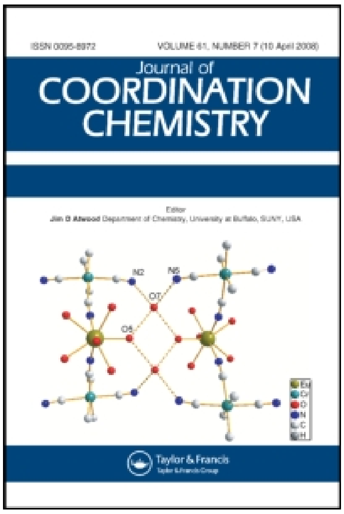

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FURTHER STUDIES ON THE KINETICS AND MECHANISM OF THE COPPER-IMIDAZOLE CATALYSED DECOMPOSITION OF HYDROGEN PEROXIDE

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The catalytic decomposition of hydrogen peroxide in the presence of the tetrakis(imidazole)copper(II) complex was investigated. The kinetics, based on the rates of oxygen evolution, indicated that a ternary copper(II)–imidazole–peroxo complex is involved in the rate-determining step. The equilibrium constant for the coordination of hydrogen peroxide to the cupric ion, and the acid dissociation constant for the coordinated H_2O_2 ligand were calculated as $1.7\,M^{-1}$ and $2.1 \times 10^{-9}\,M$, respectively. The ternary complex undergoes intramolecular electron transfer, with $k = 4\,s^{-1}$, generating Cu(I) species which can react with hydrogen peroxide or dioxygen, returning to the catalytic cycle. A complete mechanism is proposed, based on the kinetics of oxygen and on the electrocatalytic behaviour observed for the copper–imidazole complexes under a dioxygen atmosphere.

Keywords: Peroxide, copper, catalysis, kinetics, mechanism

INTRODUCTION

The catalytic activity of copper(II) complexes in reactions of hydrogen peroxide and dioxygen has been extensively investigated,[1,2] due to its implication in many chemical and biological processes.[3] The activity depends on the ligand coordinated to the metal ions, and is considerably enhanced in the case of ligands such as pyridine,[4] 2,2′-bipyridine,[5] ethylenediamine[6] and 1,10-phenanthroline.[7,8] In polymeric catalysts,[9] the coordination of copper to amino groups also increases the catalytic activity of the metal ion.

Among the factors which determine the reactivity of these complexes are their redox potentials and structural characteristics. In the catalysis by copper enzymes, such as laccase, the high potential of the active centre is attributed mainly to the great stabilization provided by the ligands.[10] It has also been reported that binuclear complexes with appropriate Cu–Cu distances exhibit a higher activity than planar mononuclear ones.[11]

The catalytic decomposition of hydrogen peroxide by copper(II)–imidazole complexes was studied by Sharma and Schubert,[12] taking into account the formation of over 20 simple, mixed and hydrolysed species existing in dynamic equilibrium at pH 6–8. The study was carried out at low imidazole (im) concentrations, *e.g.*, 10^{-4}–10^{-2} M, and the kinetics indicated that $[Cu(im)_2]^{2+}$ and $[Cu(im)_2(OH)]^{+}$ were the

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most active species in the catalysis. Another important study on the catalytic reactions of copper(II) complexes[13] showed that ternary Cu(II)–peroxo–ligand complexes are involved in the mechanism.

Here, we have extended the previous investigation[12] on the catalytic activity of copper(II)–imidazole complexes, by working under experimental conditions in which the primary species in solution is $[Cu(im)_4]^{2+}$. This species is tetracoordinated, exhibiting a planar configuration[14] and a redox behaviour[15] which is closely related to biological systems.

EXPERIMENTAL

The copper(II)–imidazole complexes were prepared in aqueous solution by adding appropriate amounts of a standardized stock solution of copper(II) nitrate to solutions of the ligand. Hydrogen peroxide free from stabilizers was kindly supplied by Peroxidos do Brasil. The solutions were prepared by dilution and analysed by reaction with sodium metavanadate.[16] All other chemicals were of analytical grade and were used without further purification.

Measurements of the catalytic decomposition of hydrogen peroxide were made manometrically,[17] using a Warburg apparatus from B. Braun (model V-85). The rates of oxygen evolution were obtained from the initial slopes of a plot of dioxygen evolved *versus* time. All kinetic experiments were carried out at 308K. The initial and final pH of the reaction solutions was checked with a Digimed DMPH-2 pH meter. Distilled, deionized water was used in all the experiments. The ionic strength was kept constant with lithium perchlorate ($I = 0.100$ M).

Electrochemical measurements were carried out with a Princeton Applied Research instrument consisting of a 173 potentiostat and a 175 universal programmer. A platinum working electrode was employed, in the presence of a platinum foil as an auxiliary electrode. Measurements were referenced to an Ag/AgCl (1 M KCl) electrode, using the conventional Luggin capillary arrangement to minimize the ohmic drop.

The electronic spectra were recorded with a Hewlett-Packard 8451-A diode array spectrophotometer.

RESULTS AND DISCUSSION

Copper(II) ions form successive complexes with imidazole in aqueous solution. Based on the stability constants reported in the literature,[18,19] it can be shown that at total imidazole concentrations above 0.10 M, the primary species in solution is the tetra-substituted complex $[Cu(im)_4]^{2+}$. For this reason, the kinetic experiments were performed at $[im] = 0.20$ M, pH = 9.45. The initial rate method was used to determine the order of the reaction with respect to the various species participating in the reaction.

In the evaluation of the influence of the catalyst concentration on the rates of dioxygen evolution (v_i), a non-catalytic step was also observed (v_0). The plot of (v_i–v_0) *versus* the total concentration of copper(II) ions (1–8 μM) was linear, at different levels of hydrogen peroxide (0.129–0.855 mM), as shown in Figure 1.

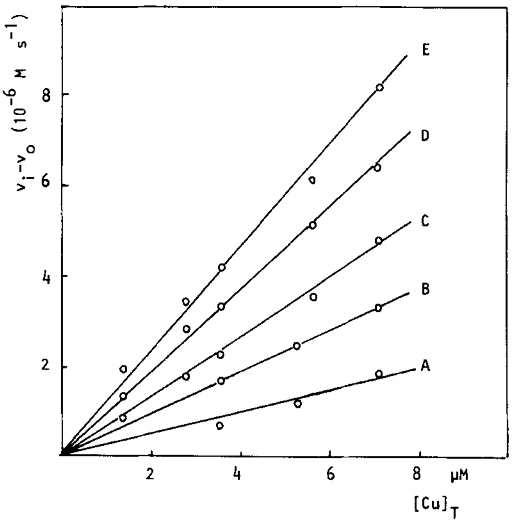

FIGURE 1 First-order dependence of the hydrogen peroxide decomposition rates on the total copper concentration; [im] = 0.200 M, 308K, I = 0.100 M($LiClO_4$), [H_2O_2] = 0.0188 M (A), 0.0243 M (B), 0.0343 M (C), 0.0635 M (D) and 0.0855 M (E).

The estimated value of the rate constant for the non-catalytic step, $v_o = 7.3 \times 10^{-7}$ M s^{-1} was independent of both catalyst and hydrogen peroxide concentrations. This step can be attributed to the slow, base-induced dismutation of hydrogen peroxide in alkaline solution. The proposed scheme for this chain reaction involves the participation of reactive free radicals,[20] including the following steps (*1*)–(*4*).

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \qquad (1)$$
$$H_2O_2 + HO_2^- \rightarrow O_2^{\cdot -} + HO\cdot + H_2O \qquad (2)$$
$$HO\cdot + H_2O_2 \rightarrow O_2^{\cdot -} + H_2O\cdot + H^+ \qquad (3)$$
$$2O_2^{\cdot -} + H_2O \rightarrow O_2 + HO_2^- + OH^- \qquad (4)$$

The rate constant for the initiation step (equation *2*) has been determined[20] as 1.88×10^{-7} M^{-1} s^{-1}. The attack of HO· radicals at the imidazole ligand, both coordinated or free, can also compete successfully with reaction (*3*) under the conditions used.

At total copper concentrations varying from 2.12 μM to 7.08 μM, the kinetics exhibited saturation behaviour with the concentration of hydrogen peroxide. Such an effect is typical of Michaelis–Menten kinetics, and the linearity of the Lineweaver–Burk plot of $1/(v_i - v_o)$ *versus* $1/[H_2O_2]$, shown in Figure 2, indicates that the reaction proceeds *via* the formation and subsequent breakdown of a ternary copper–imidazole–peroxo complex.

Only a very small dependence of v_i on the concentration of the imidazole ligand (0.15–0.50 M) was observed, as shown in Figure 3, confirming the expectation that $[Cu(im)_4]^{2+}$ plays a main role in the catalytic cycle.

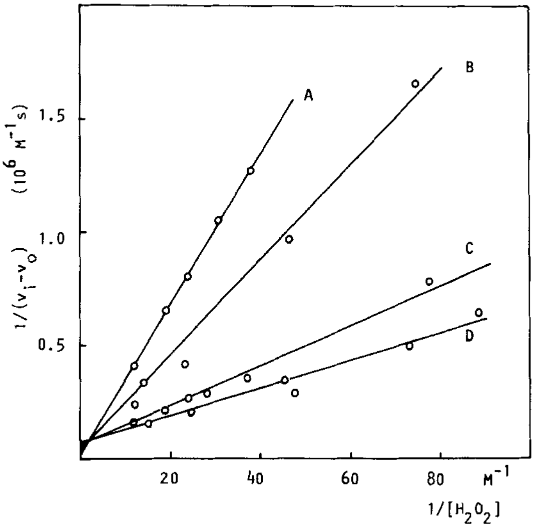

FIGURE 2 Lineweaver-Burk plots, at pH 9.45 and conditions as in Figure 1; $[Cu]_T = 2.12\,\mu M$ (A), $2.83\,\mu M$ (B), $5.66\,\mu M$ (C), and $8.85\,\mu M$ (D).

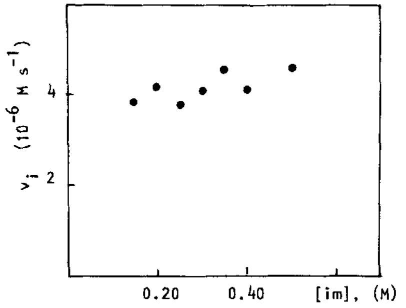

FIGURE 3 Dependence of the initial rates on the concentration of imidazole; pH 9.45, 308K, $[H_2O_2] = 0.063$ M, and $[Cu]_T = 3.54\,\mu M$.

The pH influence on the kinetics was also investigated. Over the range of pH from 8 to 11, an S-shaped curve was observed, as shown in Figure 4A. These results indicate the participation of deprotonated species in the activated complex, with a pKa of about 9. The pKa of imidazole and H_2O_2 are 14.3[13] and 11.6,[21] respectively; however, in the coordinated form their acidity may be considerably greater. The water molecules weakly interact with the $[Cu(im)_4]^{2+}$ ions, thus playing only a minor role, in contrast to those in the $[Cu(im)_2(H_2O)_2]^{2+}$ species.[12] Since hydrogen peroxide is strongly involved in the activated complex, it seems reasonable to assign the pKa = 9 to the deprotonation of the coordinated H_2O_2 molecule.

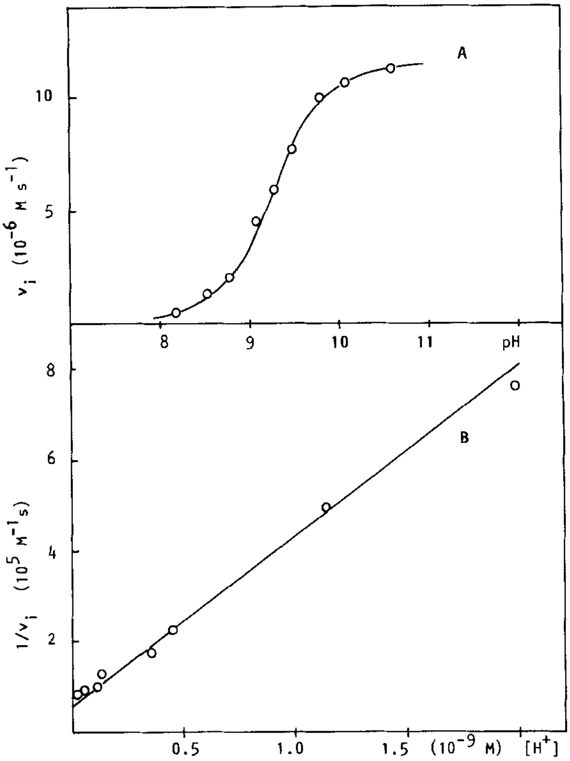

FIGURE 4 Effects of pH on the rates (v_i) of hydrogen peroxide decomposition (A) and plot of $1/v_i$ against [H^+] (B); [H_2O_2] = 0.0338 M, $[Cu]_T$ = 4.96 μM, [im] = 0.200 M.

According to the experimental results, the following scheme can be proposed for the decomposition of hydrogen peroxide catalysed by $[Cu(im)_4]^{2+}$, (*5*)–(*7*).

$$[Cu^{II}(im)_4]^{2+} + H_2O_2 \rightleftharpoons [Cu^{II}(im)_4(H_2O_2)]^{2+} \qquad K_1 \qquad (5)$$

$$[Cu^{II}(im)_4(H_2O_2)]^{2+} \rightleftharpoons [Cu^{II}(im)_4(HO_2^-)]^{+} + H^+ \qquad K_2 \qquad (6)$$

$$[Cu^{II}(im)_4(HO_2^-)]^{+} \rightarrow \text{Products} \qquad k_3 \qquad (7)$$

The initial equilibrium step involves the binding of a hydrogen peroxide molecule to the catalyst, and is followed by the acid dissociation of the coordinated peroxo ligand. The catalytically active species is then a ternary peroxy-complex, which can undergo intramolecular electron transfer, yielding Cu^I-superoxide species as immediate products in equation (*7*). Assuming the steady-state hypothesis for these species, the rate of oxygen evolution can be expressed by (*8*)

$$d[O_2]/dt = (k_3K_2K_1/[H^+])[Cu(im)_4][H_2O_2] \qquad (8)$$

or

$$d[O_2]/dt = k_{obs}\,[Cu]_T$$

where $k_{obs} = k_3[H_2O_2]/\{[H^+]/K_2K_1 + (1 + [H^+]/K_2)[H_2O_2]\}$ and $[Cu]_T$ refers to the total copper concentration.

The experimental data agree very well with equation (*8*). From the double reciprocal plot shown in Figure 5, and the pH-dependence of the plot of Figure 4B, the kinetic constant k_3 and the equilibrium constants K_1 and K_2 were evaluated as 4 ($\pm$1) s^{-1}, 1.7 M^{-1} and 2.1 × 10^{-9} M (pKa = 8.66), respectively.

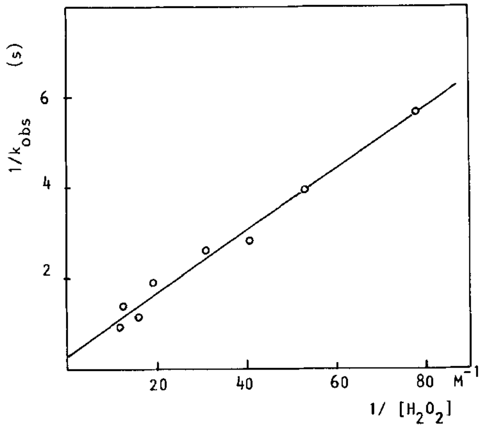

FIGURE 5 Double reciprocal plot used in the evaluation of the kinetic and equilibrium constants involved in the catalytic decomposition of hydrogen peroxide by $[Cu(im)_4]^{2+}$; [im] = 0.200 M, 308K, I = 0.100 M ($LiClO_4$).

In order to provide supplementary data for the kinetic studies, electrochemical measurements were carried out for the $[Cu(im)_4]^{2+}$ complex. The cyclic voltametric plots obtained in the presence of argon were typically reversible, as shown in Figure 6. The half-wave potentials depended on the imidazole concentration (0.05–2.0 M) according to equation (*9*)

$$E\,(V\ vs\ SHE) = 0.060(\pm 0.03) - 0.116(\pm 0.05)\log[im] \qquad (9)$$

which is the Nernst equation for the $[Cu(im)_4]^{2+}/[Cu(im)_2]^+$ redox couple[22] shown in (*10*).

$$[Cu^{II}(im)_4]^{2+} \rightleftharpoons [Cu^{I}(im)_2]^+ + 2\,im + e^- \qquad (10)$$

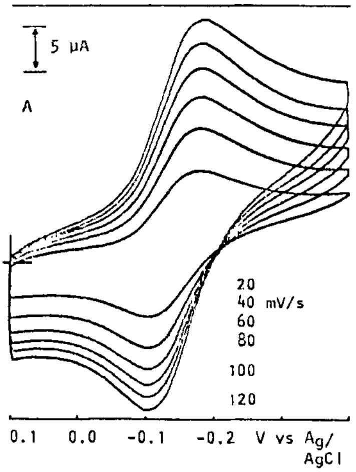

FIGURE 6 Cyclic voltammograms of the $[Cu(im)_4]^{2+}$ complex, 0.78 mM; [im] = 0.200 M, I = 0.10 M (KCl), 298K, argon atmosphere.

When the voltammetry measurements were performed in the presence of dioxygen, an increase of the cathodic peak was observed, simultaneously with the disappearance of the corresponding anodic peak, as shown in Figure 7A. The intensity of the cathodic peak increased with the oxygen concentration. The reduction and reoxidation cycle can be repeated indefinitely, by bubbling nitrogen or oxygen into the solution. The observations indicate that after the electron transfer step (equation *10*), the $[Cu^I(im)_2]^+$ species react with dioxygen yielding $[Cu^I(im)_x(O_2)]^+$ intermediates which can be further oxidized to Cu(II) and H_2O_2 products. In this way the copper(II) complex can return to the electrocatalytic cycle.

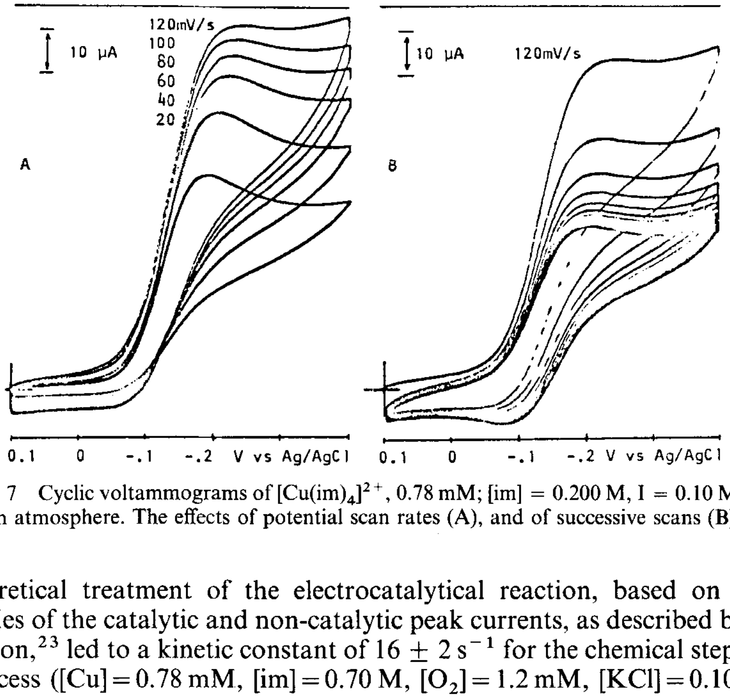

FIGURE 7 Cyclic voltammograms of $[Cu(im)_4]^{2+}$, 0.78 mM; [im] = 0.200 M, I = 0.10 M (KCl), 298K, a dioxygen atmosphere. The effects of potential scan rates (A), and of successive scans (B) are shown.

Theoretical treatment of the electrocatalytical reaction, based on the relative intensities of the catalytic and non-catalytic peak currents, as described by Shain and Nicholson,[23] led to a kinetic constant of $16 \pm 2\ s^{-1}$ for the chemical step involved in the process ([Cu] = 0.78 mM, [im] = 0.70 M, $[O_2]$ = 1.2 mM, [KCl] = 0.10 M, 298 K).

The autoxidation of the copper(I) imidazole complex has already been investigated by Zuberbuhler,[24] by following the oxygen consumption with a coated oxygen sensor, and the formation of copper(II) by means of stopped-flow techniques. The proposed rate law (equation *11*)

$$-d[O_2]/dt = 6.4 \times 10^3\ [Cu(im)_2]\ [O_2]\ [Him] \qquad (11)$$

is consistent with the $[Cu(im)_3(O_2)]^+$ composition for the reactive complex in the rate-determining step.

Under the conditions employed in this work, the calculated catalytic constant based on equation *(11)* is $15\ s^{-1}$, a result which is in excellent agreement with the electrochemical data.

The cuprous ions can also be oxidized by the hydrogen peroxide which accumulates during the reaction. On observing the effect of successive scans under a dioxygen atmosphere, in the cyclic voltammetry plots of Figure 7B, it is evident that the anodic signal is not completely restored when the dissolved O_2 near the electrode surface is depleted. This observation can be explained by considering that the oxidation of the cuprous ions can also proceed, although more slowly, by reaction with hydrogen peroxide.

Based on the results obtained for the reactions of copper–imidazole complexes with hydrogen peroxide and dioxygen, the following global mechanism (Figure 8) can be proposed for the catalytic and electrocatalytic processes.

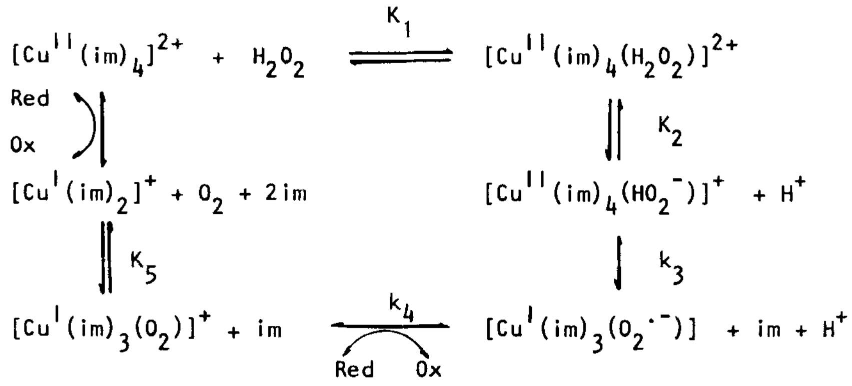

FIGURE 8 Mechanism of the $[Cu(im)_4]^{2+}$-catalysed decomposition of hydrogen peroxide.

An alternative mechanism, involving coordination of a second H_2O_2 molecule followed by the reaction of H_2O_2 and HO_2^- within the coordinated shell, has been proposed in the case of the copper(II)–2,2′-bipyridine system.[13] In our case however, it seems unreasonable, since it would lead to a quadratic law with hydrogen peroxide, in contrast to the experimental results.

The proposed mechanism is in harmony with the kinetic and electrochemical data, and in principle, it can provide a useful model for the understanding of the biological processes involving tetracoordinated copper(II) enzymes.

ACKNOWLEDGEMENTS

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