

## Notes

### Activation of Dioxygen and Catalytic Oxidation of Ethanol to Acetaldehyde and Hydrogen Peroxide by Copper(I) Complexes containing 2,2'-Bipyridyl and Tertiary Phosphine Ligands

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Reactions of  $[\text{Cu}(\text{bipy})\text{LI}]$  ( $\text{bipy} = 2,2'$ -bipyridyl;  $\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{PBU}^n_3, \text{or } \text{PEt}_3$ ) with  $\text{O}_2$  alone in dimethylformamide and  $\text{SO}_2$  plus  $\text{O}_2$  in dichloromethane lead to the formation of  $[\text{Cu}_2(\text{bipy})_2(\text{OH})_2]\text{I}_2$  and precipitation of  $\text{Cu}[\text{SO}_4]$ . The complex  $[\text{Cu}(\text{bipy})\text{LI}]$  catalyses the oxidation of ethanol by dioxygen to acetaldehyde and  $\text{H}_2\text{O}_2$  in the presence of equimolar quantities of  $\text{Na}[\text{OC}_2\text{H}_5]$ . Added phosphine acts as a strong inhibitor and the catalytic decomposition of  $\text{H}_2\text{O}_2$  by the complexes leads to their deactivation. A tentative reaction mechanism is discussed.

COPPER complexes are widely used as homogeneous catalysts in oxidation reactions involving dioxygen.<sup>1</sup> In this note we report the reaction between dioxygen and ethanol in the presence of  $[\text{Cu}(\text{bipy})\text{LI}]$  ( $\text{bipy} = 2,2'$ -bipyridyl,  $\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{PBU}^n_3, \text{or } \text{PEt}_3$ ) to give acetaldehyde and  $\text{H}_2\text{O}_2$ . The reactivity of these complexes towards dioxygen is also described. While this work was in progress, the reduction of dioxygen to water and the oxidation of alcohol catalysed by binary and ternary copper(I) complexes were reported by Munakata *et al.*<sup>2</sup> Our system and findings differ in several aspects from those reported and could be considered as an alternative model for copper(I)-containing oxidase.

#### RESULTS AND DISCUSSION

Dichloromethane solutions of  $[\text{Cu}(\text{bipy})\text{LI}]$  complexes undergo slow and irreversible oxygen absorption, accompanied by a colour change from orange-yellow to green with the eventual formation of a bluish green precipitate.

By carrying out the reaction of  $[\text{Cu}(\text{bipy})(\text{PPh}_3)\text{I}]$  (1) with  $\text{O}_2$  in dimethylformamide and by adding benzene to the resulting filtrate, analytically pure deep blue crystals of  $[\text{Cu}_2(\text{bipy})_2(\text{OH})_2]\text{I}_2$  (2) are obtained. A plausible mechanistic pathway involves the formation of a peroxo-bridged intermediate, and its subsequent hydrolysis by trace quantities of water to give the hydroxo-bridged dimer. Hydrolysis of peroxo-bridged complexes with the formation of hydroxo-bridges and  $\text{H}_2\text{O}_2$  has recently been reported.<sup>3</sup> Since peroxo-complexes are known to react with  $\text{SO}_2$  to give the corresponding sulphate complexes,<sup>3,4</sup> (1) was treated with a mixture of  $\text{SO}_2$  and  $\text{O}_2$  in the hope of trapping such an intermediate. A rapid exothermic reaction leads to the precipitation of free  $\text{Cu}[\text{SO}_4]$  identifiable on the basis of quantitative and qualitative analyses.

The complexes  $[\text{Cu}(\text{bipy})\text{LI}]$ , although totally inactive in neutral solution, are active towards ethanol oxidation with  $\text{O}_2$  when a stoichiometric amount of base such as sodium ethoxide or hydroxide is present. The formation of equal amounts of acetaldehyde and water, from the decomposition of  $\text{H}_2\text{O}_2$ , is established by gas chromatography with a thermal conductivity detector.

Although maximum activity is observed in ethanol, other alcohols can also be oxidised under the same conditions. Added phosphine acts as a strong inhibitor as can be seen from the Table. The rate of acetaldehyde formation does

Results of reactions between dioxygen and alcohol using (1) as catalyst<sup>a</sup>

Reactant	Mole ratio of catalyst to $\text{PPh}_3$	Mole ratio of carbonyl product <sup>b</sup> to catalyst
Ethanol	No $\text{PPh}_3$	38 : 1
	3.28 : 1	25 : 1
	1.64 : 1	12 : 1
	0.82 : 1	No reaction
Isopropyl alcohol	No $\text{PPh}_3$	16 : 1
n-Butanol		22 : 1
Cyclohexanol		14 : 1
Benzyl alcohol		25 : 1

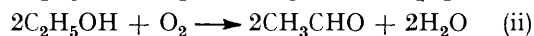
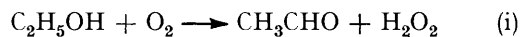
<sup>a</sup> Reaction conditions: amount of (1) = 0.16 mmol; temperature = 25 °C; oxygen pressure = 30 p.s.i.; time for reaction = 20 min. <sup>b</sup> Acetaldehyde, acetone, n-butyraldehyde, cyclohexanone, and benzaldehyde respectively.

not show any simple dependence on the concentration of the catalyst, ethanol, added phosphine, base, or the pressure of  $\text{O}_2$ . Finally, all the  $[\text{Cu}(\text{bipy})\text{LX}]$  ( $\text{X} = \text{I}, \text{Br}, \text{or } \text{Cl}$ ;  $\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{PBU}^n_3, \text{or } \text{PEt}_3$ ) complexes studied under identical conditions gave approximately the same initial rate for the formation of acetaldehyde.

Addition of sodium ethoxide to an equimolar dichloromethane-ethanol solution of (1) under a nitrogen atmosphere leads to a colour change from orange-red to yellow and the eventual formation of a brownish yellow precipitate. On the basis of its analytical data, this species is best formulated as  $[\text{Cu}_2(\text{bipy})_2(\text{OEt})\text{I}]$  (3). It has not been possible to record the n.m.r. spectrum of (3) due to its insolubility in organic solvents. It is important to note that there is no reaction between (1) and sodium ethoxide in the presence of added triphenylphosphine [in a 1 : 1  $\text{PPh}_3$ -(1) molar ratio]. Attack by ethoxide, therefore, seems to be possible only when phosphine dissociation takes place to some extent. It should be mentioned that both (2) and (3) are found to be inactive as catalysts for ethanol oxidation.

As shown below [equations (i) and (ii)], the reaction

between ethanol and dioxygen to form acetaldehyde can proceed either through a two- or a four-electron pathway giving hydrogen peroxide or water as the other product.



Establishing the stoichiometry as that of reaction (i) is complicated by the fact that  $\text{H}_2\text{O}_2$  undergoes ready catalytic decomposition by (1) into  $\text{H}_2\text{O}$  and  $\text{O}_2$ . Thus in a separate experiment, with  $\text{H}_2\text{O}_2$  and (1) in a molar ratio of 150 : 1, it is found that 99.5%  $\text{H}_2\text{O}_2$  is decomposed within 2 min. In *ca.* 20 min, a precipitate is formed whose characterisation has not been attempted, but which is catalytically inactive. However, the following iodometric method establishes, at least qualitatively, the presence of  $\text{H}_2\text{O}_2$  in the catalytic runs.

An ethanol-dichloromethane solution, with catalytic and equimolar quantities of (1) and sodium ethoxide respectively, is subjected to an oxygen pressure of 30 p.s.i.\* Samples are withdrawn at short time intervals (every 0.5 min), iodometrically titrated, and analysed for acetaldehyde and water by gas chromatography. A duplicate experiment under identical conditions is carried out; in this case however sodium ethoxide is not added. The iodometric titration value for the first experiment at a given time is always higher than the corresponding value for the second experiment. As mentioned already, in the absence of sodium ethoxide, (1) does not catalyse the oxidation of ethanol. The formation of  $\text{H}_2\text{O}_2$  in the catalytic oxidation is therefore indicated from the consistently higher values obtained for the first experiment.

Rapid catalytic decomposition of  $\text{H}_2\text{O}_2$  by  $[\text{Cu}(\text{bipy})\text{LI}]$  complexes leads to the deactivation of the catalyst, and to values very much lower than the theoretical ones for the iodometric titrations. At no point in the reaction is more than 1% of the  $\text{H}_2\text{O}_2$  undecomposed.

The similarities between the enzymatic oxidation of galactose by the copper-containing protein galactose oxidase and the present system are obvious. In both cases an alcoholic group is involved and  $\text{H}_2\text{O}_2$  is a co-product which in the absence of catalase can also cause deactivation of the enzymatic system.<sup>5</sup> Based on various physico-chemical studies, involvement of  $\text{Cu}^{\text{III}}$  in the enzymatic system was proposed by Hamilton *et al.*,<sup>5</sup> but very recently this has been seriously questioned.<sup>6</sup>

A tentative mechanism for the system described here involves formation of a mononuclear copper ethoxo-species with co-ordinative unsaturation through phosphine dissociation. Co-ordination of dioxygen as  $\text{O}_2^-$ , followed by proton transfer from the co-ordinated ethoxo-group, would produce free or bound  $\text{HO}_2^-$ , the involvement of which has been proposed in reactions of platinum dioxygen complexes.<sup>7</sup> Reaction of ethanol with  $\text{HO}_2^-$

could then produce hydrogen peroxide and ethoxide ion, thereby completing the catalytic cycle.

#### EXPERIMENTAL

The complexes  $[\text{Cu}(\text{bipy})\text{LX}]$  and  $[\text{Cu}_2(\text{bipy})_2\text{I}_2]$  were prepared by literature methods.<sup>8</sup> Microanalyses were carried out with a Carlo-Erba 1106 instrument. Infrared spectra were recorded on a Perkin-Elmer 377 grating spectrophotometer. Gas chromatographic analyses were performed with a Pye-Unicam 204 instrument. Unless otherwise specified, all the reactions were carried out under nitrogen. Ethanol and other solvents were dried and distilled before use.

*Reactions of  $[\text{Cu}(\text{bipy})\text{LI}]$ . With  $\text{O}_2$ .* The complex  $[\text{Cu}(\text{bipy})(\text{PPh}_3)\text{I}]$  (570 mg, 1 mmol) in dimethylformamide (15 cm<sup>3</sup>) was shaken under an oxygen atmosphere (30 p.s.i.) for 30 min. The colour of the solution changed from orange-red to bluish green. After filtration, benzene was added to the filtrate to obtain deep blue microcrystals of  $[\text{Cu}_2(\text{bipy})_2(\text{OH})_2]\text{I}_2$  (210 mg, 0.3 mmol) (Found: C, 33.1; H, 2.5; N, 7.6. Calc. for  $\text{C}_{20}\text{H}_{18}\text{Cu}_2\text{I}_2\text{N}_4\text{O}_2$ : C, 33.0; H, 2.5; N, 7.1%);  $\nu_{\text{OH}}$  at 3 560 cm<sup>-1</sup>. The reactions of dioxygen with other  $[\text{Cu}(\text{bipy})\text{LI}]$  (L = tertiary phosphine) complexes were carried out in a similar fashion to give  $[\text{Cu}_2(\text{bipy})_2(\text{OH})_2]\text{I}_2$  in each case.

*With  $\text{O}_2$  plus  $\text{SO}_2$ .* The complex  $[\text{Cu}(\text{bipy})\text{LI}]$  (288 mg, 0.5 mmol) was dissolved in degassed dichloromethane (20 cm<sup>3</sup>). The reaction vessel was attached to inflated bladders filled with  $\text{O}_2$  and  $\text{SO}_2$  respectively. Dioxygen was first introduced into the reaction vessel and, after 2 min,  $\text{SO}_2$  was also introduced. An exothermic reaction took place, and a bluish green precipitate of  $\text{Cu}[\text{SO}_4]$  (39 mg, 0.25 mmol) was formed which was characterised by conventional qualitative and quantitative analyses.

*With  $\text{Na}[\text{OC}_2\text{H}_5]$ .* The compound  $\text{Na}[\text{OC}_2\text{H}_5]$  (34 mg, 0.5 mmol) in ethanol (5 cm<sup>3</sup>) was added to a solution of  $[\text{Cu}(\text{bipy})(\text{PPh}_3)\text{I}]$  (288 mg, 0.5 mmol) in dichloromethane (15 cm<sup>3</sup>). An instantaneous colour change from orange-red to yellow took place, and a brownish yellow precipitate began to form. After stirring for 1 h, the suspension was filtered through a Schlenk apparatus. The complex  $[\text{Cu}_2(\text{bipy})_2(\text{OEt})\text{I}]$  which formed as the residue was washed with dry hexane and stored under vacuum (126 mg, 0.2 mmol) (Found: C, 43.5; H, 3.5; N, 9.0. Calc. for  $\text{C}_{22}\text{H}_{21}\text{Cu}_2\text{IN}_4\text{O}$ : C, 43.2; H, 3.4; N, 9.2%). The reactions of  $\text{Na}[\text{OC}_2\text{H}_5]$  with other  $[\text{Cu}(\text{bipy})\text{LI}]$  (L = tertiary phosphine) complexes were carried out in a similar fashion to give  $[\text{Cu}_2(\text{bipy})_2(\text{OEt})\text{I}]$  in each case.

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\* Throughout this note: 1 p.s.i. (lbf in<sup>-2</sup>)  $\approx 7.09 \times 10^3$  Pa.