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Autoxidation of 3,5-di-t-butylcatechol catalyzed by two pyrazolate-bridged dicopper complexes with different structural features

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Abstract

Two pyrazolate-bridged dicopper(II) complexes, $[Cu_2(LEP)_2]^{2+}$ (**1**) and $[Cu_2(BLEP)(OH)]^{2+}$ (**2**), have been studied as catalysts for the autoxidation of 3,5-di-t-butylcatechol (DTBC). Kinetic studies by the method of initial rates in 1:1 CH_3OH:H_2O revealed a rate law which is first order in the binuclear copper catalyst and O_2 and independent of DTBC concentration. Rate constants for the autoxidations catalyzed by the two complexes are 4.19×10^5 M^{-1} min^{-1} for $[Cu_2(BLEP)(OH)]^{2+}$ and 4.65×10^3 M^{-1} min^{-1} for $[Cu_2(LEP)_2]^{2+}$. The superior catalytic activity of **2** is attributed to the presence of the binucleating ligand which maintains the integrity of the dicopper structure in the reduced form and allows a more favorable mode of interaction with O_2.

Introduction

The catalysis of catechol autoxidation by binuclear copper complexes has received considerable attention [1–10] in recent years as a model reaction for the catecholase function of tyrosinase [11–13]. The two types of reactivity observed for tyrosinase are classified as monophenolase activity, the *o*-hydroxylation and subsequent oxidation of a phenol substrate (eqn. (1)), and diphenolase (or catecholase) activity, the dehydrogenation of catechol substrates (eqn. (2)).

$$\text{phenol} + O_2 \longrightarrow o\text{-quinone} + H_2O \quad (1)$$

$$2\text{catechol} + O_2 \longrightarrow 2o\text{-quinone} + 2H_2O \quad (2)$$

Both reactions utilize the four electron oxidizing capacity of O_2 and yield water as the product. Tyrosinase contains a dicopper active site which exhibits spectroscopic behavior in its met- and oxy-forms virtually identical to the corresponding forms of hemocyanin [12, 13]. The structure of the tyrosinase active site is therefore expected to be similar to that determined for hemocyanin [14, 15] in which each copper ion is coordinated to three imidazole donors and the Cu–Cu separation is *c.* 3.6 Å. The reduction potential of the tyrosinase dicopper site is 0.36 V and corresponds to the uptake of 1*e* per copper.

Several researchers have discussed the advantages of a binuclear copper species for the oxidation of catechol substrates in terms of the complementarity in the number of electrons transferred and the steric fit advantages [1, 3–7, 9, 16]. Similar arguments apply to the subsequent reaction of the reduced dicopper species with O_2. Nishida and co-workers [1] demonstrated that, in a series of copper(II) complexes, those binuclear complexes which allow a good steric match for catechol coordination with the dicopper(II) site are the best catalysts for the autoxidation of 3,5-di-t-butylcatechol (DTBC). Other workers have also reported [5, 7, 9] the superior catalytic activity of dicopper(II) species compared to similar mononuclear complexes. Few studies of catechol autoxidation, however, have proceeded beyond comparisons of reaction rates for different copper catalysts or for variations in the catechol substituents. One rather complete study was carried out by Speier [17] on the oxidation of DTBC in CH_2Cl_2 or $CHCl_3$ catalyzed by [Cu(I)Clpy]. The rate expression found was second order in Cu(I), first order in O_2 and zero order in DTBC and the rate determining step was concluded to be the reoxidation of the [Cu(I)Clpy] species [17]. Rogić and coworkers [2] also investigated many of the mechanistic details of the oxidation of catechol catalyzed by a binuclear copper(II) complex with triketonate ligands.

In this paper we describe studies of the autoxidation of DTBC catalyzed by two new binuclear copper

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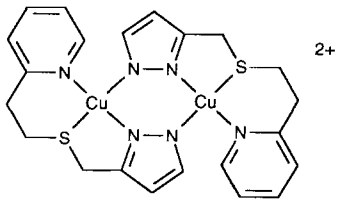
complexes, $[Cu_2(LEP)_2]^{2+}$ (**1**) and $[Cu_2(BLEP)(OH)]^{2+}$ (**2**). Although the dicopper environment in these two complexes is significantly different from that proposed for tyrosinase, **1** and **2** both exhibit Cu–Cu distances of approximately 3.7 Å and are therefore useful models for the interaction with catechol substrates. The different structural features of **1** and **2** also allow for different modes of substrate and O_2 interaction and the effect of these differences on the reaction rate is explored.



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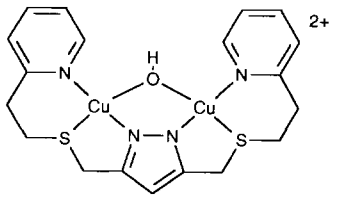

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Experimental

The synthesis, spectroscopy and structural characterization of the two binuclear copper(II) complexes used in this study, $[Cu_2(LEP)_2](ClO_4)_2$ and $[Cu_2(BLEP)(OH)](ClO_4)_2$, are described elsewhere [18]. 3,5-Di-t-butylcatechol was obtained from Aldrich Chemical Co. and 3,5-di-t-butylquinone was prepared by a literature method [19].

Kinetic studies

The kinetics of the autoxidation of 3,5-di-t-butylcatechol (DTBC) were determined by the method of initial rates by monitoring the growth of the 410 nm band of the product 3,5-di-t-butylquinone (DTBQ) spectrophotometrically or by measuring the consumption of O_2 in a sealed, thermostatted (25.0±0.1 °C) reaction cell with a Yellow Springs Instrument model 53 oxygen monitor. The initial rate studies were carried out in methanol–water (1:1 vol.:vol.) mixed solvent at 25 °C. In the spectrophotometric rate measurements the pH* of an O_2 saturated solution of DTBC was adjusted to the desired value in the spectrophotometer cell. A small aliquot containing the binuclear copper catalyst was injected with a microsyringe into the cell with stirring and the absorbance change at 410 nm was recorded. O_2 was gently bubbled into the cell to maintain saturation. The pH* of the reaction solution was remeasured following the run to insure that no significant change in $[H^+]$ had occurred. For the kinetic runs based on O_2 consumption, the $[O_2]$ was adjusted to the desired value in a solution of DTBC at the appropriate pH* in the reaction cell. The catalyst solution was injected by microsyringe into the stirred solution and the O_2 uptake was recorded. Initial rates were taken as the slopes of the tangents to either the increase in absorbance or the decrease in $[O_2]$. Plots of log(initial rate) versus log(reactant) were used to determine the reaction order for each component. The operational unit pH* is used according to Bates [20] to define the acidity of the 1:1 methanol/water mixed solvent as

$$pH^* = pa_{H^*} = pH - \delta$$

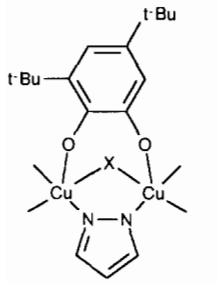
where a_{H^*} is the hydrogen ion activity referred to the standard state in the mixed solvent, pH is the value obtained by a pH meter standardized with aqueous buffer solutions, and δ is a constant for the given medium (in this case $\delta = 0.13$). Spectrophotometric measurements were made with a Cary model 14 recording spectrophotometer.

Results and discussion

The two binuclear copper complexes employed in this study exhibit contrasting structural features which are important for their possible modes of interaction with catechol substrates and with O_2. In the solid state, $[Cu_2(LEP)_2](ClO_4)_2$ is a dimeric complex with two square pyramidal coppers joined in the equatorial plane by two pyrazolate bridges producing a Cu–Cu separation of 3.70 Å [18]. One of the perchlorate counterions is coordinated in a bridging bidentate fashion to the apical positions of the two copper ions. This coordinated perchlorate presumably is replaced in solution by apical solvent donors thus maintaining the square pyramidal coordination geometry of the copper ions in $[Cu_2(LEP)_2]^{2+}$ (**1**). In $[Cu_2(BLEP)(OH)]^{2+}$ (**2**), the binucleating ligand provides tridentate coordination to each copper ion and an exogenous bridging hydroxide completes the equatorial bonding. The single, broad d–d band for $[Cu_2(BLEP)(OH)]^{2+}$ at 16 500 cm^{-1} indicates that a square pyramidal coordination geometry with apical solvent coordination is also present for the copper ions in this complex. This structure is analogous to the square pyramidal coordination found in the solid state [18] for $[Cu_2(BLEP)Cl_2(H_2O)]Cl$ in which the two coppers are bridged in the equatorial plane by a chloride ion and apical coordination to the two coppers is provided by another chloride ion and a

water molecule. The Cu–Cu distance in $[Cu_2(BLEP)Cl(H_2O)]Cl$ is 3.65 Å. In the solid state structures of both $[Cu_2(LEP)_2](ClO_4)_2$ and $[Cu_2(BLEP)Cl_2(H_2O)]Cl$ the two square pyramidal copper ions have their apical sites located on the same side of the complex. This cofacial arrangement is ideal for apical interaction of the catechol substrate with the two copper ions (**3**) in the manner suggested by Nishida and co-workers [1]. In contrast, the type of catecholate coordination found by Karlin *et al.* [21] for a phenolate-bridged dicopper(II) complex is not possible for $[Cu_2(LEP)_2]^{2+}$ and would appear to be highly strained for $[Cu_2(BLEP)(OH)]^{2+}$. In Karlin's structure the two oxygens of tetrachlorocatecholate span basal positions on the two square pyramidal copper ions [21]. The Cu–Cu distance is found to be 3.248 Å and the dihedral angle between the equatorial planes of the two Cu(II) ions is 46.4° [21]. $[Cu_2(BLEP)(OH)]^{2+}$ also offers the possibility that catecholate could replace the bridging OH^-. Owing to the constraints of the binucleating ligand, however, it seems more likely that one catecholate oxygen would occupy the bridging position with the other catecholate oxygen in an apical site (**4**).

For the reoxidation step, O_2 coordination to the reduced form of both complexes **1** and **2** is possible through one apical site or bridged through both apical sites. For reduced $[Cu_2(BLEP)(OH)]^{2+}$ the binding of O_2 in equatorial sites by the displacement of the bridging OH^- is very favorable (**5**). The μ-1,2-peroxo-bridged dicopper(II) species which results from this type of interaction has been proposed as the form of oxytyrosinase and oxyhemocyanin [12].



X = pyrazole or OH^-

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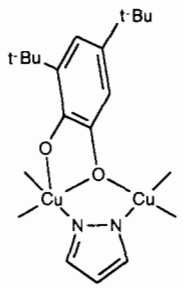

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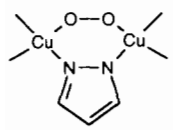

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Prior to the kinetic studies of the autoxidation of DTBC the stoichiometric reductions of the two binuclear complexes by DTBC were investigated by spectrophotometric titrations. The addition of successive aliquots of DTBC to $[Cu_2(LEP)_2]^{2+}$ in CH_3CN leads to a monotonic decrease in the d–d and charge transfer transitions until their total loss at a 1:1 DTBC:complex ratio. The titration of $[Cu_2(BLEP)(OH)]^{2+}$ with DTBC, on the other hand, reveals a more complicated interaction between the catechol and the complex ion (Fig. 1). The initial additions of DTBC (up to 40% of the required amount) lead to a shift in the position of the d–d band to lower energy accompanied by the presence of two isosbestic points in the spectra which indicate an equilibrium between two species. Furthermore, in the charge transfer region of the spectrum, the initial aliquots of DTBC lead to a rapid loss in intensity for the 24 000 cm^{-1} band (attributed to the $OH^- \rightarrow Cu(II)$ transition [18]) while the 30 000 cm^{-1} band ($S(\sigma) \rightarrow Cu(II)$ transition) is scarcely diminished. The high energy shoulder at 31 500 cm^{-1} on the $S(\sigma) \rightarrow Cu(II)$ transition also decreases sharply with the initial additions of DTBC suggesting that this spectral feature may also be associated with the bridging hydroxide. These data suggest that the initial interaction of DTBC with $[Cu_2(BLEP)(OH)]^{2+}$ results in the loss of the bridging hydroxide presumably by direct replacement by catecholate.

Another effect which may contribute to the initial rapid loss of the hydroxide bridge is the release of protons accompanying the oxidation of DTBC. This increased acidity will protonate the hydroxide and make it ineffective as a bridging group [22]. In a separate experiment the addition of one equivalent of H^+ (as $HClO_4$) to an CH_3CN solution of $[Cu_2(BLEP)(OH)]^{2+}$ causes the loss of the $OH^- \rightarrow Cu(II)$ transition while the $S(\sigma) \rightarrow Cu(II)$ transition is maintained. Further evidence of the ease of replacement of the hydroxide bridge comes from the fact that the spectrum of a CH_3CN solution of $[Cu_2(BLEP)(OH)]^{2+}$ spontaneously loses the $OH^- \rightarrow Cu(II)$ transition upon standing for several hours.

Preliminary studies of catalytic behavior

Both $[Cu_2(BLEP)(OH)]^{2+}$ and $[Cu_2(LEP)_2]^{2+}$ were found to rapidly catalyze the autoxidation of DTBC in O_2-saturated methanol as judged by the growth of an absorption band at 410 nm attributed to DTBQ. Confirmation of the oxidation product was achieved by isolation of DTBQ in 80% yield from the reaction of $[Cu_2(BLEP)(OH)]^{2+}$ (1×10^{-4} mol) with DTBC (1×10^{-3} mol) in O_2-saturated methanol. The DTBQ product was identified through comparisons of UV and IR spectra and TLC with an authentic sample of DTBQ [19]. No other oxidation products were indicated by UV spectra in

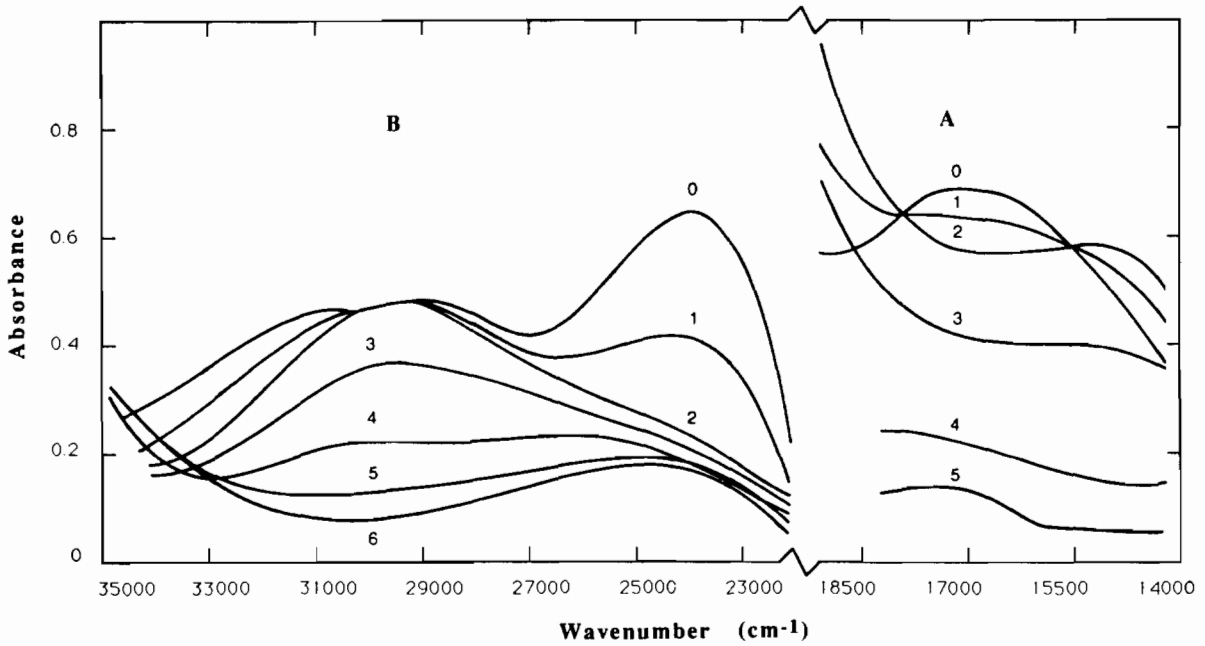

Fig. 1. Spectrophotometric titration of $[Cu_2(BLEP)(OH)]^{2+}$ with DTBC in CH_3CN. A: d–d spectral region: $[[Cu_2(BLEP)(OH)]^{2+}] = 5\times10^{-4}$ M (10 ml); each addition represents 0.02 ml of 5×10^{-2} M DTBC. B: charge transfer region: $[[Cu_2(BLEP)(OH)]^{2+}] = 2\times10^{-5}$ M (12 ml); each addition represents 0.02 ml of 2×10^{-3} M DTBC.

contrast to earlier studies of less hindered catechols [3, 4]. Preliminary studies in acetonitrile revealed much slower autoxidation rates. This observation may result from stabilization of the intermediate Cu(I)..Cu(I) species by coordination of acetonitrile thereby producing slower reoxidation by O_2. Based on the observed rapid oxidation of DTBC in methanol and the need to have a solvent system in which pH could be determined, we chose a 1:1 (vol.:vol.) methanol/water mixed solvent to carry out the kinetic studies.

Initial rate studies

The initial rates of the autoxidation of DTBC catalyzed by the binuclear copper complexes were determined either spectrophotometrically by following the growth of the DTBQ absorption band at 410 nm or amperometrically by following O_2 uptake. Data for the reaction catalyzed by $[Cu_2(BLEP)(OH)]^{2+}$ and $[Cu_2(LEP)_2]^{2+}$ are given in Tables 1 and 2, respectively. For both complexes at $pH^* = 6.4$ the rate law shows a first-order dependence on the catalyst and dioxygen concentrations and zero-order dependence with respect to DTBC concentration and may be expressed as

$$\text{rate} = k[\text{complex}][O_2]$$

The simplest interpretation of this rate law is a ping-pong mechanism which cycles between the fast oxidation of DTBC and the rate-determining reoxidation of the catalyst by O_2:

$$\text{Cu(II)..Cu(II)} + \text{DTBC} \longrightarrow \text{Cu(I)..Cu(I)} + \text{DTBQ} + 2H^+ \text{ (fast)}$$

$$\text{Cu(I)..Cu(I)} + O_2 \longrightarrow \text{Cu(II)}(O_2)^{2-}\text{Cu(II)} \text{ (slow)}$$

$$\text{Cu(II)}(O_2)^{2-}\text{Cu(II)} + 2H^+ \longrightarrow \text{Cu(II)..Cu(II)} + H_2O_2 \text{ (fast)}$$

Another mechanism in agreement with the observed rate law involves the μ-peroxo–dicopper(II) species as the direct oxidant of DTBC in the redox cycle. In this case an initial reduction of the dicopper(II) catalyst by DTBC is required prior to the redox cycle.

Initial step:

$$\text{Cu(II)Cu(II)} + \text{DTBC} \longrightarrow \text{Cu(I)..Cu(I)} + \text{DTBQ} + 2H^+$$

Redox cycle:

$$\text{Cu(I)..Cu(I)} + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Cu(II)}(O_2)^{2-}\text{Cu(II)}$$

$$\text{Cu(II)}(O_2)^{2-}\text{Cu(II)} + \text{DTBC} \xrightarrow{k_3} \text{Cu(I)..Cu(I)} + \text{DTBQ} + H_2O_2$$

Applying a steady state approximation to $[Cu(II)(O_2)^{2-}Cu(II)]$ and assuming that $k_3[DTBC] \gg k_2$ yields the rate law

TABLE 1. Rate law determination by the method of initial rates[a] for the autoxidation of DTBC catalyzed by $[Cu_2(BLEP)(OH)]^{2+}$

Dependence on $[[Cu_2(BLEP)(OH)]^{2+}]$[b]			
$[[Cu_2(BLEP)(OH)]^{2+}]$ (M)	V_o (M min^{-1})[c]	$\log[[Cu_2(BLEP)(OH)]^{2+}]$	$\log V_o$
5.98×10^{-8}	1.16×10^{-5}	−7.22	−4.93
7.97×10^{-8}	1.50×10^{-5}	−7.10	−4.83
9.96×10^{-8}	2.18×10^{-5}	−7.00	−4.66
1.99×10^{-7}	3.82×10^{-5}	−6.70	−4.42
3.98×10^{-7}	9.04×10^{-5}	−6.40	−4.04
5.98×10^{-7}	1.52×10^{-4}	−6.22	−3.82
Slope = 1.10			
Correlation coefficient (r) = 0.9974			
Dependence on $[O_2]$[d]			
$[O_2]$ (M)	V_o (M min^{-1})[e]	$\log[O_2]$	$\log V_o$
1.27×10^{-4}	1.18×10^{-5}	−3.90	−4.93
1.95×10^{-4}	1.69×10^{-5}	−3.71	−4.77
3.38×10^{-4}	2.75×10^{-5}	−3.47	−4.56
4.98×10^{-4}	3.63×10^{-5}	−3.30	−4.44
6.60×10^{-4}	5.18×10^{-5}	−3.18	−4.29
Slope = 0.87			
Correlation coefficient (r) = 0.9979			
Dependence on [DTBC][f]			
[DTBC] (M)	V_o (M min^{-1})[e]	log[DTBC]	$\log V_o$
1.00×10^{-4}	2.39×10^{-5}	−4.00	−4.62
2.00×10^{-4}	2.48×10^{-5}	−3.70	−4.61
3.98×10^{-4}	2.61×10^{-5}	−3.40	−4.58
5.98×10^{-4}	2.69×10^{-5}	−3.22	−4.57
7.97×10^{-4}	2.59×10^{-5}	−3.10	−4.59
Slope = 0.05			
Correlation coefficient (r) = 0.8523			

[a]In non-buffered 1:1 CH_3OH/H_2O at pH* = 6.40 and 25 °C. [b]$[DTBC] = 3.98\times10^{-4}$ M; $[O_2] = 5.5\times10^{-4}$. [c]Measured spectrophotometrically at 400 nm. [d]$[DTBC] = 3.95\times10^{-4}$ M; $[[Cu_2BLEP(OH)]^{2+}] = 2\times10^{-7}$ M. [e]Measured O_2 uptake amperometrically. [f]$[[Cu_2BLEP(OH)]^{2+}] = 1\times10^{-7}$; $[O_2] = 5.5\times10^{-4}$ M.

$$\text{rate} = k_1[\text{Cu(I)..Cu(I)}][O_2]$$

It is not possible to distinguish between these two mechanisms with the present data, however it seems likely that in the solvent system employed the μ-peroxo–dicopper(II) species would be rapidly protonated and would not exist long enough to oxidize DTBC. Furthermore, Gampp and Zuberbühler [23] have suggested that oxo–copper(II) species are more effective as oxidants and μ-peroxo–dicopper(II) species act as oxygenating agents. For these reasons we prefer the former mechanism to explain the observed kinetics.

The requirement of this mechanism for a 1:1 O_2:DTBQ stoichiometry was tested by measuring O_2 consumed and DTBQ produced under identical reaction conditions. Figure 2 shows good experimental agreement with this requirement and confirms that H_2O_2 is the reduction product of the O_2. In this regard the autoxidations of DTBC catalyzed by **1** and **2** differ significantly from the diphenolase reaction of tyrosinase which results in the formation of H_2O.

The rate dependence of the reaction on $[H^+]$ was also investigated. For both $[Cu_2(BLEP)(OH)]^{2+}$ and $[Cu_2(LEP)_2]^{2+}$ lower pH* values produced slower rates of autoxidation. Over the pH* range 6.0 to 7.6 a straight line dependence on $[H^+]$ was obtained for both complexes with reaction orders of −0.42 and −0.81 for $[Cu_2(BLEP)(OH)]^{2+}$ and $[Cu_2(LEP)_2]^{2+}$, respectively. This non-integral dependence probably reflects the fact that $[H^+]$ can affect the reaction in several ways. Since [DTBC] does not appear in the rate law, the effect of increased $[H^+]$ on the rate cannot be attributed to a decrease in the amount of deprotonated catechol. It is most likely that decreases in pH* influence the nature of the dicopper catalyst and make it less active. Among the possible effects of lower pH* on the two catalysts are: dissociation of the $[Cu_2(LEP)_2]^{2+}$ dimer, loss of the OH^- bridge from $[Cu_2(BLEP)(OH)]^{2+}$, and

TABLE 2. Rate law determination by the method of initial rates[a] for the autoxidation of DTBC catalyzed by $[Cu_2(LEP)_2]^{2+}$

Dependence on $[[Cu_2(LEP)_2]^{2+}]$[b] $[[Cu_2(LEP)_2]^{2+}]$ (M)	V_o (M min^{-1})[c]	$\log[[Cu_2(LEP)_2]^{2+}]$	$\log V_o$
2.00×10^{-6}	9.64×10^{-6}	−5.70	−5.02
3.98×10^{-6}	2.22×10^{-5}	−5.40	−4.65
4.98×10^{-6}	2.86×10^{-5}	−5.30	−4.54
6.97×10^{-6}	3.75×10^{-5}	−5.16	−4.43
7.97×10^{-6}	4.52×10^{-5}	−5.10	−4.34
9.96×10^{-6}	5.05×10^{-5}	−5.00	−4.30
Slope = 1.05			
Correlation coefficient (r) = 0.9930			
Dependence on $[O_2]$[d] $[O_2]$ (M)	V_o (M min^{-1})[e]	$\log[O_2]$	$\log V_o$
1.25×10^{-4}	5.55×10^{-6}	−3.90	−5.26
2.59×10^{-4}	9.34×10^{-6}	−3.59	−5.03
3.18×10^{-4}	1.46×10^{-5}	−3.50	−4.84
4.85×10^{-4}	2.13×10^{-5}	−3.31	−4.67
6.83×10^{-4}	2.66×10^{-5}	−3.17	−4.58
Slope = 0.97			
Correlation coefficient (r) = 0.9890			
Dependence on [DTBC][f] [DTBC] (M)	V_o (M min^{-1})[e]	log[DTBC]	$\log V_o$
2.00×10^{-4}	4.92×10^{-6}	−3.70	−5.31
3.98×10^{-4}	4.49×10^{-6}	−3.40	−5.35
5.98×10^{-4}	4.32×10^{-6}	−3.22	−5.36
7.97×10^{-4}	4.49×10^{-6}	−3.10	−5.35
9.96×10^{-4}	3.99×10^{-6}	−3.00	−5.40
Slope = −0.10			
Correlation coefficient (r) = 0.8879			

[a]In non-buffered 1:1 CH_3OH/H_2O at pH* = 6.40 and 25 °C. [b][DTBC] = 3.98×10^{-4} M; $[O_2] = 1.0\times10^{-3}$ M. [c]Measured spectrophotometrically at 400 nm. [d][DTBC] = 3.95×10^{-4} M; $[[Cu_2(LEP)_2]^{2+}] = 2\times10^{-7}$ M. [e]Measured O_2 uptake amperometrically. [f]$[[Cu_2(LEP)_2]^{2+}] = 1\times10^{-6}$; $[O_2] = 1.0\times10^{-3}$ M.

protonation of the terminal pyridyl arms of either ligand resulting in reduced coordination. We have no detailed explanation of this rate dependence on $[H^+]$ and therefore restrict our comments about the kinetic behavior of the other components at a single value of pH*.

Averaged values for the specific rate constants k for the two catalysts, $[Cu_2(LEP)_2]^{2+}$ and $[Cu_2(BLEP)(OH)]^{2+}$, evaluated from the data in Tables 1 and 2, are 4.65×10^3 M^{-1} min^{-1} and 4.19×10^5 M^{-1} min^{-1}, respectively. Thus $[Cu_2(BLEP)(OH)]^{2+}$, which contains the binucleating ligand, is a better catalyst than $[Cu_2(LEP)_2]^{2+}$ by almost two orders of magnitude. This difference must arise from a superior mode of interaction between the reduced form of $[Cu_2(BLEP)(OH)]^{2+}$ and O_2. $[Cu_2(BLEP)(OH)]^{2+}$ offers two major advantages over $[Cu_2(LEP)_2]^{2+}$ in the interaction with O_2. First, the ligand BLEP will maintain an intact binuclear structure for the Cu(I)..Cu(I) species whereas the dimer structure of $[Cu_2(LEP)_2]^{2+}$ may dissociate to some degree in the reduced form thus negating the advantages of a 2e transfer with O_2. Second, if the hydroxy bridge is lost upon reduction of $[Cu_2(BLEP)(OH)]^{2+}$, then a very favorable pathway exists for interaction with O_2 via the formation of a μ-peroxo–dicopper(II) species where the peroxide bridges two equatorial positions on the Cu(II) ions.

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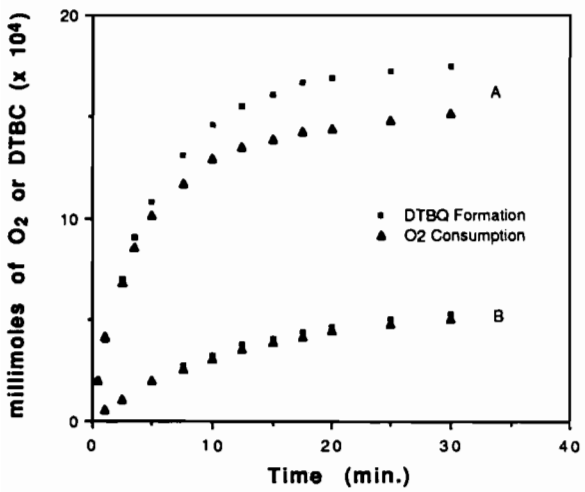

Fig. 2. Stoichiometric ratio of DTBC formation to dioxygen consumption for the autoxidation of DTBC catalyzed by 1 (B) and 2 (A).

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