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Oxidation of 3,5-ditert-butylcatechol catalyzed by copper(II) complexes. A kinetic study

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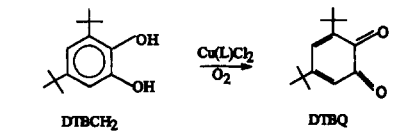
Abstract—Copper(II) complexes of the ligands (6-methyl-2,2′-dipyridyl)methane (MeDPM) and (6,6′-dimethyl-2,2′-dipyridyl)methane (diMeDPM) were prepared and used as catalysts for the oxidation of 3,5-ditert-butylcatechol to 3,5-ditert-butyl-*o*-benzoquinone. The rate of reaction was determined in the presence and absence of base (KOH) in methanol. The kinetic data are interpretated, postulating two reactive species towards molecular oxygen: a copper(I) complex and a species described as a ternary copper(II) catecholate complex. © 1997 Elsevier Science Ltd

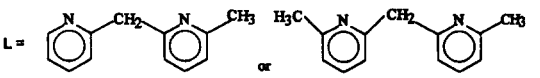
Keywords: oxidation; catalysis; 3,5-ditert-butylcatechol; copper(II) complexes; kinetics; dioxygen.

One of the interests in copper–dioxygen chemistry arises from the occurrence of several metalloproteins that contain copper as the central metal atom. These proteins have different functions, such as dioxygen transport, mono-oxygenation, dioxygenation, oxidation and superoxide dismutation [1–3].

Interest in studying small molecular weight copper(II) complexes as models for copper oxidase enzymes has led to the synthesis of many dinuclear and mononuclear copper(II) complexes, with the idea that these complexes might mimic the reactions of several copper-containing proteins, such as tyrosinase. One of the functions of tyrosinase is to catalyze the oxidation of catechols to quinones. In the model systems that have been studied, geometric factors around the copper ions have been cited as the most dominant feature in determining the catalytic activity of the copper complexes. Mononuclear copper(II) complexes with a distorted tetrahedral and trigonal bipyramidal structure, and binuclear complexes with two metal centers separated by 3–4 Å, catalyze the oxidation process. Square-planar mononuclear complexes and binuclear complexes with a larger copper–copper distance have been shown to be unreactive [4–16].

We have investigated the catalytic activity of two non-planar copper(II) complexes with (6-methyl-2,2′-dipyridyl)methane and (6,6′-dimethyl-2,2′-dipyridyl)methane ligands for the oxidation of 3,5-ditert-butylcatechol ($DTBCH_2$) by molecular oxygen in methanol solution. Only 3,5-ditert-butyl-*o*-benzoquinone (DTBQ) was isolated as the oxidation product.





On the basis of the kinetic results obtained, a plausible reaction scheme for the oxidation of the catechol, catalyzed by the copper(II) complexes, is proposed.

EXPERIMENTAL

Materials

All reagents and solvents were of high purity grade and were purchased from commercial sources and

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used as received unless noted otherwise. (6-Methyl-2,2′-dipyridyl)methane (MeDPM) and (6,6′-dimethyl-2,2′-dipyridyl)methane (diMeDPM), and the corresponding copper(II) complexes were prepared by literature methods [17,18].

Measurements

The C, H, N elemental analyses were performed on a Fison–Carlo Erba EA1108 model analyzer; ^{1}H NMR spectra were recorded on a Bruker Advance DRX300 instrument, using $CDCl_3$ as solvent with tetramethylsilane as internal standard. Electronic spectroscopy was performed on a Perkin–Elmer Lambda 11 spectrophotometer using methanol (Chrom AR HPLC, Mallinckrodt) as solvent, and IR spectra were obtained on a Bruker spectrophotometer. X-Band ESR spectra were recorded on a Bruker ECS106 spectrometer at room temperature.

Electrochemistry was performed in methanol solution using 0.1 M tetra-n-butylammonium perchlorate as electrolyte. The cyclic voltammograms were recorded at a glassy carbon electrode, with a saturated calomel reference electrode and a Pt wire as an auxiliary electrode, on an EG&G Parr model 362 scanning potentiostat.

Kinetic measurements were made spectrophotometrically on a Perkin–Elmer Lambda 11 spectrophotometer, following the appearance of DTBQ over time (400 nm absorbance maximum, $\varepsilon = 1600$ M^{-1} cm^{-1} in methanol).

Oxidation method

Reactions were carried out in 50 cm^3 flasks with a gas inlet tube, a condenser with a drying tube and a dropping funnel under an oxygen atmosphere, at a controlled temperature. In a typical experiment the copper(II) complex (2 mmol) was dissolved in 20 cm^3 of methanol. The oxidation reaction was started by adding a methanolic solution of DTBC (10 mmol) to the catalytic solution by means of the dropping funnel. The reaction mixture was left for 7 h and analyzed by GLC. The only reaction product formed was DTBQ, which was obtained in essentially quantitative yield, and characterized by elemental analysis, melting point, IR and NMR data.

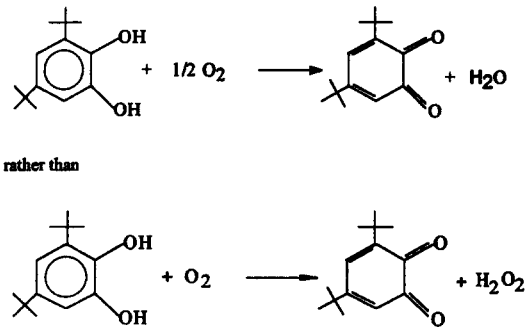
Oxygen absorption measurements

Oxygen absorption measurements were conducted in a constant-pressure gas absorption apparatus consisting of a reaction vessel with a magnetic stirrer connected to a gas buret and a U-tube manometer. The whole reaction system was saturated with oxygen for 30 min under vigorous stirring. When equilibrium was attained, the $DTBCH_2$ solution was added with a syringe to the catalytic solution in the thermostated reaction vessel. Oxygen consumption was measured after the reaction mixture had achieved a new equilibrium.

RESULTS AND DISCUSSION

Data on the catalyzed oxidation of $DTBCH_2$ show that only DTBQ was produced almost quantitatively and that other oxidation products, such as carbon–carbon bond cleavage products, were not obtained.

The O_2 uptake experiments showed that the stoichiometry of the copper(II) complex-catalyzed oxidation of catechol was $DTBCH_2:O_2 = 2:1$. The stoichiometry for the oxidation of $DTBCH_2$ conforms to the equation:



Cyclic voltammetric data

Upon oxidizing catechol, both tyrosinase and the copper(II) complexes are reduced to copper(I). Cyclic voltammetry was used to determine the ease of reduction of the complexes studied here, since the redox potential should be such as to permit the subsequent reoxidation by molecular oxygen of the reduced species in order to maintain the catalytic cycle. Therefore, it was of interest to compare the redox properties of the copper(II) complexes with their catalytic activity.

The cyclic voltammograms for the systems studied are shown in Figs 1 and 2. Only the curves corresponding to the $Cu(MeDPM)Cl_2$ catalyst are shown, since $Cu(diMeDPM)Cl_2$ exhibits similar behavior.

The electrochemical data show that the reduction potentials of the two copper(II) complexes do not depend on the number of methyl groups substituted at the pyridine rings of the ligands. Both complexes have positive reduction potentials, which compare well with the reported value of 0.36 V vs the standard calomel reference for the enzyme tyrosinase isolated from mushroom (*Agaricus bisporus*) [19].

$$Cu(MeDPM)^{2+} + e \underset{0.38\,V}{\overset{0.30\,V}{\rightleftharpoons}} Cu(MeDPM)^{+} \quad (1)$$

$$Cu(diMeDPM)^{2+} + e \underset{0.37\,V}{\overset{0.27\,V}{\rightleftharpoons}} Cu(diMeDPM)^{+} \quad (2)$$

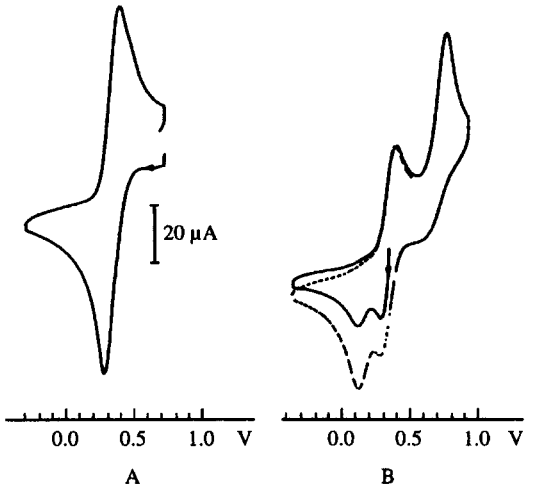


Fig. 1. Cyclic voltammograms for: (A) $Cu(CuMeDPM)Cl_2$ 1.0×10^{-3} M. (B) $Cu(MeDPM)Cl_2$ and $DTBCH_2$ 0.5×10^{-3} M, scanning towards reduction. Electrolyte: 0.1 M tetraethylammonium perchlorate in methanol.

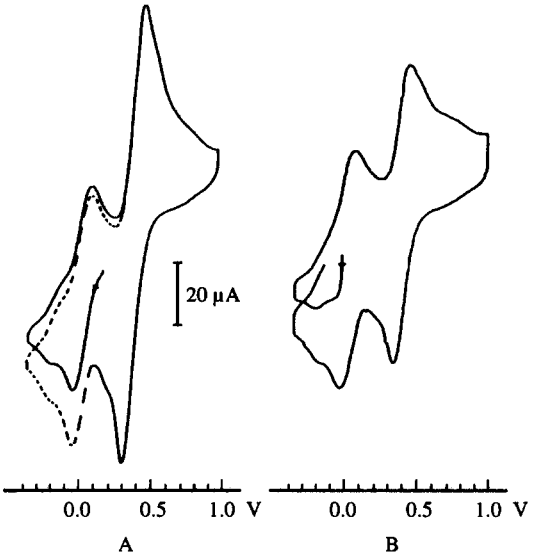


Fig. 2. Cyclic voltammograms for solutions of $Cu(MeDPM)Cl_2$ and $DTBCH_2$ 0.5×10^{-3} M in the presence of KOH. (A) Molar ratio 2:1:2, (B) molar ratio 1:1:2. Electrolyte: 0.1 M tetraethylammonium perchlorate in methanol.

These results suggest that these ligands are weaker than other pyridine-containing ligands, and that, therefore, the coordination environment of the complexes is softer (Table 1).

The addition of $DTBCH_2$ to a solution of the copper(II) complex alters the peaks observed in the voltammogram. Towards reduction, a peak at 0.12 V appears, and corresponds to the reduction potential of DTBQ in acid medium.

$$DTBQ + 2H^+ + 2e \xrightarrow{0.12\,V} DTBCH_2 \qquad (3)$$

During the first sweep towards oxidation a signal at 0.38 V appears, which corresponds to the reoxidation of the copper(I) formed by the reaction with catechol. The addition of increasing quantities of catechol, until a ratio of $1:10 = Cu^{II}L : DTBCH_2$ is reached, only reduces the intensity of the reduction peak at 0.30 V.

The above experimental data can be explained by the following equilibrium:

$$2\,Cu^{II}L + DTBCH_2 \longleftrightarrow 2\,Cu^{I}L + DTBQ + 2\,H^+ \qquad (4)$$

The addition of base to the system produces a new reduction peak at −0.04 V, which corresponds to the process,

$$Cu^{I}L + DTBQ + e \underset{0.02\,V}{\overset{-0.04\,V}{\rightleftharpoons}} Cu^{II}L(DTBC^{2-}) \qquad (5)$$

When the ratio $Cu^{II}L : DTBCH_2 : OH^- = 2:1:2$ is reached the voltammogram only shows this redox couple, together with $Cu^{II}L/Cu^{I}L$, and it is identical

Table 1. Electrochemical data for copper complexes with pyridine-derived ligands

	$E_{red.}$(V)	References
$Cu(MeDPM)Cl_2$	0.30[a]	This work
$Cu(diMeDPM)Cl_2$	0.27[a]	This work
$Cu(BP)Cl_2$	0.07[b]	20
$Cu(phen)Cl_2$	−0.02[b]	20
$Cu(tpyma)Cl_2$	−0.32[c]	16
$Cu(tpyca)Cl_2$	−0.04[c]	16

MeDPM = (6-methyl-2,2′-dipyridyl)methane; diMeDPM = (6,6′-dimethyl-2,2′-dipyridyl)methane; BP = 2,2′-bipyridine; phen = 1,10-phenanthroline; tpyma = tris(2-pyridylmethyl)amine; tyrea = tris (2-pyridylethylamine).

[a]In EtOH.

[b]In DMF.

[c]In H_2O.

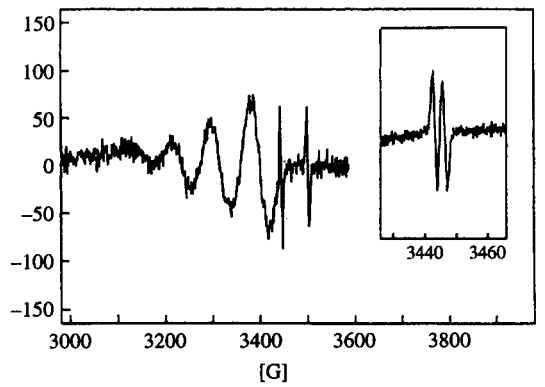


Fig. 3. EPR spectrum of a solution of a mixture of $Cu(MeDPM)Cl_2$ (2.0×10^{-3} M) $DTBCH_2$ and KOH in a molar ratio of 1 : 1 : 2, in methanol. Insert: details of the band assigned to the semiquinonate species.

with the scan obtained for a solution of $Cu^{I}L$ with DTBQ. When the ratio $Cu^{II}L : DTBCH_2 : OH^- = 1 : 1 : 2$ is reached, the first reduction scan does not show peaks, while towards oxidation the peak at 0.02 V, corresponding to the oxidation of $Cu^{II}L(DTBC^{2-})$, is observed, followed by the reoxidation of the $Cu^{I}L$ produced.

EPR spectroscopy

Spectroscopic studies confirmed the data obtained by cyclic voltammetry. A solution of $Cu^{II}L : DTBCH_2 : OH^- = 2 : 1 : 2$ is EPR inactive, thus indicating that the species present are $Cu^{I}L$ and DTBQ [Eq. (4)], while a solution of $Cu^{II}L : DTBCH_2 : OH^- = 1 : 1 : 2$ shows a signal corresponding to $Cu^{II}L(DTBC^{2-})$ (Fig. 3). At room temperature the EPR spectrum of the solution shows a four-line pattern with hyperfine coupling to the two di(2-pyridyl)methane nitrogen atoms on the high field portions of the signal.

With respect to the charge distribution of this type of compound, it has been pointed out that an equilibrium with a semiquinonate (SQ) copper(I) species can take place [21]. Since the original complex has a distorted tetrahedral geometry, the reduction to copper(I) is favored, since this geometry is preferred by the reduced form of copper.

$$Cu^{II}L(DTBC^{2-}) \longleftrightarrow Cu^{I}L(SQ^{\cdot -})$$

This type of equilibrium depends on the donor atoms that bond to the copper center [22]. Nitrogen donor ligands tend to favor a catecholate species, while phosphorus donor ligands favor a semiquinonate species. Besides, the reactivity of these species would correspond more to complexes of copper(I) than copper(II). In the specific case studied, the EPR spectrum shows a signal of low intensity at 3445 G, with a coupling constant of approximately 3 G (Fig. 3), being indicative of a semiquinonate copper(I) complex [23].

This experimental fact is a proof of the counter ligand dependence of the charge distribution in copper–catecholate complexes. The bipyridine and phenanthroline ligands permit the isolation of mixed ligand–copper(II) complexes with catecholate [24], while the di(2-pyridyl)methane ligands used in this work permit the detection of both the catecholate and semiquinonate species in equilibrium in methanol solution.

UV–visible spectroscopy

The $Cu^{II}L$ species presents an absorption band at 782 nm ($\varepsilon = 115\ M^{-1}\ cm^{-1}$). This band suffers a shift to higher energies, 754 nm, when catechol is added, indicating that an interaction between the copper ion and the substrate takes place. Besides, the addition of catechol to a solution of the copper(II) complex is accompanied by the appearance of an absorption band at *ca* 390 nm. This band is a shoulder of a more intense absorption in the ultraviolet region. This same spectrum is obtained when copper(I) is mixed with quinone in acid medium.

When base is added the band corresponding to $Cu^{II}L$ disappears and the shoulder at 390 nm is intensified. This increase in absorbance continues until a ratio of $Cu^{II}L : DTBCH_2 : OH^-$ of 2 : 1 : 2 is reached. This spectrum is equivalent to the one obtained with a solution of $Cu^{I}L$ and DTBQ under the same conditions.

It is important to emphasize that the absorption band at 530 nm ($\varepsilon = 2 \times 10^3\ M^{-1}\ cm^{-1}$) of the copper(II) catecholate is not observed, as has been reported for the copper(II) catecholate bipyridine complex [24].

When the ratio $Cu^{II}L : DTBCH_2 : OH^- = 1 : 1 : 2$ the spectrum is completely different, showing an absorption band at *ca* 500 nm, which can be assigned to a charge-transfer band owing to copper(II) catecholate species. This behavior is reversible.

Kinetic studies

Since DTBQ shows a characteristic band at 400 nm, and the concentration of copper(II) complex is too small to interfere with the measured absorbance value, this absorbance at 400 nm can be a good measure for the progress of the oxidation of the substrate, $DTBCH_2$.

Kinetic date for the system without added base (KOH). The kinetic law was determined by the method of initial rates, and the appearance of the reaction product was followed spectrophotometrically. The behavior of the system is similar for both catalysts; therefore, the figures in the text refer mostly to $Cu(MeDPM)Cl_2$.

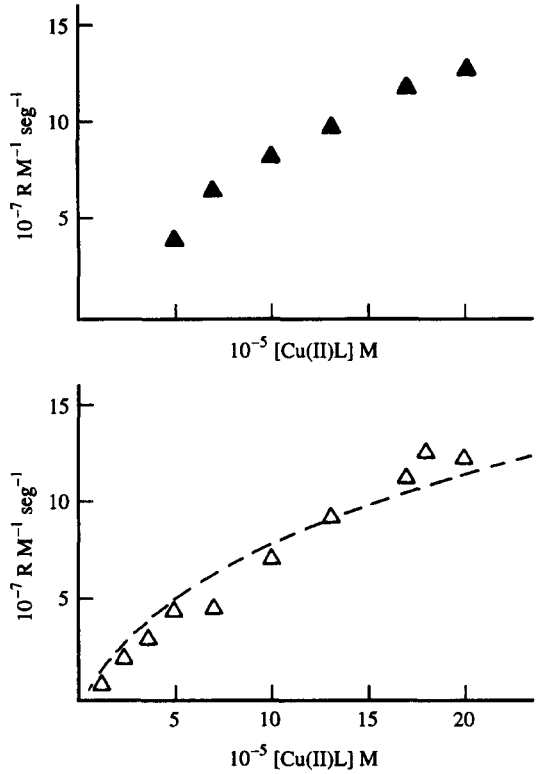


Fig. 4. Rate of oxidation versus concentration of copper catalyst at constant concentration of $DTBCH_2$ (1×10^{-3} M). ◁: experimental data for $Cu(MeDPM)Cl_2$; ----: simulated curve using $K_i = 1 \times 10^{-10}$; ▲: experimental data for $Cu(diMeDPM)Cl_2$.

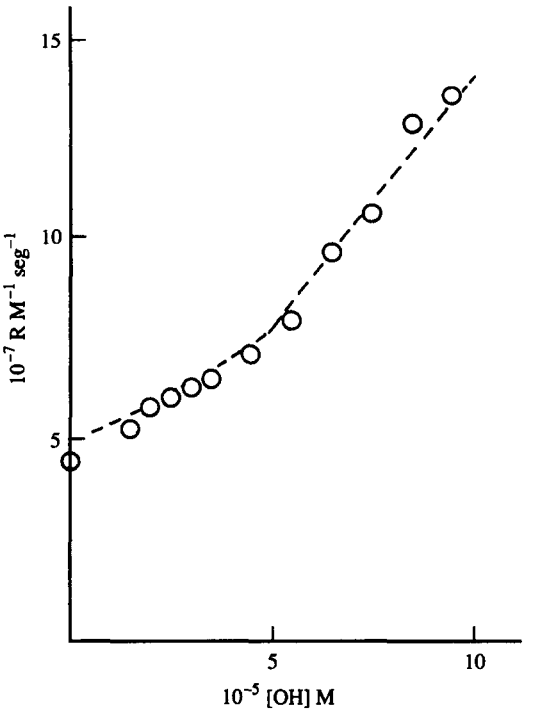


Fig. 5. Rate of oxidation versus concentration of KOH at constant concentration of catalyst $Cu(MeDPM)Cl_2$ (5.0×10^{-5} M) and $DTBCH_2$ (1.0×10^{-3} M). ----: simulated curve using $K_i = 1 \times 10^{-10}$.

Figure 4 shows the data obtained for a concentration range of copper(II) complex of $1.0–2.0 \times 10^{-5}$ M, and at a constant concentration of $DTBCH_2$ (1.0×10^{-3} M).

Kinetic data for systems with added base (KOH). When KOH is added to the system, the reaction rate of oxidation of $DTBCH_2$ increases. This may be owing to the fact that in the presence of base the reactant, $DTBCH_2$, may be partially dissociated; these species being considered to interact more easily with the copper(II) catalyst [25]. Kinetic runs, carried out with concentrations of $Cu^{II}L$ at a constant value of 5.0×10^{-5} M and of $DTBCH_2$ at 1.0×10^{-3} M, showed a behavior which is depicted in Fig. 5. The base was varied in the concentration range 0–10.0×10^{-5} M. As the concentration of base increases, the rate (R) increases, until a molar ratio of $Cu^{II}L$: OH of 1 : 1 is reached. The dependence of R on [OH] becomes linear between a ratio of 1 : 1 and 1 : 2.

Further kinetic experiments were carried out in order to obtain insight into the mechanism of oxidation of the catechol. The concentration of catechol was maintained at 1.0×10^{-3} M, while the ratio of catalyst to base was kept constant at 1 : 1 and 1 : 2. For the 1 : 1 ratio, the concentration of catalyst was varied from 2.0–20 $\times 10^{-5}$ M, while for the 1 : 2 ratio, it was varied from 1.0–10 $\times 10^{-5}$ M (Fig. 6).

Figure 6 shows the linear dependence of the rate of oxidation with concentration of $Cu(MeDPM)Cl_2$ catalyst (molar ratio 1 : 1 and 1 : 2, respectively). These data allow the calculation of the rate constants $k = 1.5 \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k' = 2.8 \times 10^{-2}\ M^{-1}\ s^{-1}$. A similar linear dependence was observed for the $Cu(diMeDPM)Cl_2$ catalyst, and the calculated rate constants were: $k = 1.2 \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k' = 1.76 \times 10^{-2}\ M^{-1}\ s^{-1}$.

The experimental data suggest that there are two reactive species towards oxygen: $Cu^{I}L$ and a ternary complex described as $Cu^{II}L$ ($DTBC^{2-}$) or $Cu^{I}L(SQ^{-})$. This is rationalized by supposing the following equilibria:

$$2\,Cu^{II}L + DTBCH_2 \overset{K_i}{\longleftrightarrow} 2\,Cu^{I}L + DTBQ + 2H^+ \quad \text{(i)}$$

$$H^+ + OH^- \longleftrightarrow H_2O \quad \text{(ii)}$$

$$Cu^{I}L + \tfrac{1}{2}Q + \tfrac{1}{2}DTBCH_2 + OH^- \longleftrightarrow Cu^{II}L(DTBC^{2-}) + H_2O \quad \text{(iii)}$$

This last equilibrum is equivalent to:

$$Cu^{II}L + DTBCH_2 + 2\,OH^- \longleftrightarrow Cu^{II}L(DTBC^{2-}) + 2H_2O \quad \text{(iv)}$$

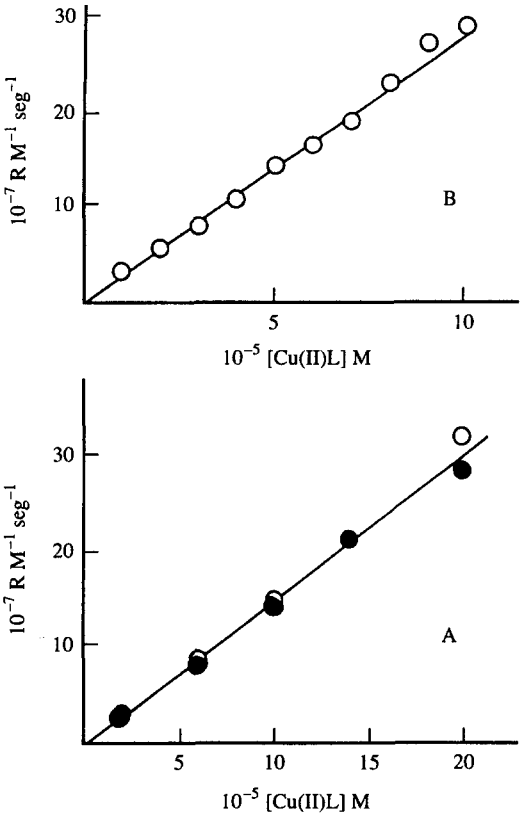


Fig. 6. Rate of oxidation at constant $DTBCH_2$ concentration (1.0×10^{-3} M) versus concentration of $Cu(MeDPM)Cl_2$ catalyst, in the presence of KOH, at constant molar ratio catalyst : OH. (A) ○: molar ratio 1 : 1; ●: $Cu(MeDPM)^+$ generated *in situ*. (B) ○: molar ratio 1 : 2.

Equilibria (i), (iii) and (iv) were shown to exist by cyclic voltammetry.

To verify the assumption that $[(Cu^{II})L]$ is present as $[Cu^{I}L]$, when the molar ratio of complex to base is 1 : 1, a set of kinetic experiments were performed generating the catalyst *in situ* with $[Cu(AN)_4)]ClO_4$, MeDPM and TEAC(1 : 1 : 2 molar ratio), AN = acetonitrile TEACl = tetraethyl ammonium chloride The copper(I) catalyst concentration varied from 2.0–20×10^{-5} M, while the $DTBCH_2$ concentration was maintained at 1×10^{-3} M. These results are superimposed on the data obtained previously, and show the same linear dependence (Fig. 6). In the presence of acid the rate of oxidation decreased, as is expected from equilibrium (i), which indicates that protons displace the equilibrium to the left, thus decreasing the concentration of the copper(I) complex.

Mechanism

The tendency of the oxidation rate versus the analytical concentration of copper(II) complex given in Figs 4 and 5, can be explained by taking into account equilibrium (i). The effect of added base shown in Fig. 5 can be explained by the fact that at low concentration of base (catalyst : OH > 1 : 1) equilibria (i) and (ii) are responsible for the increase in the concentration of copper(I). For molar ratios between 1 : 1 and 1 : 2, the active species will be both copper(I) and copper(II) catecholate generated by equilibria (iii) or (iv).

The experimental data detailed in the preceeding sections permit the postulation of the following mechanism:

$$Cu^{I}L + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu^{I}L \cdot O_2$$

$$Cu^{I}L \cdot O_2 + DTBCH_2 \xrightarrow{k_2} Cu^{I}L + Q + H_2O_2$$

$$Cu^{II}L(DTBC^{2-}) + O_2 \xrightarrow{k_3} Cu^{II}L + Q + O_2^{2-}$$

If the steady state is applied to the oxygen adduct, which is considered as a transient species, then

$$[Cu^{I}L \cdot O_2] = \frac{k_1[Cu^{I}L][O_2]}{k_{-1} + k_2[DTBCH_2]}$$

$$R = k_2[Cu^{I}L \cdot O_2][DTBCH_2] + k_3[Cu^{II}L(DTBC^{2-})][O_2]$$

$$= \frac{k_1k_2[Cu^{I}L][O_2][DTBCH_2]}{k_{-1} + k_2[DTBCH_2]} + k_3[Cu^{II}L(DTBC^{2-})][O_2]$$

If $k_2[DTBCH_2] \gg k_{-1}$, then

$$R = k_1[Cu^{I}L][O_2] + k_3[Cu^{II}L(DTBC^{2-})][O_2]$$

According to equilibria (i)–(iv), between the $Cu^{II}L$: OH^- ratios of 1 : 1 and 1 : 2, the last equation takes the form:

$$R = A + B[OH^-]$$

which correlates with the experimental results.

Kinetic data for the catalytic oxidation of $DTBCH_2$ reveal that the reaction shows no dependence upon $DTBCH_2$, when the latter is in excess. Since no accumulation of hydrogen peroxide is detected experimentally, it can be inferred that it is decomposed to water.

In this mechanism two reactive species towards oxygen have been proposed: a copper(I) complex and a species described as a ternary copper(II) catecholate complex, or as a ternary copper(I) semiquinonate complex. A simulation of the kinetic data was carried out considering a set of values for the equilibrium constant K_i. The calculated values are shown in Figs 4 and 5, and the agreement with the experimental points is obtained with values of K_i of the order of 1×10^{-10}.

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