Reaction of Copper(I) Chloride Pyridine Complexes with Dioxygen. A Kinetic Study

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Summary

Copper(I) complexes \([\text{CuClI}_L\] \((L = \text{Py}, \text{4-PhPy}, \text{4-MePy}, \text{4-Me}_2\text{NP}, \text{and} \ 4\text{-PhCOPy})\) react with dioxygen in dichloromethane according to the rate law:

\[ r = K_D^{1/2} k_2 [\text{CuClI}_L]^{1/2} [\text{O}_2] \]

where \(K_D\) is the dissociation constant of the equilibrium \([\text{CuClI}_L] \rightleftharpoons 2\text{CuCl} + k_2\) the second order rate constant of the reaction of the latter with dioxygen.

The \(K_D\) values were determined by molecular weight measurements in dichloromethane and a correlation has been developed between the experimental rate constants obtained and the acid dissociation constants (\(pK_a\)) for the ligands. The reaction fits a Hammett linear free energy relationship and the acid dissociation constants (\(pK_a\)) for the ligands. The reaction fits a Hammett linear free energy relationship and the acid dissociation constants (\(pK_a\)) for the ligands.

Introduction

The interaction of low molecular weight copper(I) complexes with dioxygen has attracted interest in recent years because of its biological relevance to many copper-containing enzymes\(^{(1)}\). Copper(I) halide amine complexes have been used successfully as reagents and/or catalysts for different oxidations with dioxygen as oxidant, such as the oxidative coupling of acetylenes\(^{(2)}\), phenols\(^{(3)}\) and the oxidative ring cleavage of aromatic amines\(^{(4)}\), phenols\(^{(5)}\), catechols\(^{(6,7)}\), and o-quinones\(^{(8)}\). The kinetics of the reaction of copper(I) chloride with dioxygen has been also followed in several solvents\(^{(9-12)}\).

We have now undertaken a kinetic study of the reaction of \([\text{CuClI}_L]_2\) complexes with dioxygen in dichloromethane and pyridine. Using different 4-substituted pyridine derivatives as ligands, the validity of the Hammett relationship for the oxygenation has been tested. No effort has been made to elucidate the composition of the actual product(s) of the oxygenation. This aspect was described in a separate study, carried out in ether and the primary dioxygen adducts CuI2Cl2 were isolated\(^{(13)}\). In solvents such as dichloromethane, pyridine, methanol, and chloroform a number of secondary products are
formed which equilibrate with the primary ones depending on the nature of the solvent. Some of the secondary products could be isolated. In all solvents the stoichiometry of the reaction is, however, Cu(I) : O₂ = 4 : 1.

Results and Discussion

Complexes of type [CuXL]₂ (X = Cl or Br; L = pyridine, 4-Me-pyridine, 4-Ph-pyridine, 4-PhCO-pyridine, and 4-Me₂N-pyridine) were prepared in an analytically pure, crystalline form by mixing equimolar amounts of CuX and L in dichloromethane, from which the [CuXL]₂ compounds were precipitated by slowly adding ether to the clear solution. These compounds are relatively stable towards dioxygen, at least if well dried, and so their handling did not require rigorous conditions; they can be stored under argon for several months without decomposition.

The complexes were dissolved in dichloromethane and the dioxygen consumption was measured by volume at constant temperature (0-18°C) and dioxygen pressure (0.25-1 bar). The concentration of dissolved dioxygen was determined with a Beckmann oxygen sensor. A plot of initial dioxygen consumption versus the square root of the concentration of [CuClL]₂ complexes is linear up to ca. 90% of reaction. The one half order dependence on [CuXL]₂ may be confirmed also by the initial reaction rate method; the linear plots so obtained are illustrated in Figure 1. The reaction rates are slightly dependent upon different substituents on the C-4 position of the pyridine ligands. A first order dependence on the dioxygen concentrations was established for similar experiments by applying various dioxygen pressures for the oxygenation of [CuClPy]₂ in dichloromethane, as shown in Figure 2.

We have further found that the reaction order with respect to the copper(I) complex is solvent dependent. In pyridine the reaction order with respect to copper is unity for [CuClPy]₂ and [CuBrPy]₂ (as shown in Figure 3). This change in order can be easily explained by the dinuclear nature of the [CuXL]₂ complexes in dichloromethane. We have measured the molecular weights of these compounds by the vapour pressure method in this solvent and from these data their degree of dissociation and the dissociation constants could be calculated. The data are presented in Table 1, from which it seems obvious that the K_D values are in the 10⁻³-10⁻⁵M range, which means that the copper(I) complexes are present mainly as dimers (≥ 50%) and monomers when dissolved in dichloromethane. In solvent pyridine, however, the complexes are present almost quantitatively in their mononuclear form as CuXL₂.