Binuclear Copper(II) Complexes as Oxidase Catalysts

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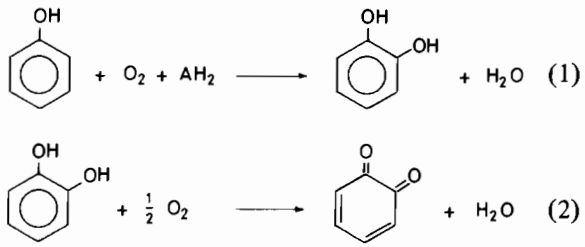
The essential role of Cu(II) ions in the enzymatic systems of plants and animals has long been of interest. Tyrosinase is an enzyme, widely distributed in nature, mainly involved in the biosynthesis of melanins and other polyphenolic compounds. It catalyzes both the *o*-hydroxylation of monophenols (eqn. (1)) and the oxidation of *o*-diphenols to *o*-quinones (eqn. (2)).



The two enzymatic activities are commonly referred to as cresolase or monophenolase and catecholase or diphenolase activities, respectively. The involvement of copper as the prosthetic group in tyrosinase is firmly established [1]. The proposed mechanism of oxidation is based on the fact that the two coupled Cu(II) ions are needed as coordination sites for the *o*-hydroxyl oxygens in *o*-diphenols and the binding of the dioxygen [2]. The ability of some binuclear Cu(II) complexes to behave catalytically like naturally occurring metallo-enzymes and to be chemical models for enzymatic oxidations has been the subject of much interest [3]. We have studied the catecholase activity of [Cu(*o*-CACOO)$_2$] complex (*o*-CACOOH = *ortho*-hydroxycinnamic acid), the preparation and magnetic characterization of which have already been reported [4].

Experimental

Electronic spectra were taken on a Jasco UVIDEC 610 spectrophotometer and the oxidation studies were carried out on a Gilford 252 system equipped with constant temperature control.

Results and Discussion

Kinetic Studies

A 10^{-1} M solution of catechol and 10^{-3} M of [Cu(*o*-CACOO)$_2$] complex were made up in tetrahydrofuran. The fresh catechol solution was stored in a dark container during the study to minimize photooxidation.

The complex solution (0.3 ml) was placed in a 1 cm quartz cell and allowed to equilibrate in the spectrophotometer cavity which was at a constant temperature of 25 °C. A 2.0 ml sample of catechol was added and the solution was stirred. The ability to catalyze the dioxygen oxidation of catechol to *o*-quinone in air was followed spectrophotometrically, monitoring the increase in absorbance at 390 nm (1451 M^{-1} cm^{-1} molar absorptivities) on the *o*-quinone peak (λ_{max} = 370 nm), as a function of time.

We found that the complex shows catecholase activity and the oxidation reaction stops at the production of *o*-quinone. Figure 1 shows the absorbance *versus* time during the first 20 min for the oxidation of pyrocatechol catalyzed by [Cu(*o*-CACOO)$_2$] complex, for which it is possible to find an oxidase activity of 0.088 U/mg (as μmol of substrate catechol transformed in 1 min at 25 °C).

We are pursuing the study of the interaction of catechol and different substituted catechols with several binuclear Cu(II) complexes that might serve as synthetic models and mimic both known spectroscopic properties as well as the chemical behaviour of some dicopper enzymes.

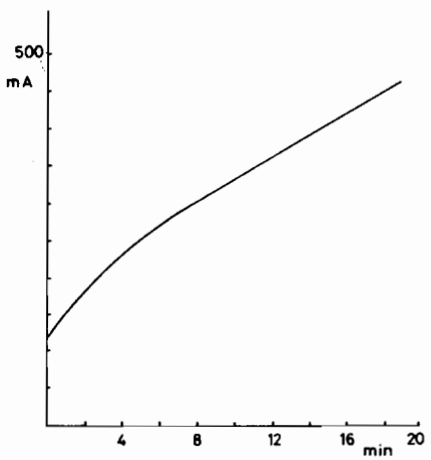


Fig. 1. The absorbance *vs.* time spectrum of the Cu(II) complex (10^{-3} M) catalyzed oxidation of catechol (10^{-1} M).

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