Characterization of a Novel Low Oxidation State Transition-metal Peroxide from the Reaction of Copper(I) Chloride with Oxygen in Pyridine

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Summary The reaction of copper(I) chloride with oxygen in pyridine results in the formation of a novel copper(I) peroxide complex and copper(II) chloride.

The addition of pyridine to solid copper(I) chloride in the presence of oxygen at room temperature results in the formation of a brown solution which is an active catalyst in the homogeneous oxidative coupling of acetylenes, amines, and phenols.[1] We have found that the stoicheiometry of this reaction, as determined by oxygen uptake experiments, is $\Delta(\mathrm{Cu^I})/\Delta(\mathrm{O_2}) = (4{\cdot}0 \pm 0{\cdot}2)$ (20 determinations), at final molar pyridine:copper ratios, $R > 0{\cdot}5$.[1] No deviations from this stoicheiometry were evident up to $R = 80$, consistent with negligible pyridine co-oxidation (confirmed by spectral (u.v.–visible, i.r.) inspection of the products).

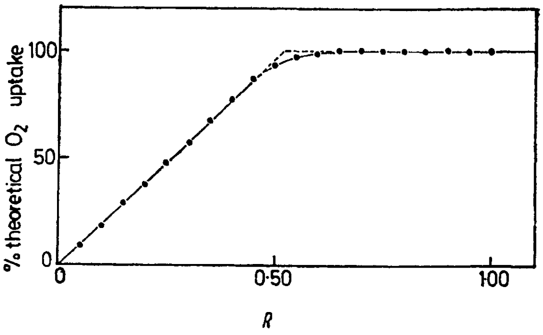

Figure. Effect of R (see text) on the percentage of theoretical oxygen uptake expected for equation 1 in *o*-dichlorobenzene. 2·02 m moles of copper(I) chloride were suspended in 30 ml of *o*-dichlorobenzene at 27°; pyridine (2·02 m moles, dissolved in 10 ml *o*-dichlorobenzene) was added in 0·5 ml aliquots, the system was equilibrated and the amount of oxygen absorbed was measured manometrically, with appropriate corrections, after each addition.

The products of the reaction were separated by gel permeation chromatography on a 90 cm × 1 cm diameter column of Biobeads SX-12 (200–400 mesh) resin (Biorad Laboratories) with pyridine as the eluant at room temperature. (Other chromatographic supports such as alumina and silica cause decomposition under these conditions). Elution of the product mixture results in two bands; the first is brown and catalytically active, and the second is green but does not result in visible polymerization of 2,6-xylenol under standard conditions.[2] The brown component saturates the column and a pretreated column was employed for subsequent separations.† The retention volumes, V_R, of the first and second components were 38·7 and 42·5 ml, respectively, at a flow rate of 0·29 ml min^{-1}. V_R for the green component was identical to that of $\mathrm{Cu(py)_2Cl_2}$ under identical chromatographic conditions. The formation of this product was confirmed by quantitative e.s.r. measurements [calibrated with standard copper(II) chloride solutions in pyridine],[3] which were consistent with the overall reaction (equation 1).‡

$$4\mathrm{Cu^I} + \mathrm{O_2} \xrightarrow{\text{pyridine}} 2\mathrm{Cu^{II}} + \mathrm{Cu_2O_2} \qquad (1)$$

Beer's law is obeyed by the product solution and by the separated components in pyridine over the copper atom concentration range 10^{-2}—10^{-4} M. Analysis of the spectra at 433 nm [ϵ (mixture) 338 ± 10, ϵ(peroxide) 633 ± 20, $\epsilon(\mathrm{Cu^{II}})$ 1 ± 0·4 (g atom Cu)$^{-1}$ cm^{-1}] and 735 nm [ϵ(mixture) 82 ± 3, ϵ(peroxide) 29·2, $\epsilon(\mathrm{Cu^{II}})$ 136 ± 2, (g atom Cu)$^{-1}$ cm^{-1}] confirm the above stoicheiometry within experimental error and show that the reaction products may be separated without appreciable decomposition.

The identity of the brown, catalytic component solution was established by gravimetric determination of the sulphate[4] formed (equation 2),‡

$$\mathrm{Cu_2O_2} + \mathrm{SO_2} \xrightarrow[\text{pyridine}]{\mathrm{N_2}} \mathrm{Cu_2SO_4} \qquad (2)$$

which is that expected for a transition-metal peroxide.[5] The existence of co-ordinated peroxide was confirmed by the detection of a polarographic wave (Pt electrodes) at −0·95 V for the brown component in 0·1 M tetramethylammonium perchlorate solution in pyridine (−0·95 V for $\mathrm{H_2O_2}$) and by the presence of a characteristic, sharp band at 856 cm^{-1} in the Raman spectrum in pyridine (876 cm^{-1} for $\mathrm{H_2O_2}$).[6] These bands are infra-red inactive in pyridine. Conductance measurements were consistent with the presence of a non-electrolyte in pyridine.

The brown component has no spectral maxima in the range 800–305 nm (the limit of pyridine solvent transparency); $\epsilon(340)$ $2{\cdot}3 \times 10^3$ (g atom Cu)$^{-1}$ cm^{-1} is similar to that due to the proposed peroxide grouping in oxyhemocyanin[7] but no discrete peroxide band is evident.§ No e.s.r. spectrum is observed for a 10^{-2} M solution in pyridine, and the spectra are unaffected by high vacuum or by bubbling nitrogen through the solution.

Although pyridine solutions of the peroxide compound are stable over long periods of time, attempts to isolate a solid (for example by freeze-drying in the absence of excess $\mathrm{O_2}$) always resulted in the precipitation of an insoluble black material, which was shown by analysis to be CuO. Co-ordination of pyridine to the complex was confirmed

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† The green band is a mixture of blue bis-(pyridyl)copper(II)chloride and the brown component, due to column saturation by the latter. Spectral analysis of a representative fraction of the green band using the known extinction coefficients of pyridine solutions of copper(II) chloride and the brown component gave $[\mathrm{Cu^{II}}] = 1{\cdot}8 \times 10^{-3}$ M and $[\mathrm{Cu^{I}}] = 1{\cdot}2 \times 10^{-4}$ M.

‡ Equations 1 and 2 represent only observed stoicheiometries: chloride and pyridine ligands have been omitted for clarity.

§ Oxyhemocyanin has been formulated as a copper(II) peroxide species on the basis of its visible spectrum: $\epsilon(700)$ 75; $\epsilon(570)$ 500; $\epsilon(440)$ 65.[7,11]

from the ^{1}H n.m.r. spectrum of a 0·3 M solution. The spectrum shows a very marked broadening of the α-proton signal of the solvent and significant broadening of the β and γ signal at room temperature. These results are similar to those for copper(II) chloride in pyridine, and differ sharply from the minor broadening due to copper(I) chloride. Kinetic measurements indicate that pyridine ligand exchange in the peroxide is much too slow ($t_{\frac{1}{2}} > 1$ week at 50°) to account for this broadening, which must result from the marked electron delocalization which stabilizes this complex. Excess pyridine is necessary to stabilize the peroxide; thus, decomposition results on attempted extraction of pyridine solutions with purified non-polar solvents at room temperature. Decomposition of the complex to copper(II) is slow in the presence of water, but is greatly accelerated by small amounts of aqueous acid.

Since the peroxo complex cannot be isolated as a pure solid, we are unable to establish its complete chemical identity with respect to pyridine co-ordination. Ligand exchange, *e.g.* with 2,9-dimethyl-1,10-phenanthroline [a copper(I) specific ligand] at 50° is accompanied by oxidation of the substituting ligands. However, observations on the stoicheiometric effect of varying pyridine:copper ratios, particularly in benzene co-solvent,[8] suggest that the minimum number of pyridine ligands required for stabilization of the peroxo species is 2. This conclusion is supported by the data in the Figure, where the percentage of theoretical oxygen uptake in *o*-dichlorobenzene shows a linear dependence on R when $R < 0{\cdot}5$, which is consistent with the requirement for pyridine co-ordination by copper(I),[9] and is confirmed by a lack of evidence for pyridine co-ordination at copper(II) chloride at $R = 0{\cdot}5$ in *o*-dichlorobenzene.

The above results are consistent with the formation of the species (py)$_n$CuOOCu(py)$_n$ ($n \geqslant 1$) in the reaction of copper(I) chloride with oxygen in pyridine. This species is formally a copper(I) peroxide complex which is evidently strongly stabilized by electron delocalization. To our knowledge, it is the first example of a peroxo-compound of a transition metal in a low oxidation state. Very few copper-peroxide species have been reported, and these are exclusively copper(II) complexes.[10] We are currently investigating other co-ordinating solvent media in an attempt to explain this unusual behaviour. These studies may have some bearing on the mechanisms of reaction of those copper-proteins (tyrosinase, laccase) which promote similar amine and phenol oxidative reactions *in vivo*.[11]

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