2-1.8) \times 10^{-2}$ mol dm^{-3} 2,2'-bipyridyl and $(0-2) \times 10^{-2}$ mol dm^{-3} perchloric acid.

The results have been shown to be consistent with the following rate law for the reaction:

$$d[Cu^I]/dt = k_a K_a[Cu(Bipy)_2^{2+}] + k_b K_b[Cu(Bipy)_2^{2+}][Cu(Bipy)_2^+]/[H^+] + k_c K_c[Cu(Bipy)_2^+][H^+] - k_d[Cu(Bipy)_2^+]P_{O_2}.$$

At low acid concentrations the reaction proceeds by two pathways: one independent of the copper(I) species and the other autocatalysed by them in a mechanism exhibiting inverse dependence on the acid concentration. A third, acid catalysed pathway becomes significant at greater acid concentrations. In all cases the results are consistent with a rate-determining step involving the homolytic cleavage of copper–oxygen bonds. The relative amounts of the copper(I) and copper(II) species at equilibrium are strongly dependent on the concentration of oxygen initially present.

There have been a number of studies on the reduction of aqueous copper(II) in the presence of various conventional reducing agents, but few at temperatures > 323 K. The kinetics and mechanism of the reaction between carbon monoxide and copper(II) in aqueous solution at 393 K and carbon monoxide pressures up to 1.38×10^5 kPa were studied by Byerley *et al.*[1, 2] Similar studies of the oxidation of formaldehyde by copper(II) in aqueous solution [3] and the copper catalysed autoxidation of sulphite [4] have been carried out at 433 and 298 K, respectively. Brackman and Gaasbeek [5, 6] studied the kinetics and mechanism of the oxidation of methanol by copper(II) *o*-phenanthroline ions catalysed by di-tert-butyl nitroxide at 303 K.

A knowledge of the behaviour of compounds such as copper(II) + 2,2'-bipyridyl complexes at elevated temperatures is desirable because of the potential use of N-containing compounds as ligands to chelate metal ions which could otherwise cause problems in high pressure steam generating plants.[7]

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This paper reports a kinetic and mechanistic investigation of the reduction of copper(II) in aqueous solution in the presence of 2,2'-bipyridyl at 473 K.

EXPERIMENTAL

Analytical grade 2,2'-bipyridyl (Fluka), copper(II) perchlorate (Fluka) and AnalaR perchloric acid were used without further purification. The solutions employed in the kinetic study were prepared by diluting freshly prepared standard solutions.

The kinetic runs were followed spectrophotometrically using a high temperature, Teflon lined cell fitted with quartz windows and heated in an aluminium furnace as described previously.[8] The temperature in the cell, which was controlled to ± 1 K, was measured by means of an iron–constantan thermocouple extending to the surface of the inner cell.

The required amounts of copper(II) perchlorate and 2,2'-bipyridyl solution were first mixed and placed in the reaction cell. With the cell and contents in the spectrophotometer the temperature was raised to 473 K. Systematic readings at 450 nm were taken once the temperature exceeded 373 K. The cell reached 473 K after $\approx$ 20 min. The reaction was then followed until the absorbance was too great to be measured accurately ($\approx$ one absorbance unit) or until it reached completion.

In autoclave tests solutions of copper(II) perchlorate (1×10^{-3} mol dm^{-3}) and 2,2'-bipyridyl (5×10^{-3} mol dm^{-3}) were heated at 473 K for 1 h and cooled to room temperature. Red crystals were deposited from the test solution and were found to correspond to $Cu(Bipy)_2ClO_4$.

The spectrum of the products of reaction of copper(II) perchlorate (1.0×10^{-3} mol dm^{-3}) and 2,2'-bipyridyl (5.0×10^{-3} mol dm^{-3}) at 373 K is shown in fig. 1 together with that representing changes after 1 h at 473 K. The spectrum of the bis(2,2'-bipyridyl) copper(I) complex showed a broad peak over the range 400-500 nm. At 450 nm the absorbance of the Cu^{II} complex was negligible and this wavelength was chosen to follow the reaction. The measured absorbance was found to be directly proportional to the concentration of the copper(I) complex at this wavelength.
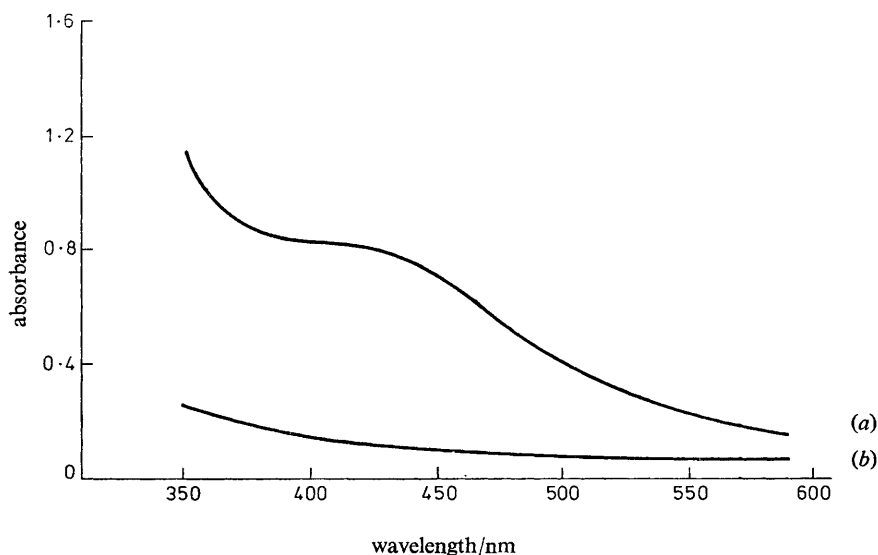

FIG. 1.—Spectra of copper(II) +2,2'-bipyridyl complex at 373 K and the reaction product at 473 K Cu(ClO$_4$)$_2$: 1×10^{-3} mol dm^{-3}; bipy: 5.0×10^{-3} mol dm^{-3}. (a) 200, (b) 100°C.

RESULTS

Plots of absorbance against time representing the reduction of copper(II) to copper(I) showed a characteristic S shape for all reactions studied under various conditions. This indicated the presence of an initial slow reaction followed by a rapid autocatalytic reduction of copper(II) to copper(I). Graphical differentiation gave curves which are nearly symmetrical about the point where 50 % reaction had occurred regardless of the initial copper(II) concentration. The maximum rate $(d[Cu^I]/dt)_{max}$ obtained at the point of 50 % reaction was used for comparison between kinetic runs as it was relatively reproducible and enabled a greater range of copper concentrations to be used.

For a second order autocatalytic reaction of the form shown in eqn (1) going to equilibrium the rate law shown in eqn (2) can be derived,

$$Red + Cu^{II} + Cu^{I} \overset{k_1}{\rightleftharpoons} 2Cu^I + Ox \tag{1}$$
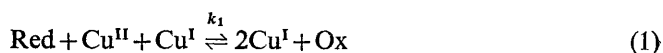
$$\frac{1}{[Cu^I]_e} \ln \left\{ \frac{[Cu^I]_e}{b} \times \frac{[Cu^I]_t - [Cu^I]_0}{[Cu^I]_e - [Cu^I]_t} \right\} = k_1 t \tag{2}$$

time/10^{-3} s
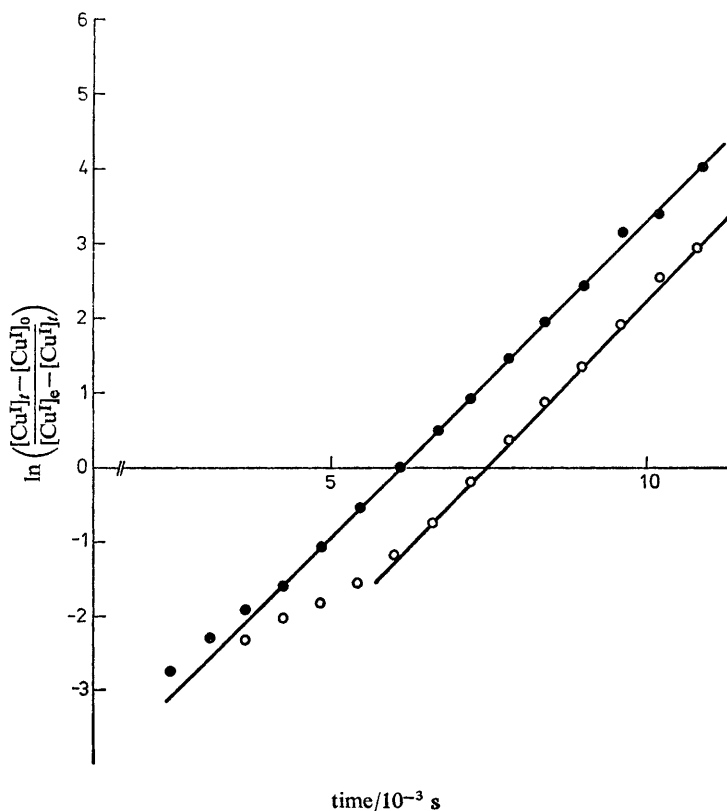
Fig. 2.—Plots of $\ln \{([Cu^I]_t - [Cu^I]_0)/([Cu^I]_e - [Cu^I]_t)\}$ against time for a second order autocatalytic reaction going to an equilibrium. $\bigcirc$, $Cu(ClO_4)_2$: 0.2×10^{-3}, bipy: 1.1×10^{-3}; $\bullet$, $Cu(ClO_4)_2$: 0.5×10^{-3}, bipy: 1.15×10^{-2} mol dm^{-3}.

where $[Cu^I]_e$ is the concentration of product at equilibrium, b is the very small initial concentration of product necessary to start the autocatalytic reaction, $[Cu^I]_t$ is the concentration of product at time t and k_1 is the constant for the forward reaction forming the product.

Plots of $\ln\{([Cu^I]_t - [Cu^I]_0)/([Cu^I]_e - [Cu^I]_t)\}$ against time shown in fig. 2, at total copper concentrations of 0.2×10^{-3} and 0.5×10^{-3} mol dm^{-3}, are linear over most of the reaction.
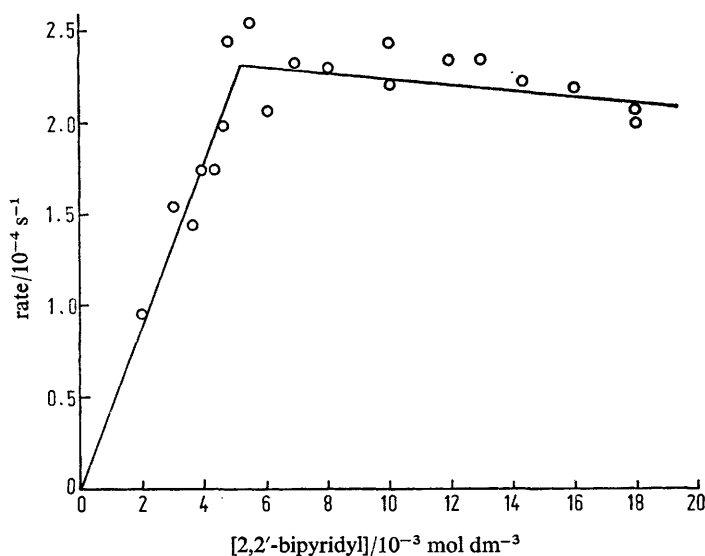

FIG. 3.—Dependence of maximum rate on 2,2'-bipyridyl concentration.   Cu(ClO$_4$)$_2$: 1.0×10^{-3};
bipy: 0–0.02 mol dm^{-3}.

The rapid increase in maximum rate observed with increasing 2,2'-bipyridyl concentration over the concentration range 0–5.5×10^{-3} mol dm^{-3}, at a constant copper(II) concentration of 1.0×10^{-3} mol dm^{-3}, is shown in fig. 3.   The figure also shows the slight decrease in this rate which occurred with further increase in 2,2'-bipyridyl concentration up to 2.0×10^{-2} mol dm^{-3}.

Fig. 4 shows plots of the concentrations of the species Cu(Bipy)$^{2+}$, Cu(Bipy)$_2^{2+}$ and Cu(Bipy)$_3^{2+}$ at 473 K calculated using the formation constants in table 1.   These constants were determined using formation constants and heats of formation for the Cu^{2+}+2,2'-bipyridyl system determined at 298 K [9, 10] and the Van't Hoft isochore $-\mathrm{d}\ln K/\mathrm{d}t = \Delta H/RT^2$.   As the concentration of copper ions is quite small relative to the ligand concentration the latter was assumed to be constant.

Plots of the maximum rates obtained (fig. 3) against the concentrations of the species (fig. 4) showed that the linear relationship given in eqn (3) existed over the concentration range of Cu(Bipy)$_2^{2+}$ of 0–8×10^{-4} mol dm^{-3}

$$(\mathrm{d}[Cu^I]/\mathrm{d}t)_{\max} = 0.327[Cu(Bipy)_2^{2+}]. \tag{3}$$

A smooth curved rapid increase in rate $[(0.8\text{-}3.5) \times 10^{-4}\ \mathrm{s}^{-1}]$ occurred with increasing initial copper(II) concentration over the measured range of 0–2.5×10^{-3} mol dm^{-3} copper(II) and at an experimental 2,2'-bipyridyl concentration determined using eqn (4)

$$[2,2'\text{-bipyridyl}]_{\mathrm{tot}} = 1.0 \times 10^{-2} + 3[Cu^{II}]_{\mathrm{tot}}. \tag{4}$$

A value of the extinction coefficient of the Cu^I species was found by the following method. Solutions of copper(II) perchlorate (1×10^{-4} mol dm^{-3}) and 2,2'-bipyridyl [(0.05-0.25) mol dm^{-3}] were prepared with varying amounts of sodium sulphite [$(0.516-2.78) \times 10^{-3}$ mol dm^{-3}]. The latter caused complete reduction of the copper(II)
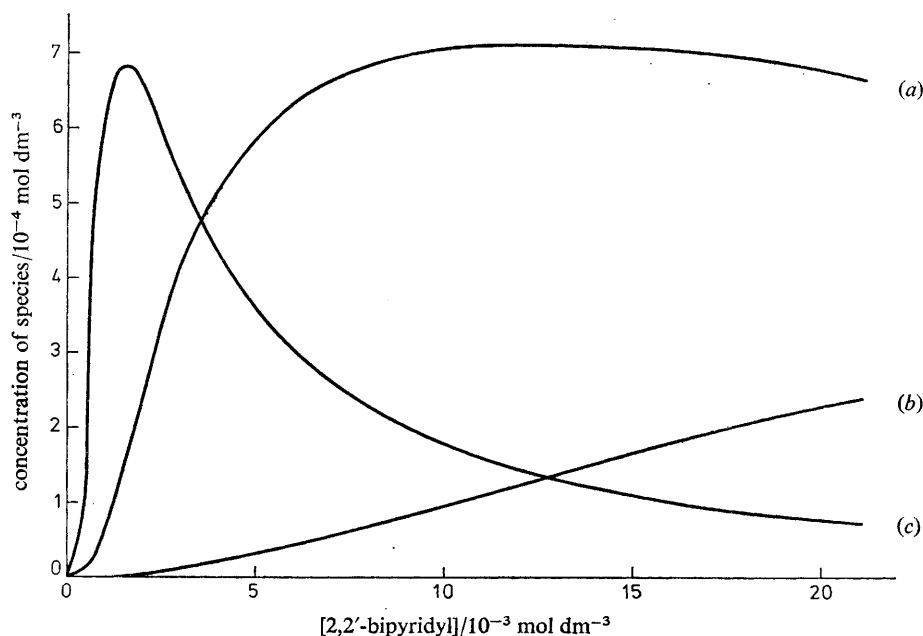

FIG. 4.—Effect of 2,2'-bipyridyl concentration on the concentration of copper(II) complexes in an aqueous solution of copper(II) perchlorate (1.0×10^{-3} mol dm^{-3}) and 2,2'-bipyridyl (0-0.02 mol dm^{-3}) at 473 K. (a) Cu (Bipy)$_2^{2+}$, (b) Cu(Bipy)$_3^{2+}$, (c) Cu (Bipy)$^{2+}$.

TABLE 1.—THERMODYNAMIC DATA [9, 10] FOR THE COPPER(II)+2,2'-BIPYRIDYL COMPLEXES AT 298 AND 473 K

| | enthalpy of formation | stepwise equilibrium constants (K_n) | |
	ΔH_{298}/kJ mol^{-1}	298 K	473 K
K_1	-58.51	10^8	10 742
K_2	-41.69	3.98×10^5	591
K_3	-30.94	3.02×10^3	24

to copper(I) and scavenged any oxygen present. The solutions were allowed to equilibrate in the cell at 473 K, the equilibrium absorbance was measured and an extinction coefficient of 4050 ± 100 calculated by use of the Beer–Lambert law.

At the point of maximum rate the influence of the concentration of Cu^I species involved in reaction can be determined. At this point of 50 % reduction the contribution of the initial reaction to the overall rate was so small as to be negligible.

A linear dependence of the maximum rate on the term $[Cu^{II}][Cu^{I}]$ was then exhibited over the range $[Cu^{II}]_{tot}$ $0\text{-}2.5 \times 10^{-3}$ mol dm^{-3} [eqn (5)]

$$(d[Cu^{I}]/dt)_{max} = 2.14 \times 10^{4}[Cu^{I}][Cu^{II}]. \tag{5}$$

Using the initial rates of reaction from the results with increasing initial copper(II) concentration a linear dependence of rate on $Cu(Bipy)_2^{2+}$ concentration [shown in eqn (6)] was obtained over the range $[Cu(Bipy)_2^{2+}]$ $(0.15\text{-}1.8) \times 10^{-3}$ mol dm^{-3} for the slow initial reaction

$$(d[Cu^{I}]/dt)_{init} = 6.78 \times 10^{-2}[Cu(Bipy)_2^{2+}]. \tag{6}$$

Addition of acid $(0\text{-}0.2$ mol dm$^{-3})$ at constant copper concentration $(2 \times 10^{-3}$ mol dm$^{-3})$ and 2,2′-bipyridyl concentration calculated according to eqn (7)

$$[Bipy]_T = 3[Cu^{II}]_T + [H^+]_T + 1 \times 10^{-2} \tag{7}$$

produced a pronounced minimum in the maximum rate at 10^{-3} mol dm^{-3} (as shown in fig. 5) up to an acid concentration of 0.25×10^{-2} mol dm^{-3} the maximum rate was found to be inversely proportional to this concentration [eqn (8)]

$$(d[Cu^{I}]/dt)_{max} = 1.218 \times 10^{-8}/[H^+] + 0.66 \times 10^{-4}, \tag{8}$$

while above it a direct proportion was indicated [eqn (9)]

$$(d[Cu^{I}]/dt)_{max} = 5.38 \times 10^{-3}[H^+] + 0.65 \times 10^{-4}. \tag{9}$$
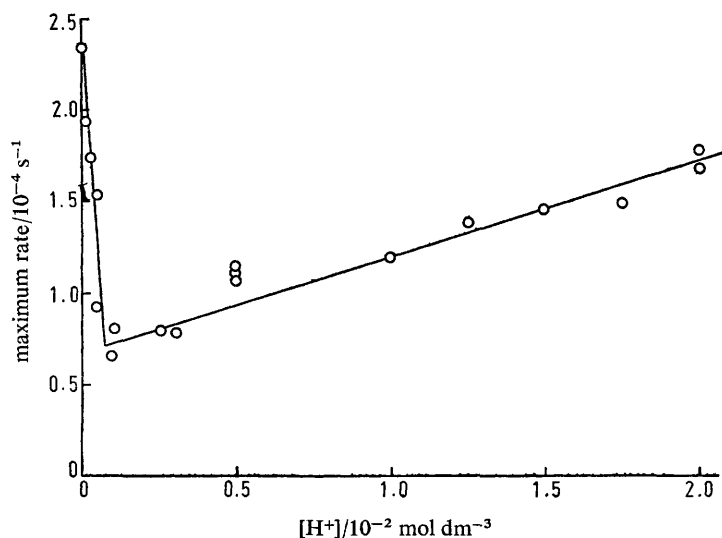
FIG. 5.—Dependence of the maximum rate on the total acid concentration. $Cu(ClO_4)_2$: 1×10^{-3} mol dm^{-3}; bipy: $(1.0 \times 10^{-2} + [H^+]_{tot} + 3[Cu^{II}]_{tot})$ mol dm^{-3}; $HClO_4$: $0\text{-}0.02$ mol dm^{-3}.

Experiments in which the concentration of copper was also systematically varied showed that eqn (9) can be written as eqn (10) for the higher range of acid concentrations

$$(d[Cu^{I}]/dt)_{max} = 3.40 \times 10^{2}[Cu^{I}][H^+] + 0.62 \times 10^{-4}. \tag{10}$$

Under both the high and low acid conditions the majority of the acid present was in the form of the 2,2-bipyridyl cation. Calculations using the formation constants in table 1 and a value of K_a of 4.78×10^{-4} previously determined at 473 K [11] showed

that over the range of acid studied the concentration of each of the copper complexes is virtually constant. A selection of the results is shown in table 2.

The effect of oxygen concentration on the system was assessed qualitatively by varying the methods of deoxygenation of the water prior to commencement of the reaction. Table 3 gives the results of runs carried out using various different methods of deoxygenation under the same conditions of copper and 2,2'-bipyridyl concentration. With increasing deoxygenation the induction period for reaction and the maximum rate were largely unaffected, but the final absorbance was markedly increased.

TABLE 2.—CONCENTRATIONS/10^{-4} mol dm^{-3} OF COMPLEXES PRESENT IN THE SYSTEM COPPER(II) + 2,2'-BIPYRIDYL + PERCHLORIC ACID

| [H$^+$]total	[HL$^+$]	[CuL^{2+}]	[CuL$_2^{2+}$]	[CuL$_3^{2+}$]
1	0.958	1.31	7.11	1.56
50	48	1.29	7.11	1.59
100	96	1.27	7.11	1.62
150	144	1.25	7.10	1.64
200	193	1.23	7.10	1.67

TABLE 3.—END POINT ABSORBANCES AND MAXIMUM RATES FOR RUNS AT DIFFERENT DEGREES OF INITIAL DEOXYGENATION

run*	end point (absorbance)	maximum rate /10^{-5} s^{-1}
A	0.24	5.7
B	0.29	5.7
C	0.41	5.8
D	0.47	7.1

* Conditions: copper(II): 0.2×10^{-3} mol dm^{-3}; 2,2'-bipyridyl: 3.1×10^{-3} mol dm^{-3}; increasing deoxygenation in the order A < B < C < D.

RATE LAW AND PROPOSED MECHANISM

The results are consistent with water acting as the reductant and oxygen being generated according to eqn (11): during the reaction the equilibrium would move to the left with increasing total oxygen concentration, resulting in a lower final copper(I) concentration

$$4Cu^{II} + 2H_2O \rightleftharpoons 4Cu^{I} + 4H^+ + O_2. \tag{11}$$
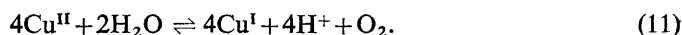
A rate equation consistent with the observations summarised above is given in eqn (12)

$$d[Cu^I]/dt = k_1[Cu^{II}] + k_2[Cu^{II}][Cu^I]/[H^+] + k_3[Cu^I][H^+] - k_4[Cu^I]P_{O_2}. \tag{12}$$

In the absence of added acid the symmetrical S-form of the experimental curves is indicative of the $k_1[Cu^{II}]$ term initially controlling the rate but increasing control and eventual predominance of the term $k_2[Cu^{I}][Cu^{II}]$ as the concentration of Cu^{I} increases. The linear relationship evident in eqn (6) and the results shown in fig. 2 and eqn (5) support this assertion.

From these results it is evident that the acid affects different paths of the reaction depending on the concentration. Below 0.25×10^{-2} mol dm^{-3} an acid/copper-2,2'-bipyridyl competition exists and above 0.25×10^{-2} mol dm^{-3} acid catalysis predominates.
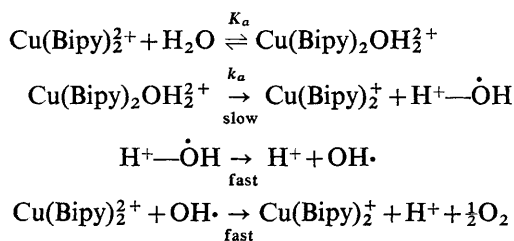
At low concentrations of added acid (up to 0.25×10^{-2} mol dm^{-3}) the linear relationship shown in eqn (8) holds and, at the point of maximum rate, this relationship should be associated with the $[Cu^{I}][Cu^{II}]$ term [and thus with the second term in eqn (12)]. The non-zero intercept indicated by eqn (8) and (9) for the dependence on acid at " low " and " high " acid concentrations, respectively, substantiates the participation of the pH independent component $k_1[Cu^{II}]$ in the rate equation. This component was not evident in the form of eqn (5) and (6) which related to the dependence on copper concentrations.

The linear rate dependence on " high " acid concentration given in eqn (9) indicates that an acid catalysed path exists in competition with the contribution from the second term of eqn (12) and eqn (10) further indicates that this term involves Cu^{I} and H^+ species hence the term $k_3[Cu^{I}][H^+]$ in the rate equation.
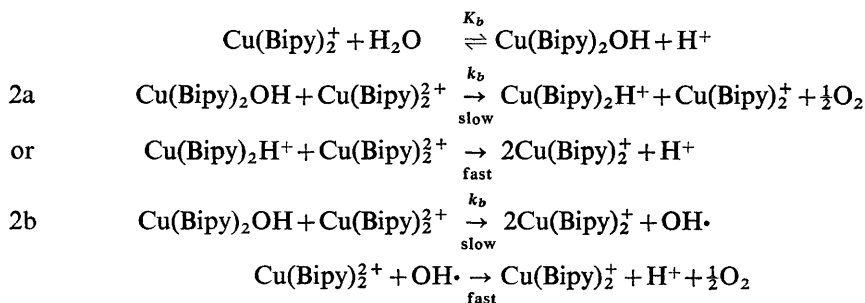
The final term of eqn (12) has not been derived experimentally in this study: the nature of high temperature aqueous spectrometry and the experimental constraints imposed by available apparatus precluded quantitative investigation. The term, however, describes the type of reaction thought to occur in the system considered.

A reaction mechanism consistent with eqn (12) and involving three pathways may be postulated as below:

PATH 1 (INDUCTION)

$$Cu(Bipy)_2^{2+} + H_2O \underset{}{\overset{K_a}{\rightleftharpoons}} Cu(Bipy)_2OH_2^{2+}$$

$$Cu(Bipy)_2OH_2^{2+} \underset{slow}{\overset{k_a}{\rightarrow}} Cu(Bipy)_2^+ + H^+{-}\dot{O}H$$

$$H^+{-}\dot{O}H \underset{fast}{\rightarrow} H^+ + OH\cdot$$

$$Cu(Bipy)_2^{2+} + OH\cdot \underset{fast}{\rightarrow} Cu(Bipy)_2^+ + H^+ + \tfrac{1}{2}O_2$$

PATH 2 (AUTOCATALYSIS)

$$Cu(Bipy)_2^+ + H_2O \underset{}{\overset{K_b}{\rightleftharpoons}} Cu(Bipy)_2OH + H^+$$

2a $$Cu(Bipy)_2OH + Cu(Bipy)_2^{2+} \underset{slow}{\overset{k_b}{\rightarrow}} Cu(Bipy)_2H^+ + Cu(Bipy)_2^+ + \tfrac{1}{2}O_2$$

or $$Cu(Bipy)_2H^+ + Cu(Bipy)_2^{2+} \underset{fast}{\rightarrow} 2Cu(Bipy)_2^+ + H^+$$

2b $$Cu(Bipy)_2OH + Cu(Bipy)_2^{2+} \underset{slow}{\overset{k_b}{\rightarrow}} 2Cu(Bipy)_2^+ + OH\cdot$$

$$Cu(Bipy)_2^{2+} + OH\cdot \underset{fast}{\rightarrow} Cu(Bipy)_2^+ + H^+ + \tfrac{1}{2}O_2$$

PATH 3 (ACID CATALYSIS)

$$Cu(Bipy)_2^+ + H_3O^+ \overset{K_c}{\rightleftharpoons} Cu(Bipy)_2(H_3O)^{2+}$$

$$Cu(Bipy)_2(H_3O)^{2+} \underset{slow}{\overset{k_c}{\rightarrow}} Cu(Bipy)_2H^+ + H^+ - \overset{\bullet}{O}H$$

$$Cu(Bipy)_2H^+ + Cu(Bipy)_2^{2+} \underset{fast}{\rightarrow} 2Cu(Bipy)_2^+ + H^+$$

$$H^+ - \overset{\bullet}{O}H \underset{fast}{\rightarrow} H^+ + OH\cdot$$

$$Cu(Bipy)_2^{2+} + OH\cdot \underset{fast}{\rightarrow} Cu(Bipy)_2^+ + \tfrac{1}{2}O_2 + H^+.$$

To account for the overall equilibrium situation the reoxidation of $Cu(Bipy)_2^+$ by oxygen could follow the mechanism

$$Cu(Bipy)_2^+ + O_2 \overset{rapid}{\rightleftharpoons} Cu(Bipy)_2O_2^+$$

$$Cu(Bipy)_2O_2^+ + Cu(Bipy)_2^+ + 2H^+ \overset{k_d}{\rightarrow} 2Cu(Bipy)_2^{2+} + H_2O_2.$$
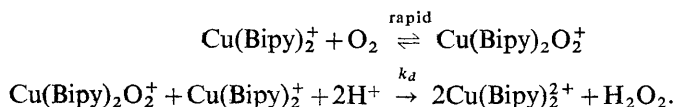
Other pathways [10, 13, 14] have been postulated for the oxidation of the Cu^I species under other conditions, some of which could account for the system existing in this study.

The overall rate law derived from the above paths is shown in eqn (13)

$$d[Cu^I]/dt = k_aK_a[Cu(Bipy)_2^{2+}] + k_bK_b[Cu(Bipy)_2]^{2+}[Cu(Bipy)_2^+]$$
$$/[H^+] + k_cK_c[Cu(Bipy)_2^+][H^+] - k_d[Cu(Bipy)_2^+]P_{O_2}. \tag{13}$$

The proposed mechanism indicates that path 1 is predominant initially but after a short induction time to build up a sufficient concentration of the copper(I) complex the autocatalytic reaction in path 2 rapidly takes over. In the presence of acid the equilibrium in path 2 will be suppressed and the autocatalytic reaction then goes *via* path 3, an acid catalysed pathway. The concentration of the copper(I) complex will increase until its rate of oxidation by oxygen is in balance with the rate of reduction so that an equilibrium situation is attained.

The observations (table 3) that oxygen concentration has little effect on the rate of reduction of copper(II) to copper(I) indicates that products of the oxidation of Cu^I to Cu^{II} by oxygen are not involved in the rate determining steps in the reduction reactions of Cu^{II} to Cu^I shown in paths 1, 2 and 3.

DISCUSSION

The experimental results are consistent with the hypothesis that in water the primary process (path 1) involves the homolytic cleavage of a Cu^{II}–solvent bond. Such reactions have been postulated in the photo-reduction of the bis(2,9-dimethyl-1, 10-phenanthroline) copper(II) complex ion at 298 K[12] and it seems reasonable to assume at least one labile water molecule is coordinated to $Cu(Bipy)_2^{2+}$.[15] This slow spontaneous reduction will lead to the formation of further copper(I) complexes *via* a mechanism of the type shown in path 2. During the induction period the concentration of $Cu(Bipy)_2^+$ will slowly increase until the considerably faster path 2 becomes predominant. The autocatalytic route (path 2) postulates the rapid formation of an equilibrium concentration of $Cu(Bipy)_2OH$. The involvement of this type of species in the rate determining step is indicated by the increase in rate with acid con-

centration and the inverse dependence on acid concentration shown in eqn (8). The two alternative pathways for the reduction of $Cu(Bipy)_2^{2+}$ are kinetically indistinguishable. In both cases the slow step is the attack on a Cu—O bond by copper(II). In path 2(a) the slow step implies the transfer of an H atom or hydride ion. Removal of a hydride ion from H_2 to form CuH^+ has already been postulated for the mechanism of hydrogen reduction by copper.[16] [The available thermodynamic data indicate that the formation of alternate products such as copper atoms and a proton are energetically inconsistent ($341\ kJ\ mol^{-1}$) with the activation energy of $109\ kJ\ mol^{-1}$ observed for the reduction of copper(II) by molecular hydrogen in which CuH^+ is the proposed intermediate].[17, 18] The CuH^+ species is decomposed rapidly by reaction with another copper(II) species. The alternative mechanism involves the cleavage of the copper–oxygen bond to yield hydroxyl radicals which react (in what is regarded a fast reaction) with further copper(II) ions.

In the presence of increasing acid the formation of the $Cu(Bipy)_2OH$ complex will gradually be inhibited resulting in the observed decrease in rate of reaction, but with increasing acid concentration an acid catalysed reaction (Path 3) begins to predominate. Little is known about the reactivity of the copper(I) complexes but it seems likely that there is a rapid equilibrium with a hydronium ion under strong acid conditions. The rate determining step is then the formation of a $Cu(Bipy)_2H^+$ species and this is rapidly decomposed by reaction with another copper(II) species.

The effect of the initial oxygen concentration on the point of equilibrium can be understood provided the rate law for the oxidation is dependent on the oxygen concentration. This is clearly supported by work on the oxidation of cuprous-ammine complexes [13] and of the compound $Cu(CH_2CN)_4ClO_4$,[14] for both of which reaction is dependent on oxygen concentration, and on the oxidation of bis(2,2'-bipyridyl) copper(I) by oxygen, which shows a first order dependence on the copper complex and oxygen concentration.[19] The mechanism of the oxidation of the bis(2,2'-bipyridyl) copper(I) complex in this study is unclear and could involve a number of alternative pathways.[13, 14, 19, 20]

Previous studies involving the reduction of Cu^{II} to Cu^I in the presence of N containing ligands such as histidine,[21] imidazole [22] and o-phenanthroline [20] indicated that only copper(I) species with less than three coordinated N-ligands are active although the bis(2,2'-bipyridyl) copper(II) complex [23] has been considered as a catalytically active species in the decomposition of hydrogen peroxide. Although Cu^{2+}–bidentate ligand 1:2 complexes are not usually considered as active species, in this study the bis(2,2'-bipyridyl) copper(II) complex clearly is active in relation to the mono(2,2'-bipyridyl) copper(II) analogue. Apparently the geometry of the coordination sphere of Cu^{2+} can have unexpected effects which strongly depend on the kind of ligand bound. The main requirement for effective catalytic activity would seem to relate to the rate at which the copper(II) and copper(I) coordination spheres can be made to resemble each other on each side of the catalytic cycle. This would be facilitated by the rapid loss of weakly bound ligands such as H_2O or H_3O^+.

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