The Stoichiometric and Catalytic Oxidation of Various Substrates with a Novel Macrocyclic Binuclear Copper(I) Dioxygen Complex as an Intermediate

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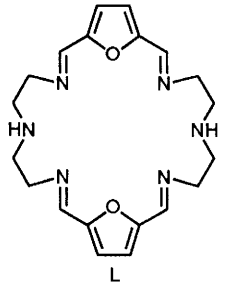
The stoichiometric oxidations of hydroquinones, phenols, 3,5-di-*tert*-butylcatechol and 3,4-dimethylaniline with a macrocyclic Cu^{I} dioxygen complex and with a Cu^{II} complex show that in some cases the substrate is oxidized both by the Cu^{I} dioxygen complex and by the corresponding Cu^{II} complex, while in other cases the Cu^{II} complex shows no activity; the combination of the Cu^{I} dioxygen complex and the Cu^{II} complex as oxidants results in catalytic oxidation of the substrate, but no catalysis is observed when only the Cu^{I} dioxygen complex is active.

In a previous investigation[1] spectroscopic evidence was presented for the generation of a relatively long lived Cu^{I} dioxygen complex, **1**, when a solution containing the Cu^{I} complex of the tetra-Schiff base L was exposed to dioxygen at room temperature. Although several binuclear Cu^{I} dioxygen complex model systems for haemocyanin and tyrosinase have been prepared,[2–8] relatively few studies[9–11] have reported their reactivities in relation to externally introduced substrates. Presented here is a study of the oxidation reactions of hydroquinones, phenols, 3,5-di-*tert*-butylcatechol and 3,4-dimethylaniline with the oxygenated Cu^{I} complex, $[Cu_2L]^{2+}$.

For both stoichiometric and catalytic oxidations by Cu^{I} the ligand L was dissolved in degassed methanol, under argon, prior to the addition of 2 equiv. of $Cu(MeCN)_4PF_6$ in deoxygenated acetonitrile. The oxygen complex was generated by treating the system with dioxygen for 5 min. For the stoichiometric reactions the excess of oxygen was removed by purging with argon for 10 min before introducing the substrate in tenfold excess. The reaction mixture was stirred until oxygen uptake ceased. The Cu^{II} binuclear complex was prepared by dissolving the ligand L in methanol followed by the addition of 2 equiv. of $CuCl_2$ in methanol. The substrate

Table 1 Initial rates in the Cu^{I}–dioxygen and Cu^{II} oxidations of substrates

Substrate	Product	Initial, pscudo-first-order rate/s^{-1}	
		$Cu^{I} + O_2$	Cu^{II}
Hydroquinone	Benzoquinone	1.1×10^{-4}	2.2×10^{-5}
tert-Butylhydroquinone	*tert*-Butylbenzoquinone	1.2×10^{-4}	1.6×10^{-5}
2,6-Di-*tert*-butylphenol	3,3′,5,5′-Tetra-*tert*-butyldiphenoquinone	2.4×10^{-4}	5.8×10^{-5}
2,6-Dimethoxyphenol	3,3′,5,5′-Tetramethoxydiphenoquinone	7.4×10^{-3}	5.6×10^{-5}
3,5-Di-*tert*-butylcatechol	3,5-Di-*tert*-butyl-1,2-benzoquinone	1.4×10^{-8}	~0
3,4-Dimethylaniline	3,4-Dimethylnitrosobenzene	6.5×10^{-5}	~0



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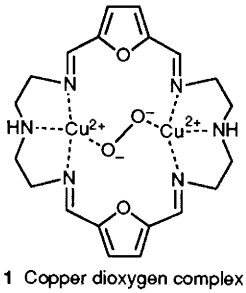
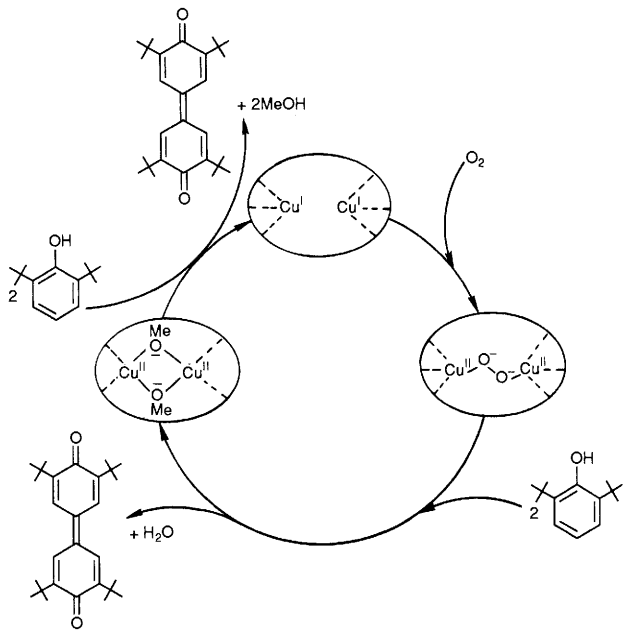


1 Copper dioxygen complex

was introduced as a solution in methanol and the reaction mixture was stirred for about 2 h. For both Cu^{I} and Cu^{II} oxidations, at the end of the reaction, the crude mixture was concentrated and chromatographed on silica gel. The products were identified by ^{1}H and ^{13}C NMR spectroscopy and melting point determination. In the study of the formation rates of products, specific wavelengths characteristic of the products were chosen to follow the progress of the reaction (3,3′,5,5′-tetra-*tert*-butyldiphenoquinone, 424 nm: 3,3′,5,5′-tetramethoxydiphenoquinone, 428 nm, hydroquinone 360 nm; tetrabutylhydroquinone, 370 nm).

Since the stoichiometric oxidation reactions were generally first order in the binuclear Cu^{I} macrocyclic dioxgen complex, and in the concentration of the substrate, a large excess of the substrate was employed. Thus, the data listed in Table 1 may be considered as pseudo-first-order reaction rates. Initial rates were taken to avoid the complication of the oxidation by the Cu^{II} complex, which is formed in the Cu^{I} dioxygen complex reaction with the substrate. Also the initial rates avoided the effects of the slow but gradual degradation of the Cu^{I} dioxygen complex, which also produces a Cu^{II} complex in solution. Since the Cu^{II} catalysed oxidations were carried out in the absence of dioxygen the Cu^{I} binuclear complex that would be formed would not cause any further oxidation of the substrate so that the first of the two problems with the Cu^{I} dioxygen oxidation is not a factor in the Cu^{II} oxidations. Of course, the degradation of the Cu^{I} dioxygen complex is also not a factor in the Cu^{II} oxidations. The initial first-order rates listed in Table 1 show that the macrocyclic binuclear Cu^{I} dioxygen complexes are from 5 to 100 times more rapid as oxidants than the binuclear Cu^{II} macrocyclic complexes. Probably the most interesting aspect of the data in Table 1 is the fact that 3,5-di-*tert*-butylcatechol and 3,4-dimethylaniline are assigned oxidation rate constants for the macrocyclic binuclear Cu^{I} dioxygen complex only, and that the oxidation rates for the Cu^{II} complex are immeasurably small, or non-existent. This observation correlates with the fact that only the first four substrates listed in Table 1, which have appreciable oxidation rates assigned to the Cu^{II} macrocyclic complex, show catalytic activity in the presence of excess dioxygen. Thus, it seems that the Cu^{II} catalysed oxidation is a necessary part of the reaction cycle, and the Cu^{I} complex generated by the Cu^{II} oxidation forms an oxygen complex under conditions of excess oxygen so that the cycle can then be repeated. Thus, in cases where the Cu^{II} macrocyclic complex is not an effective oxidant, the reaction cannot be catalytic in nature. A typical mechanism



Scheme 1

Table 2 Catalytic activity of $[Cu_2L]^{2+}$ in the oxidation of various substrates

Substrate	Turnover/h	Time of reaction/min
Hydroquinone	7	60
tert-Butylhydroquinone	5	43
2,6-Di-*tert*-butylphenol	25	5
2,6-Dimethoxyphenol	30	10

for the catalytic reaction for di-*tert*-butylphenol as a substrate is indicated in Scheme 1. A cyclic process is shown in which the binuclear Cu^{I} macrocyclic complex combines with molecular oxygen to form the dioxygen complex which then oxidizes 2,6-di-*tert*-butylphenol to the corresponding diphenoquinone with the concomitant formation of a Cu^{II} complex. This then oxidizes an additional 2 mol of di-*tert*-butylphenol to the corresponding diphenoquinone with the concomitant formation of the original Cu^{I} binuclear complex.

The substrates to which the proposed mechanism in Scheme 1 applies are listed in Table 2, with the turnover rates and the times over which the reaction was observed. It is noted that only those systems for which the Cu^{II} macrocyclic complex formed is active can be catalytic, since both Cu^{II} complexes and Cu^{I} dioxygen complexes are involved in the proposed reaction mechanism.

While the proposed mechanism does not go into detail concerning how di-*tert*-butylphenol combines with itself to form the diphenoquinone, one should mention the fact that Kitajima *et al.*[10] have proposed that the phenols form bridges

between the two Cu^{II} centres followed by electron transfer to give two Cu^{I} centres and two phenolate radicals, which are then close enough to combine to give the diphenoquinone. This is an interesting concept but it should be pointed out that it is not necessary for the phenolate ions to be bridging groups. Coordination of a phenolate ion with each of the copper centres would probably give the same result.

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