Role of a Copper Complex in an Oxygen-atom Transfer Reaction from Dioxygen to Triphenylphosphine

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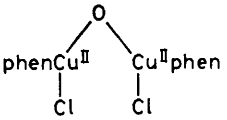
Summary Unexpectedly, 1,10-phenanthroline–Cu^{I}Cl (phenCuCl) reacts with dioxygen to give only one oxygenated complex (yield 95%), the stoicheiometry of which is $(phenCuCl)_2O$; the quantitative transfer of an oxygen atom from this complex to triphenylphosphine is also reported.

In homogeneous solutions of methylene dibromide, the compound 1,10-phenanthroline–Cu^{I}Cl (phenCuCl) reacts with molecular oxygen to give a single complex (yield 95%), isolated in an inert atmosphere. The dixoygen absorption by phenCuCl has been followed by gas volumetry: (*a*) 20 ml of CH_2Br_2 plus 833 mg of phenCuCl absorbed 0·742 mmol of O_2 (O_2/Cu 0·249); (*b*) 20 ml of CH_2Br_2 plus 762 mg of phenCuCl absorbed 0·685 mmol of O_2 (O_2/Cu 0·251); (*c*) 10 ml of CH_2Br_2 plus 564 mg of phenCuCl absorbed 0·487 mmol of O_2 (O_2/Cu 0·248). The reactions were carried out at 20 °C and were complete within 1 h. The dioxygen uptake firmly established that 4 copper atoms are necessary to absorb one molecule of oxygen. The formation of a single product is surprising because in previous work, under slightly different conditions,[1] but with the same oxygenation stoicheiometry, two compounds with the formula $[LCuCl_2]_x$ and $[LCuO]_y$ were obtained. The data reported in the literature show that the aprotic oxygenation of CuCl can lead to either of these two complexes (L = pyridine)[2] or to one only (L = *N*-methylpyrrolidin-2-one).[3]

$$2\ \text{phenCuCl} + \tfrac{1}{2}\ O_2 \xrightarrow{CH_2Br_2} (\text{phenCuCl})_2O \qquad (1)$$

(1)



The elemental analysis of the complex (**1**)† confirms the stoicheiometry of the reaction established by gas volumetry. It was not possible to detect the Cu–O i.r. vibration using $^{18}O_2$, as the spectrum of the complex thus obtained was identical with that of the complex prepared from $^{16}O_2$ (characteristic vibrations, ν 642, 480 br., 425, and 295 cm^{-1}).‡ The possibility of an equimolecular mixture of $phenCuCl_2$ and phenCuO being present, which would give the same elemental composition, can be discarded. Indeed, the characteristic vibrations of the independently prepared $phenCuCl_2$ complex (ν 295 and 318 cm^{-1}) could not be detected in the i.r. spectra. Complex (**1**) is hygroscopic and must be handled only in an inert atmosphere.

The addition of triphenylphosphine (TPP) to complex (**1**), dissolved in dimethylformamide (DMF), caused a colour change (from green to carmine red). After the solution had been left for 2 h at 100 °C in an argon atmosphere, the solvent was evaporated off, and the solid residue was washed with diethyl ether to extract TPP and TPP-oxide from the copper complex. The reaction was carried out with an excess of TPP (5 equiv.) which showed that the TPP-oxide yield is 100% with respect to the oxygen from the complex (determined by ^{31}P n.m.r. spectroscopy on a mixture of TPP and TPP-oxide of known weight) and that the reaction follows the stoicheiometry of equation (2). The oxygen-transfer reaction has also been carried out with the complex prepared using a mixture of $^{16}O_2/^{18}O_2$ in which the isotopic ratio was 1:1. In this case, TPP-oxide was obtained with the same isotopic ratio of $^{16}O/^{18}O$ (determined by mass spectroscopy). The complex (**2**), formed after the transfer of the oxygen atom, was found to be phenCuCl(TPP), as it had the same properties (elemental analysis,§ spectroscopic data, and m.p.) as this compound, independently prepared by the method of Jardine *et al.*[4] The stoicheiometry of

$$3\ \text{TPP} + (\text{phenCuCl})_2O \rightarrow \text{TPP=O} + 2\ \text{phenCuCl(TPP)} \qquad (2)$$

(2)

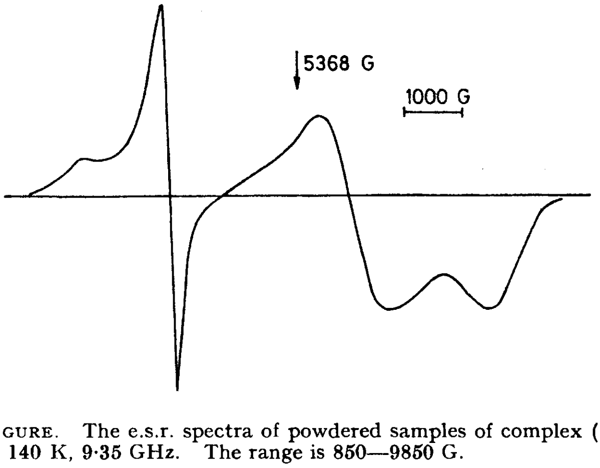


Figure. The e.s.r. spectra of powdered samples of complex (**1**) at 140 K, 9·35 GHz. The range is 850—9850 G.

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† Satisfactory C, H, Cl, Cu, and N analyses were obtained for this complex (Found: C, 50·8; H, 2·8; Cl, 11·35; Cu, 21·9; N, 9·55. Calc. for $C_{24}H_{16}Cl_2Cu_2N_4O$: C, 50·17; H, 2·78; Cl, 12·4; Cu, 22·1; N, 9·75%).

‡ It may be supposed that the Cu–O vibrations would be masked by ligand vibrations in the ν 600—400 cm^{-1} range.

§ Satisfactory C, H, N, Cl, Cu, and P analyses were obtained for this complex (Found: C, 65·5; H, 4·35; Cl, 6·35; Cu, 10·95; N 4·9; P, 6·0. Calc. for $C_{30}H_{23}ClCuN_2P$: C, 66·54; H, 4·25; Cl, 6·56; Cu, 11·74; N, 5·17; P, 5·73%).

the reaction is confirmed; 2 equiv. of complex (**2**) were quantitatively isolated for 1 equiv. of TPP-oxide.

These results indicate that two copper atoms must be bonded to the oxygen atom and suggest that the oxygenated complex (**1**) has a μ-oxo-bridge. Additional support for this structure is given by its e.s.r. spectra. The e.s.r. spectrum of this compound, recorded at 140 K, is shown in the Figure. First, we assumed that the band at *ca.* 3000 G resulted from the simple paramagnetism of a monomeric impurity present in our samples.[5] Second, the two high-field lines at 7000 and 8600 G and the low-field one at 1800 G are indicative of a binuclear structure. The intensity of the low-field line decreased dramatically by increasing the temperature. The e.s.r. data demonstrate that the copper atoms in the dimeric complex are exchange-coupled with a triplet ground state.[5–7] At present the insolubility of the complex in many solvents and its thermal instability have prevented us from obtaining suitable crystals for a crystallographic study to confirm its structure.

The fact that the same isotopic ratio is observed in the TPP-oxide and in the starting dioxygen is good evidence for the activation of molecular oxygen by the copper(I) complex. Isolation of the intermediate complex gives rise to the hypothesis of a bimetallic reduction of the oxygen atom, in which each copper atom provides an electron. This study constitutes the first example of a direct oxygen-transfer to an organic substrate from an oxygenated copper complex.

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