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

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### Summary

Copper(I) complexes [CuCIL]<sub>2</sub> (L = Py, 4-PhPy, 4-MePy, 4-Me<sub>2</sub>NPpy, and 4-PhCOPy) react with dioxygen in dichloromethane according to the rate law:

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

where  $K_D$  is the dissociation constant of the equilibrium  $[\text{CuCIL}]_2 \rightleftharpoons 2 \text{CuCIL}$  and  $k_2$  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 ( $\text{p}K_a$ ) for the ligands. The reaction fits a Hammett linear free energy relationship and the rate-determining step is attributed to the first electron transfer to the dioxygen molecule from the mononuclear copper(I) complex, which is influenced by changes in the electron density on the copper.

### 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<sup>(1)</sup>. 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<sup>(2)</sup>, phenols<sup>(3)</sup> and the oxidative ring cleavage of aromatic amines<sup>(4)</sup>, phenols<sup>(5)</sup>, catechols<sup>(6, 7)</sup>, and *o*-quinones<sup>(8)</sup>. The kinetics of the reaction of copper(I) chloride with dioxygen has been also followed in several solvents<sup>(9–12)</sup>.

We have now undertaken a kinetic study of the reaction of [CuXL]<sub>2</sub> 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 Cu<sub>4</sub>Cl<sub>4</sub>L<sub>3</sub>O<sub>2</sub> were isolated<sup>(13)</sup>. In solvents such as dichloromethane, pyridine, methanol, and chloroform a number of secondary products are

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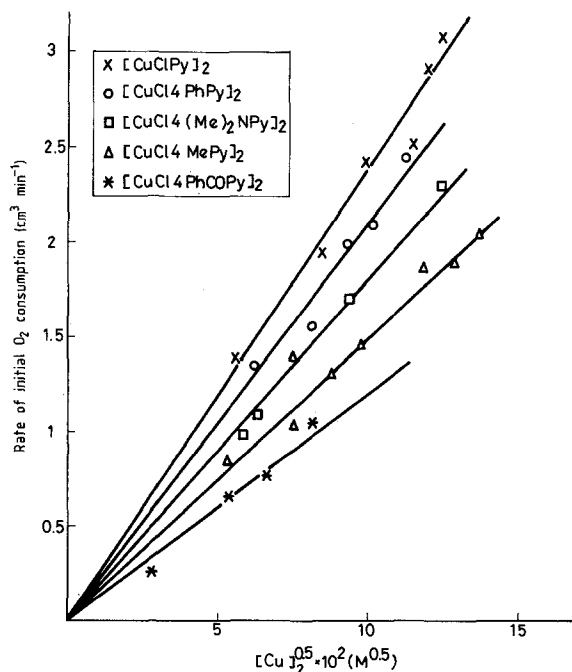
formed which equilibrate with the primary ones depending on the nature of the solvent. Some of the secondary products could be isolated<sup>(7, 14-16)</sup>. In all solvents the stoichiometry of the reaction is, however,  $\text{Cu(I)} : \text{O}_2 = 4 : 1$ .

### Results and Discussion

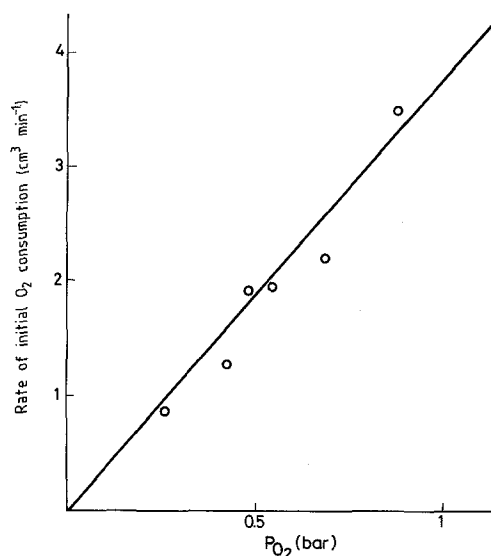
Complexes of type  $[\text{CuXL}]_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{L} = \text{pyridine}$ , 4-Me-pyridine, 4-Ph-pyridine, 4-PhCO-pyridine, and 4-Me<sub>2</sub>N-pyridine) were prepared in an analytically pure, crystalline form by mixing equimolar amounts of  $\text{CuX}$  and  $\text{L}$  in dichloromethane, from which the  $[\text{CuXL}]_2$  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  $[\text{CuClL}]_2$  complexes is linear up to *ca.* 90% of reaction. The one half order dependence on  $[\text{CuXL}]_2$  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  $[\text{CuClPy}]_2$  in dichloromethane, as shown in Figure 2.

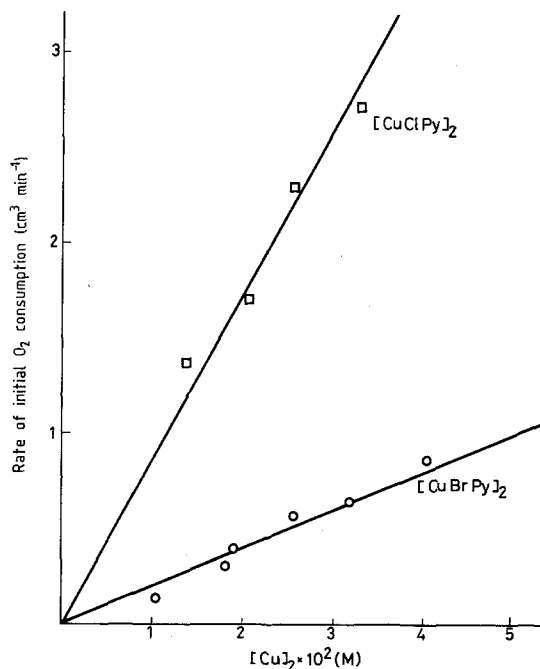
We have further found that the reaction order with respect to the copper(I) complex is solvent dependent. In pyridine the reaction order with respect to copper is unity for  $[\text{CuClPy}]_2$  and  $[\text{CuBrPy}]_2$  (as shown in Figure 3). This change in order can be easily explained by the dinuclear nature of the  $[\text{CuXL}]_2$



**Figure 1.** Rate of initial dioxygen consumption *vs.* the concentration of different  $[\text{CuClL}]_2$  complexes at 10°C in  $\text{CH}_2\text{Cl}_2$ ,  $[\text{O}_2] = 2.3 \times 10^{-4}$  M.



**Figure 2.** Dependence of the rate of dioxygen consumption on the dioxygen pressure at 10°C in  $\text{CH}_2\text{Cl}_2$ ,  $[\text{CuClPy}]_2 = 1.6 \times 10^{-2}$  M.



**Figure 3.** Dependence of the rate of oxygen consumption on the  $[\text{CuXPy}]_2$  concentration in pyridine at 18°C,  $[\text{O}_2] = 4.4 \times 10^{-3}$  M.

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  $10^{-3}$ – $10^{-5}$  M range, which means that the copper(I) complexes are present mainly as dimers ( $\geq 50\%$ ) and monomers when dissolved in dichloromethane. In solvent pyridine, however, the complexes are present almost quantitatively in their mononuclear form as  $\text{CuXL}_3$ .

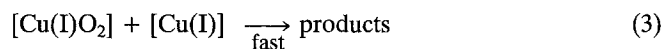
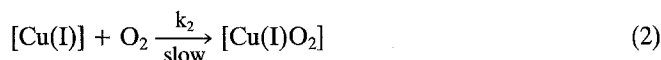
All the copper(I) compounds studied so far exhibit a first order dependence on dioxygen and first and/or second order dependence on the copper(I) complexes<sup>(17-19)</sup>. Our results however, indicate an overall half order dependence on the

**Table 1.** Molecular weights and dissociation constants of [CuCIL]<sub>2</sub> complexes as determined by the vapour pressure method in CH<sub>2</sub>Cl<sub>2</sub> between 0 and 37 °C<sup>a)</sup>

Compounds	M.W. (calcd.)	M.W. (obs) <sup>b)</sup>	Degree of Dissociation (%)	10 <sup>3</sup> K <sub>D</sub> (M)
[CuClPy] <sub>2</sub>	356.16	249	43.3	2.3 ± 0.6
[CuCl(4PhPy)] <sub>2</sub>	508.34	332	53.1	2.7 ± 0.7
[CuCl(4MePy)] <sub>2</sub>	384.22	282	36.2	0.77 ± 0.17
[CuCl(4Me <sub>2</sub> NPy)] <sub>2</sub>	442.30	415	6.6	0.011 ± 0.003
[CuCl(4PhCOPy)] <sub>2</sub>	564.36	370	52.5	0.74 ± 0.05

a) With a Knauer Vapour Pressure Osmometer assuming no dissociation of the pyridine ligands; the dependence of K<sub>D</sub> on the temperature was small, insignificant and within the errors of the determination; b) Average of three independent measurements.

copper concentration. The kinetic data can be accommodated by the following equations:

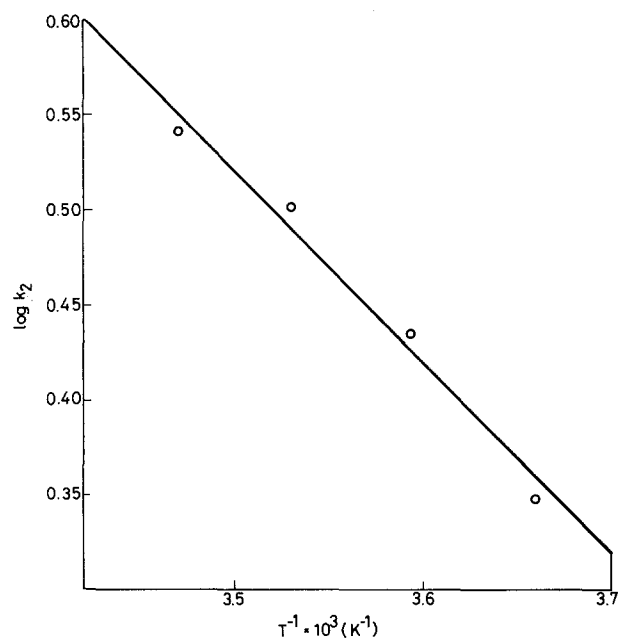


and this mechanism is consistent with the rate Equation (4):

$$r = K_D^{1/2} k_2 [\text{Cu(I)}]_2^{1/2} [\text{O}_2] \quad (4)$$

A good Arrhenius plot was obtained for oxygenations of [CuClPy]<sub>2</sub> in dichloromethane (Figure 4). The activation parameters are: ΔH<sub>2</sub><sup>‡</sup>, 17 ± 3 kJ mol<sup>-1</sup> and ΔS<sub>2</sub><sup>‡</sup>, -167 ± 5 kJ K<sup>-1</sup> mol<sup>-1</sup>.

In the reaction sequence [Equations (1)–(3)] the rate-determining step (2) is preceded by dissociation of the halogen-bridged dinuclear copper(I) complexes to give mononuclear copper(I) species. Since the dissociation constants, K<sub>D</sub>, are

**Figure 4.** Arrhenius plot for the oxygenation of [CuClPy]<sub>2</sub>.

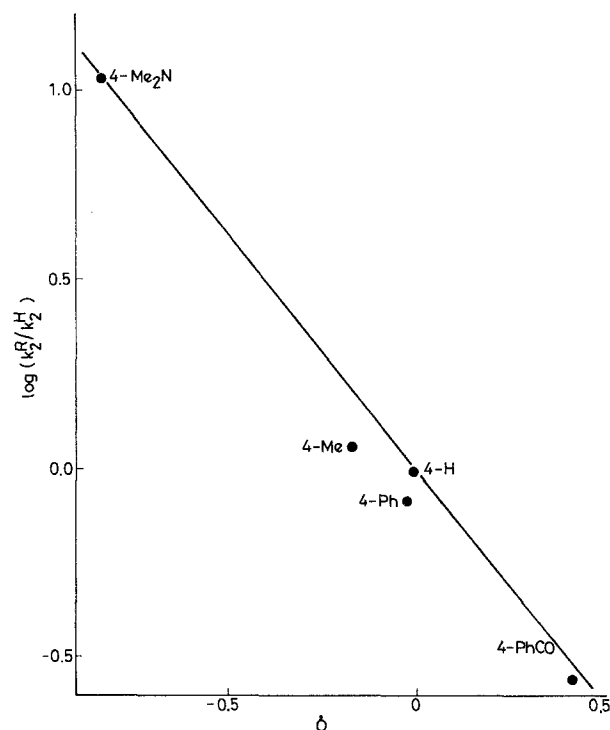
small and equilibrium (1) is not shifted much to the right, one part of the copper(I) (≥ 50%) remains dimeric in dichloromethane solution. The opposite is valid for pyridine solutions, where the total amount of copper(I) appears to be the mononuclear CuXPy<sub>3</sub>. The first order dependence with respect to dioxygen and copper(I) indicates that a plausible pathway for the redox reaction would be a slow rate-limiting one electron reduction of dioxygen by the copper(I) complexes (Reaction 2), followed by a fast, more favourable second electron transfer from another copper(I) forming O<sub>2</sub><sup>2-</sup>. (The redox potential of the O<sub>2</sub>/O<sub>2</sub><sup>-</sup> and O<sub>2</sub><sup>-</sup>/O<sub>2</sub><sup>2-</sup> couples are in the +0.2 to 0.5 V<sup>(20, 21)</sup> and -1.8 V<sup>(22, 23)</sup> range respectively in aprotic solvents.)

The second order rate constants (k<sub>2</sub><sup>R</sup>) (where R = the substituent on position 4 of the pyridine ring) are summarized in Table 2 and fit a Hammett linear free energy relation of the type shown in Equation (5):

$$\log (k_2^R/k_2^H) = \sigma \rho \quad (5)$$

**Table 2.** Second-order rate constants for the oxygenation reaction of [CuXL]<sub>2</sub> (X = Cl or Br) complexes.

L	X	Temp. (°C)	Solvent	k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )	pK <sub>a</sub>
Py	Cl	0	CH <sub>2</sub> Cl <sub>2</sub>	2.2 ± 0.3	
Py	Cl	5	CH <sub>2</sub> Cl <sub>2</sub>	2.7 ± 0.4	
Py	Cl	10	CH <sub>2</sub> Cl <sub>2</sub>	3.2 ± 0.4	5.19
Py	Cl	15	CH <sub>2</sub> Cl <sub>2</sub>	3.5 ± 0.4	
Py	Br	18	Py	0.17 ± 0.01	
Py	Cl	18	Py	0.73 ± 0.01	
4-PhPy	Cl	10	CH <sub>2</sub> Cl <sub>2</sub>	2.6 ± 0.3	5.35
4-MePy	Cl	10	CH <sub>2</sub> Cl <sub>2</sub>	3.5 ± 0.4	5.99
4-Me <sub>2</sub> NPy	Cl	10	CH <sub>2</sub> Cl <sub>2</sub>	35 ± 4	9.60
4-PhCOPy	Cl	10	CH <sub>2</sub> Cl <sub>2</sub>	0.89 ± 0.03	3.35

**Figure 5.** Hammett plot showing the substituent effect for the reaction of [CuCIL]<sub>2</sub> with O<sub>2</sub> where L = Py, 4-PhPy, 4-MePy, 4-Me<sub>2</sub>NPy, and 4-PhCOPy.

$\sigma$  is  $\log(K_a^R/K_a^H)$  and can be taken as a measure of the donor or acceptor ability of the substituents. The reaction constant  $\rho$ , the slope of the Hammett plot, is a measure of the susceptibility of the reaction to the influence of substituents on the parent ligand. Equation (5), plotted in Figure 5, gave a  $\rho$  value of  $-1.24$ .

This correlation of the oxygenation rate with the Hammett values provides evidence, that the rate-determining step is sensitive to factors which vary the electron density available to the copper from the ligand. The enhanced basicity of the nitrogen atoms correspondingly increases the electron density at the metal site. An increase of the electron density on the central metal atom makes electron transfer to the dioxygen in the transition state easier. This conclusion is in accordance with the mechanism postulated in Equations (1)–(3).

### Experimental

$\text{CH}_2\text{Cl}_2$  and Py were purified by standard methods, degassed and stored under Ar. 4-Methylpyridine, 4-phenylpyridine, 4-dimethylaminopyridine and 4-benzoylpyridine (Fluka AG) were used as supplied.

### Preparation of the $[\text{CuXL}]_2$ complexes

The copper(I) halide (50 mmol) and ligand (53 mmol) were stirred in  $\text{CH}_2\text{Cl}_2$  (50  $\text{cm}^3$ ) under Ar at  $25^\circ\text{C}$  until a clear yellow solution resulted. To this solution  $\text{Et}_2\text{O}$  (40  $\text{cm}^3$ ) was slowly added. The complexes crystallized as yellow needles in 95% yields. They were filtered under argon, washed with  $\text{Et}_2\text{O}$ , dried *in vacuo*, and stored in Schlenk tubes under argon. They were found to be analytically pure and were used without recrystallization.

Molecular weight measurements of the  $[\text{CuXL}]_2$  complexes were carried out on a Knauer (Berlin) vapour pressure osmometer in  $\text{CH}_2\text{Cl}_2$  between 0 and  $37^\circ\text{C}$  in the  $2.5\text{--}15 \times 10^{-3}\text{M}$  concentration range. Three independent measurements for several readings were made and an average value calculated.

### Kinetic measurements

The concentrations of the dissolved dioxygen in  $\text{CH}_2\text{Cl}_2$  were measured at atmospheric pressure with a Beckman Oxygen Analyser. The following values were obtained:  $3.5 \times 10^{-3}$

( $0^\circ\text{C}$ );  $5.6 \times 10^{-3}$  ( $5^\circ\text{C}$ ),  $5.7 \times 10^{-3}$  ( $10^\circ\text{C}$ ),  $6.4 \times 10^{-3}$  ( $15^\circ\text{C}$ ) M, and in pyridine at  $18^\circ\text{C}$ :  $4.4 \times 10^{-3}$  M.

Standard volumetric methods were used in the kinetic experiments. The solvent was placed under dioxygen in a thermostated reaction vessel, connected to a gas burette and stirred until saturated and the vapour pressure had equalized. The consumption of dioxygen was measured at constant  $\text{O}_2$  pressure up to 80–90% conversions after adding and dissolving the  $[\text{CuXL}]_2$  complex. Kinetic data were evaluated from at least three parallel runs.

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