Inorganica Chimica Acta, 71 (1983) 95–99

A Spectrophotometric Study of the Reactions of the Phenolic Oxidative Coupling Initiator $py_4Cu_4Cl_4O_2$ and of $py_4Cu_4Cl_6O$ with Pyridine

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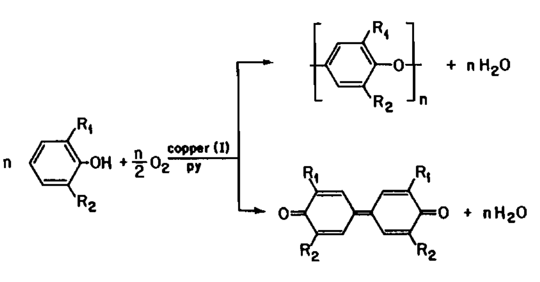
Received October 1, 1982

The species $py_4Cu_4Cl_4O_2$ is an active initiator for phenolic oxidative coupling by dioxygen while its disproportionation product $py_4Cu_4Cl_6O$ is not. Spectrophotometric titration shows that the active complex has a very high relative affinity for pyridine, which is known to influence the distribution of products from copper-catalyzed phenolic oxidative coupling.

Introduction

Our studies of the rates and products of aprotic oxidation of copper(I) complexes by dioxygen are aimed at developing molecular mechanisms for copper-catalyzed reactions of dioxygen [2]. The catalyzed systems include the oxidative coupling of phenols, eqn. 1, which are initiated under mild conditions by the brown solution obtained from the oxidation of copper(I) halide slurries in pyridine by dioxygen [3]. Much work has been done on maximization of the rate of dioxygen consumption and of the polymer yield in analogs of catalyzed reaction 1 [4] and on the mechanism of polymer growth [5]; the result has been the development of a range of commercial engineering plastics with outstanding electrical and thermal properties [6].



(1a)

(1b)

The large existing literature [4] on phenolic oxidative coupling reactions contains many indications of possible molecular mechanisms for these processes. For example, it seems clear that 1) the actual phenolic oxidants are peroxo- or oxo-copper(II) species produced by the oxidation of copper(I) centers by dioxygen [4, 7–9]; 2) that such species probably deprotonate phenolic substrates and thereby facilitate their oxidation by copper(II) [4, 9, 10]; 3) that the resulting copper(I) species might be coordinated by the large excess of substrate in the catalytic system [1, 4, 9, 11].

Polymer production, reaction 1a, is favored by 1) small R groups, 2) low temperatures, 3) high copper/phenol ratios and 4) high pyridine/copper ratios [4, 9, 12]. The first two factors would be expected to favor substrate coordination by copper, while the third and fourth would reduce its extent. The origin of experimental control of the product distribution in eqn. 1 evidently lies in the coordination and redox chemistry of the actual phenolic oxidants. One obvious difference between these species and common, inactive copper(II) complexes is that the products of aprotic O_2 reduction by copper(I) must inevitably be coordinated to copper(II) [2, 8]; this factor will influence the coordination chemistry of catalytic systems and needs to be investigated.

Some years ago we showed that the oxidation of copper(I) halide slurries in pyridine by dioxygen produces polymeric $[py_mCuO]_n$ oxidative coupling initiators *via* eqns. 2 and 3 [13]. Polymerization of the primary product from eqn. 2 via eqn. 3 is rapid and greatly complicates mechanistic studies of the initiation of phenolic oxidative coupling.

$$4CuCl(s) + O_2 \xrightarrow[py]{} 2py_2CuCl_2 + [py_mCuO]_2 \qquad (2)$$

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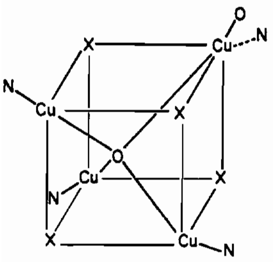

Fig. 1. Proposed [16] core structure for $py_3Cu_4X_4O_2$ and $py_4Cu_4X_4O_2$ reactants ($X = Cl$ in this paper).

$$2[py_mCuO]_2 \rightarrow [py_mCuO]_4, \textit{etc.} \qquad (3)$$

The $[py_mCuO]_n$ polymers are not amenable to isolation as solids [13, 14] but kinetic studies of their reactions with acids HY in pyridine showed that they are considerably more basic than the solvent [13].

There are reports in the literature that copper(I) halides can be heterogeneously oxidized with dioxygen at molar pyridine/copper(I) ratios near $py/Cu^{I}_{T} = 1.0$ [12, 15]. The brown products are quite soluble and stable in anhydrous nitrobenzene and methylene chloride solution [16]. It has been suggested that their characteristic 'two maxima' near infrared absorption spectra correspond to the presence of two difference copper(II) species in equilibrium, the one predominating at low py/Cu^{II}_{T} being responsible for catalysis of reaction 1b [12]. Addition of pyridine caused spectral changes consistent with an equilibrium shift and also resulted in a higher relative yield of polymer in reaction 1. At high py/Cu^{II}_{T} the titrated solutions exhibited a maximum near 740 nm [12], which is characteristic of the presence of py_2CuCl_2 [13–15], eqn. 2; however, the latter is not an initiator for the oxidative coupling of phenols by dioxygen, eqn. 1 [4, 8, 12–15].

Recent cryoscopic measurements in nitrobenzene have shown that the reactions of dioxygen with copper(I) chloride at $py/Cu^{I}_{T} = 0.75$ and 1.0 give the discrete, tetranuclear complexes $py_3Cu_4Cl_4O_2$ and $py_4Cu_4Cl_4O_2$, respectively [16]. Both species initiate reaction 1b, as expected from the earlier studies [12]. Although these complexes disproportionate to give inactive, crystalline $py_4Cu_4Cl_6O$ [17] on attempted crystallization, available spectral and other evidence indicates that all three complexes have the 'μ_4-oxo' core structure of Fig. 1 [2, 16].

In this paper we report the results of spectrophotometric titrations of $py_4Cu_4Cl_4O_2$ and $py_4Cu_4Cl_6O$ with pyridine in methylene chloride and nitrobenzene. The data reveal the high relative affinity of $py_4Cu_4Cl_4O_2$ species for pyridine ligands and provide indirect evidence for the stoichiometry and structure of the $[py_mCuO]_n$ species in eqn. 3.

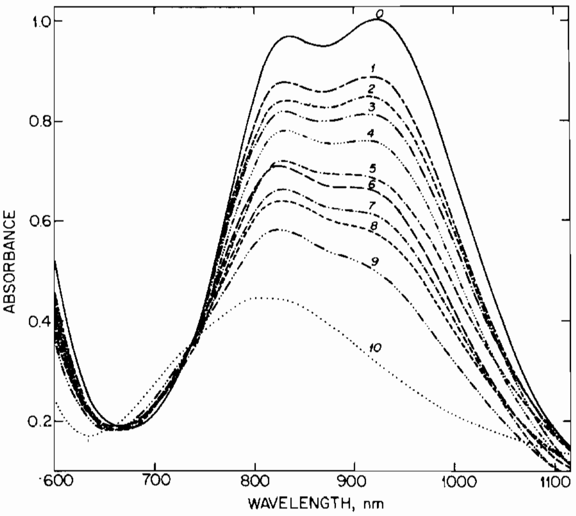

Fig. 2. Spectra for solutions of $py_4Cu_4Cl_4O_2$ (1.25×10^{-3} *M*) in nitrobenzene containing the following concentrations ($\times 10^{-3}$ *M*) of added pyridine, $[py]_{added}$: 0, 0.0; 1, 0.618; 2, 0.865; 3, 1.11; 4, 1.24; 5, 1.48; 5, 1.73; 8, 2.23; 9, 2.47; 10, 1000. The spectrum at $[py]_{added} = 0$ is due to the presence of only one component, $py_4Cu_4Cl_4O_2$ (see text).

Experimental

The purification of reactant materials and solvents and the syntheses of $py_3Cu_4Cl_4O_2$ and $py_4Cu_4Cl_4O_2$ were as previously described [16]. The crystalline disproportionation product $py_4Cu_4Cl_6O$ was independently synthesized by the method of Dieck [17]; its elemental analysis and spectral properties agreed closely with literature values. Spectrophotometric titrations of oxocopper(II) complexes with pyridine were carried out by standard techniques at 25 °C in the thermostatted cell compartment of a Beckman DK-IA spectrophotometer using matched quartz cells. Standard least-squares techniques were used for data reduction. Gel permeation chromatography of reaction products on Bio-Rad SX-12 resin with pyridine as eluant was performed as previously described [13].

The species titrated and their reaction products were tested as initiators for the oxidative coupling of 2,6-dimethylphenol under standard conditions [10].

Results and Discussion

Typical spectral changes observed during the titrations are illustrated in Fig. 2. They are of the same form as previously reported for titration of '$pyCuClOCH_3$' with pyridine in *o*-dichlorobenzene [12]

TABLE I. Equilibrium Parameters for Reactions of Oxocopper(II) Complexes with Pyridine at 25 °C.

Reactant	Solvent	n^a	$K^{a,b}$
$py_4Cu_4Cl_6O$	CH_2Cl_2	4.24 ± 0.04	0.69 ± 0.18
$py_4Cu_4Cl_6O$	nitrobenzene	4.46 ± 0.01	2.0 ± 0.1
$py_4Cu_4Cl_4O_2$	nitrobenzene	4.23 ± 0.07	(2.1 ± 0.8) × 10^8

[a] Error shown is 1 standard deviation. [b] Units are M^{-2}.

and for copper(I) halide oxidation products at various py/Cu_T^{II} ratios [15].

The occurrence of reaction 4 through cryoscopic identification of the reaction products [16] and previous identification of reaction 2 in neat pyridine [13] leads us to suggest eqn. 5 to account for the spectral changes in Fig. 2 [18].

$$m\,py + 4CuCl(s) + O_2 \xrightarrow[PhNO_2]{} py_mCu_4Cl_4O_2 \qquad (4)$$

$$(m = 3 \text{ or } 4)$$

$$py_4Cu_4Cl_4O_2 + n\,py \xrightleftharpoons[\text{or } PhNO_2]{CH_2Cl_2} 2py_2CuCl_2 + py_n(CuO)_2, K \qquad (5)$$

Subsequent polymerization of $py_n(CuO)_2$ via eqn. 3 has little effect on the molar absorptivity of this species [8, 13], which is in any case small in comparison to those of the $py_4Cu_4Cl_4O_2$ reactant or the py_2CuCl_2 co-product in the spectral range investigated [8, 13].

At fixed wavelength, it can be shown that the concentration of py_2CuCl_2 present at equilibrium in 5 is given by eqn. 6.

$$[py_2CuCl_2]_e = x = \frac{[Cu_T^{II}](A_o - A)}{(A_o - A_\infty)} \qquad (6)$$

Here, A_o, A and A_∞ are absorbances at $[py]_{added}$ equal to zero, an intermediate value and infinity, respectively and $[Cu_T^{II}]$ represents the initial molar concentration of $py_4Cu_4Cl_4O_2$. This same relationship holds for the titration of $py_4Cu_4Cl_4O$, which also produces 2 mol of py_2CuCl_2 in the presence of a large excess of pyridine (see below).

The equilibrium constant K in eqn. 5 is given by eqn. 7. Taking logarithms of both sides of eqn. 7 and rearranging gives eqn. 8. The spectral changes illustrated in Fig. 2 are rapid. The absorbance changes at fixed wavelength were used to characterize the systems as follows. Since large excesses of pyridine are required to significantly alter the spectrum of $py_4Cu_4Cl_6O$, eqn. 8 was first plotted with $[py]_{added}$ = [py] and –n was obtained from the slope of the linear plot for this system. The free pyridine concentration, [py], was next obtained from eqn. 9. Replotting eqn. 8 gave virtually the same plot since $[py] \approx [py]_{added}$ is a close approximation in

$$K = \frac{4x^3}{([Cu_T^{II}] - x)[py]^n} \qquad (7)$$

$$\ln\left(\frac{[Cu_T^{II}] - x}{x^3}\right) = \ln\frac{4}{K} - n \ln [py] \qquad (8)$$

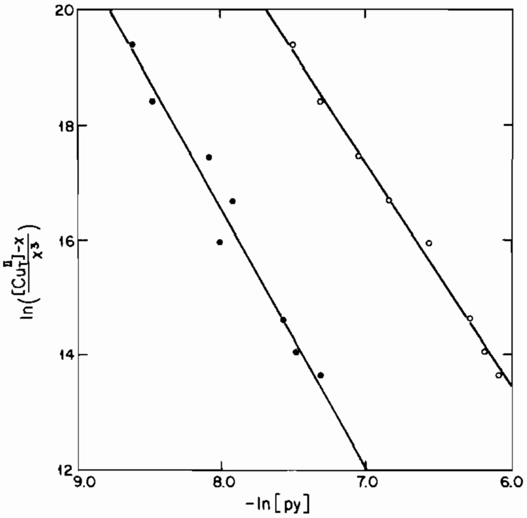

Fig. 3. Plot of $\ln\{([Cu_T^{II}] - x)/x^3\}$ *vs.* ln[py] from the data in Fig. 2 at 950 nm. Open circles are based on the approximation $[py] = [py]_{added}$; closed circles are based on [py] calculated from eqn. 9. In each plot a lest-squares line has been drawn through the points.

$$[py] = [py]_{added} + (2 - n)x \qquad (9)$$

this particular system. Finally, the equilibrium constant K was calculated from eqn. 7 with n from the slope of the plot and [py] from eqn. 9. The results in methylene chloride and nitrobenzene are collected in Table I.

The same procedure was followed in the titration of the initiator $py_4CuCl_4O_2$ in nitrobenzene. The correction embodied in eqn. 9 is much more significant in this system, *i.e.* $[py]_{added} \neq [py]$ for most of the titration. Figure 3 illustrates that the slopes of the plots of eqn. 8 with $[py] = [py]_{added}$ and [py] then given by eqn. 9 are very similar; the value of n in Table I comes from application of eqn. 9 and subsequent calculation of an average equilibrium constant K from eqn. 7.

The two important conclusions summarized in Table I are 1) that n is close to 4 but is non-integral and 2) that $py_4Cu_4Cl_4O_2$ has a much higher affinity for pyridine than does $py_4Cu_4Cl_6O$. We now consider these conclusions in turn.

As mentioned above, py_2CuCl_2 is a well-established decomposition product in these systems. If n were 4, then the other product in eqn. 5 would be $(py_2CuO)_2$. Removal of two moles of py_2CuCl_2 on reaction of the proposed core structure with pyridine would leave the unit Cu–O–Cu–O intact but with distinct copper(II) centers. Terminal copper(II) centers would be expected to coordinate more pyridine ligands than O–Cu–O units, with the primary decomposition product $py_3Cu–O–Cu(py)_2–O$ leading to n = 5. The fact that n is closer to four than to five is consistent with extensive, rapid polymerization of oxocopper(II) products even under the dilute conditions used for titration [19]. The fact that $n \gtrsim 4$ for reaction of $py_4Cu_4Cl_6O$ is not unexpected in that the primary oxocopper(II) product might be anticipated to be $py_2Cu(Cl)O(Cl)Cupy_2$, *i.e.* n is at least 4. It is, of course, possible that both oxocopper(II) core structures Cu–O–Cu–O and Cu–O–Cu are highly polymerized and that $n > 4$ for both systems because of weak association of pyridine with py_2CuCl_2 [19].

It is clear from Table I that $py_4Cu_4Cl_4O_2$ has a much higher affinity for pyridine than does catalytically inactive $py_4Cu_4Cl_6O$. The two most obvious reasons for this difference are 1) that $py_4Cu_4Cl_6O$ lacks the terminal oxo group in Figs. 1 and 2) that the six halo ligands occupy the six tetrahedral edges of the Cu_4 unit in $py_4Cu_4Cl_6O$ (and are thus 2-coordinate) whereas they occupy the four tetrahedral faces of the Cu_4 unit in $py_mCu_4Cl_4O_2$ (and are thus 3-coordinate). The stabilization achieved by reduction of the halide coordination number from 3 to 2 may be an important driving force for the formation of $py_4Cu_4Cl_6O$ on attempted crystallization of $py_mCu_4Cl_4O_2$ [16] and may also favor the coordination of phenolic substrates [20].

Gel permeation chromatography of the products obtained by treating $py_4Cu_4Cl_4O_2$ and $py_4Cu_4Cl_6O$ with a large excess of pyridine gave the following results. The first complex behaved exactly as would be expected from our earlier work: it gave an equimolar mixture of py_2CuCl_2 and $[py_mCuO]_n$ which was easily separated [13]. We were able to detect 2 mol of py_2CuCl_2 from the reaction of $py_4Cu_4Cl_6O$ with pyridine by gel permeation chromatography. One of the practical difficulties in identification of the Cu–O–Cu entity from this reaction of $py_4Cu_4Cl_6O$ is the low solubility of the latter in pyridine, which greatly limits the amount of product that can be separated by gel permeation chromatography [13]. The molecularity of this product will be established by cryoscopic measurements when sufficient, undecomposed material has been accumulated [10, 13, 16]. The oxocopper(II) product from this system is, at best, a very poor initiator for phenolic oxidative coupling. We intend to report on its characterization in a subsequent paper.

In conclusion, the characteristic 'two maxima' near infra-red spectra noted by earlier workers [12, 15] at low py/Cu_T^I are not due to two species at equilibrium but correspond to tetrameric oxocopper(II) species that initiate reaction 1b. Addition of pyridine to such species results in the production of $[py_mCuO]_n$ polymers that initiate reaction 1a at high pyridine concentrations.

Acknowledgements

We gratefully acknowledge support from Biomedical Research Support Grant RR07143 from the Department of Health and Human Services and Faculty Research Grant 7590 from Northeastern University.

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17 H. T. Dieck, *Inorg. Chim. Acta, 7,* 397 (1973) and references therein.
18 The complexes $py_mCu_4Cl_4O_2$ (m = 3 or 4) have virtually identical spectra in the range 500–850 nm [16] and so the species with m = 4 was used as the starting material for titration.
19 Note that, with this interpretation of the data, n → 4 with increasing initiator polymerization. Neutral pyridine, rather than chloride, loss is to be expected on polymerization in aprotic solvents of low polarity.
20 This presumed halide coordination factor is, of course, irrelevant to $[(py)_mCuO]_n$ phenolic oxidative coupling initiation. However, both $py_mCu_4Cl_4O_2$ and $[py_mCuO]_n$ have terminal oxogroups which will deprotonate phenols and thereby facilitate their coordination.