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Importance of Intermediate Charge-transfer Complex Formation in the Model Reaction for Laccase

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Abstract

The catalytic activities of binuclear copper(II), cobalt(II) and manganese(II) complexes with 2,6-bis-[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol were compared for the oxidation reaction of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine by dioxygen molecules. The highest activity was observed for the copper(II) complex, supporting the importance of intermediate charge-transfer complex formation in the reaction.

Introduction

N,N,N',N'-Tetramethyl-*p*-phenylenediamine (TMPD) is a one-electron donor and its oxidized compound $TMPD^+$ (called Wurster's blue salt) shows a strong blue color [1]. TMPD itself exhibits low reactivity toward the $^3O_2$ molecule and very slow oxidation of TMPD occurs in dilute solution under aerobic conditions. In 1980, Nishida *et al.* [2] found that some binuclear copper(II) complexes can catalyze the rapid oxidation of TMPD under aerobic conditions and pointed out that reaction (1) can be a model reaction for laccase (and also cytochrome *c* oxidase), because the binuclear complexes function as a two-electron carrier which transfers two electrons from two molecules of TMPD to the dioxygen molecule [3].

$$\text{TMPD} \xrightarrow[O_2,\ Cu(II)]{} \text{TMPD}^+ \qquad (1)$$

In this article we have investigated the catalytic activities of binuclear copper(II), cobalt(II) and manganese(II) complexes with 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (hereafter abbreviated as H(L)) in order to obtain more detailed knowledge of the reaction mechanism of reaction (1).

Experimental

Materials

The binuclear copper(II) and cobalt(II) complexes $[Cu_2(L)(CH_3COO)](PF_6)_2$ and $[Co(L)(CH_3COO)](ClO_4)_2$ were obtained by the published method [4, 5]. A new manganese(II) complex was obtained in this study. To a methanol solution of the ligand (0.001 mol) was added the methanol solution containing $Mn(CH_3COO)_2\cdot4H_2O$ (0.002 mol), triethylamine (0.001 mol) and NH_4PF_6 (220 mg). After one day, gray needles precipitated. *Anal.* Found: C, 48.96; H, 4.32; N, 9.26; Mn, 11.74. Calc. for $[Mn_2(L)(CH_3COO)_2]PF_6$: C, 49.24; H, 4.36; N, 9.31; Mn, 12.17%.

Catalytic Activity

In typical runs, the metal complex ($[M^{2+}] = 2.5 \times 10^{-5}$ mol dm^{-3}) and TMPD (2.5×10^{-4} mol dm^{-3}) were dissolved in DMF/CH_3OH (1/7, *v/v*) and the increase of the absorbance at 560 nm (due to the $TMPD^+$ formed) of the solution was monitored at 288 K (1-mm cell). The spectra were measured on a Shimadzu Model UV-240 spectrophotometer.

Results and Discussion

The results obtained in this study are shown in Fig. 1. It is clear that the binuclear manganese(II) complex exhibits no activity for reaction (1), because

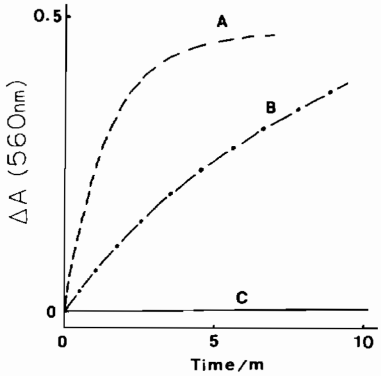

Fig. 1. Time course of absorbance at 560 nm (due to $TMPD^+$ formed) in the reaction mixture of TMPD and the metal complex (for experimental conditions, see text). A, $[Cu_2(L)(CH_3COO)](PF_6)_2$; B, $[Co_2(L)(CH_3COO)](ClO_4)_2$; C, $[Mn_2(L)(CH_3COO)_2]PF_6$.

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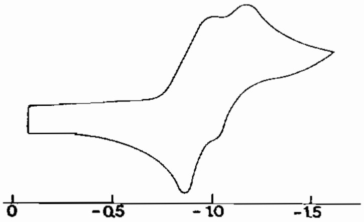
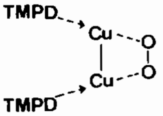


Fig. 2. Cyclic voltammogram of $[Cu_2(L)(CH_3COO)](PF_6)_2$ (in DMF at 288 K; potential was referenced to redox potential of ferrocene).

no formation of $TMPD^+$ was observed under the experimental conditions. Both the copper(II) and cobalt(II) complexes show high activity, and it is noteworthy that the activity of the copper(II) complex is much higher than that of the cobalt(II) complex in the initial stage.

The manganese(II) complex used in this study is rather stable in air (not oxidized to manganese(III) species under aerobic conditions). In contrast to this, it is known that the cobalt(II) complex used in this study readily reacts with dioxygen molecules to yield a dioxygen complex in air [5]. The cyclic voltammogram revealed that the copper(II) complex is reduced to the copper(I) state at moderately low potential, as shown in Fig. 2. In previous papers [2–4], Nishida *et al.* inferred that the two-electron transfer reaction from two molecules of TMPD to the dioxygen molecule proceeds concertedly in the following manner: (i) at the first stage, a weak charge-transfer state $2TMPD + Cu^{II}_2 \rightarrow 2TMPD^{+\delta} \cdots\cdots Cu^{II-\delta}_2$ is formed; and (ii) two-electron transfer occurs via the intermediate complex formation, as illustrated below. The importance of charge-transfer complex formation is clearly supported by the present result that the manganese(II) complex exhibits no activity for reaction (1), because the formation of a manganese(I) state is unfavourable (no reduction wave corresponding to Mn(II) → Mn(I)) was observed in the range $0 \sim -1.8$ V *versus* ferrocene [6]).



In the cobalt(II) complex, the formation of a cobalt(I) state is also unfavorable. However, this complex can combine with $^3O_2$ to yield a dioxygen complex [5]. Thus, the lower activity of the cobalt(II) complex than that of the copper(II) complex in the initial stage clearly indicates that the electrons of TMPD molecules are not transferred directly to dioxygen but via the metal ions. The cobalt(II)–dioxygen complexes can be alternatively considered to be a peroxide adduct of the cobalt(III) ion, and this cobalt(III) species may function as a redox center in the catalytic reaction. This will explain the lower activity of the cobalt(II) complex in the initial stage, since the catalytic activity of the complex depends on the quantity of cobalt(III) formed in the solution.

In the reaction of laccase, it is believed that the two-electron transfer reaction proceeds 'concertedly'; that is, electron transfer from the reduced Type I and Type II to Type III copper occurs only when the dioxygen molecule is present in the system [7]. The reaction features observed for the oxidation of TMPD catalyzed by the binuclear copper(II) complexes [2–4] are very similar to those observed with laccase. Although our understanding of the 'concerted electron transfer' reaction is very limited, we propose that intermediate charge-transfer complex formation plays an important role in biological systems where the electron transfer occurs 'concertedly' and in the long range [8].

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