acetone, ^1H NMR spectra reveal the averaged signals ascribed to B_1 and B_2 except in rigorously dry acetone solution.

Effect of Water Coordination on Observed Chemical Shifts. From the results discussed above, it is concluded[35] that a compound having apical water molecules has spectra with the isotropic shifts larger than those of compounds with no apical water molecules. The coordination of water reduces the antiferromagnetic interaction of the two copper ions and/or changes the spin densities transmitted via metal–ligand bonds.[36]

The coordinate geometries of the compounds studied here are approximately square-pyramidal when the apical ligand is bound to copper. In this structure, if a strong ligand such as water is coordinated to copper(II), the copper atom slightly deviates from the N_2O_2 coordination plane. For instance, Cu1 atom sits 0.09 Å out of the mean plane described by N1, N3, O1, and O2 in Figure 5. An analogous compound having an apical water ligand also indicates a deviation, 0.15 Å,[31] from the square-planar mean plane. This structural variation may reduce the overlap of a $d_{x^2-y^2}$ orbital with two oxygen (oxo and hydroxy) orbitals, leading to reduction[37] of the antiferromagnetic exchange interaction and/or change on spin densities from the orbital. At the present stage it is hard to conclude which is most possible because the isotropic shifts are very sensitive to both cases. Even if the antiferromagnetic interaction is mainly changed by this structural variation, it may be quite small. It can be said that NMR spectroscopy is the most useful of the few methods used to detect such a subtle event.

The methanolic solution of **1b** gives a simple ^1H NMR spectrum, in which only one species is observed. This compound undergoes no solvent effect because the apical chloride anion is tightly bound to copper ion.

Acknowledgment. This work was supported in part by Grant-in-Aid for Scientific Research No. 63740347 from the Ministry of Education, Science, and Culture of Japan.

Supplementary Material Available: Full listings of atomic and thermal parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and torsion angles, figures showing the plot of the chemical shifts of signals B in Figure 4 vs $[D_2O]/[CD_3OD]$ in titration experiments and the ^1H NMR spectra monitoring the titration with D_2O, and figure captions (7 pages); a table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(35) Even for **2** and **3**, it is possible to conclude that more water molecules afford isotropic shifts greater than those for compounds having less water molecules.

(36) The isotropic shift is sensitive to the spin densities[5] distributed on the nuclei in question.

(37) (a) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173. (b) Crawford, V. H.; Richardson, W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

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Kinetic Proof That the Tetranuclear Oxocopper(II) Complex $(py)_3Cu_4Cl_4O_2$ Initiates and Catalyzes the Oxidative Coupling of 2,6-Dimethylphenol by Dioxygen in Nitrobenzene

Mohamed A. El-Sayed,*[†] Atieh Abu-Raqabah,[‡] Geoffrey Davies,* and Ahmed El-Toukhy[†]

Received January 11, 1989

Copper(I) chloride reacts with equimolar pyridine, py, in ambient-temperature nitrobenzene under dinitrogen to give solutions of the tetranuclear copper(I) complex $(py)_4Cu_4Cl_4$ (I). Stoichiometric, cryoscopic, and kinetic measurements indicate that I is oxidized to the tetranuclear oxocopper(II) complex $(py)_4Cu_4Cl_4O_2$ (IIa) by dioxygen in nitrobenzene in a second-order process whose rate is independent of the concentration of 2,6-dimethylphenol, [DMP]. Insertion of O_2 into the tetranuclear halo core of I is the proposed rate-determining step. Slurry oxidation of CuCl with dioxygen at the molar ratio [py]/[CuCl] = 0.75 in nitrobenzene gives the tetranuclear oxocopper(II) complex $(py)_3Cu_4Cl_4O_2$ (IIb). The rate of direct, first-order oxidation of excess DMP to stoichiometric yields of 3,3′,5,5′-tetramethyl-1,4-diphenoquinone (DPQ) and water by IIa or IIb (9.45×10^{-5} M) in nitrobenzene is independent of which oxidant is used, of $[DMP]_0 = (2.2–12.2) \times 10^{-3}$ M, and of $[O_2]$. The system becomes catalytic at higher $[DMP]_0$ or lower $[II]_0$ because destruction of II and inhibition of copper(I) reoxidation by coproduct water are prevented through interaction of the latter with excess phenol. Data at different [DMP] indicate that conversion of a strong complex of stoichiometry IIb·2DMP to products DPQ, water, and copper(I) is the rate-determining catalytic step. Properties of IIa and IIb likely to be responsible for this behavior are discussed.

Introduction

Metal-catalyzed reactions of dioxygen are very important processes, and there is sustained interest in their products and mechanisms.[1-11]

Natural oxidation systems have evolved from the biosynthesis of oxidatively stable, polydentate ligands for metals that can confer reaction specificity as subtle as the difference between dioxygen transport and oxygenase or dehydrogenase activity. Part of this specificity has to do with the extent of dioxygen reduction.[1-6] Active-site models based on carefully chosen polydentate ligands have been especially helpful in clarifying cobalt,[4] iron,[5] and copper[6] dioxygen systems. Such metals are tightly held at each active site, and there are excellent prospects of determining catalytic mechanisms from direct kinetic measurements, as emphasized in recent reviews.[1-6]

[†] On leave of absence from the Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

[‡] Current address: Department of Chemistry, University of Leicester, Leicester LE1 7RH, England.

(1) (a) Hayaishi, O., Ed. *Molecular Mechanisms of Oxygen Activation*; Academic Press: New York, 1976. (b) Spiro, T. G., Ed. *Metal Ion Activation of Dioxygen*; Wiley: New York, 1980. (c) Endicott, J. F.; Kumar, K. *ACS Symp. Ser.* **1982**, *No. 198*, 425. (d) Basolo, F.; Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1976**, *9*, 175. (e) McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *18*, 125. (f) Wilkins, R. G. *Adv. Chem. Ser.* **1971**, *No. 100*, 111. (g) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265. (h) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 140. (i) Martell, A. E. *Acc. Chem. Res.* **1982**, *15*, 155. (j) Sawyer, D. T.; Nanni, E. J.; Roberts, J. L., Jr. *Adv. Chem. Ser.* **1982**, *No. 201*, 585.

(2) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

(3) (a) Martell, A. E., Sawyer, D. T., Eds. *Oxygen Complexes and Oxygen Activation by Metal Complexes*; Plenum: New York, 1988. (b) Ho, C., Ed. *Electron Transport and Oxygen Utilization*; Elsevier-North-Holland: Amsterdam, 1982. (c) Ando, W., Moro-oka, Y., Eds. *The Role of Oxygen in Chemistry and Biochemistry*; Elsevier: Amsterdam, 1988. (d) King, T. E., Mason, H. E., Morrison, M., Eds. *Oxidases and Related Redox Systems*; Liss: New York, 1988.

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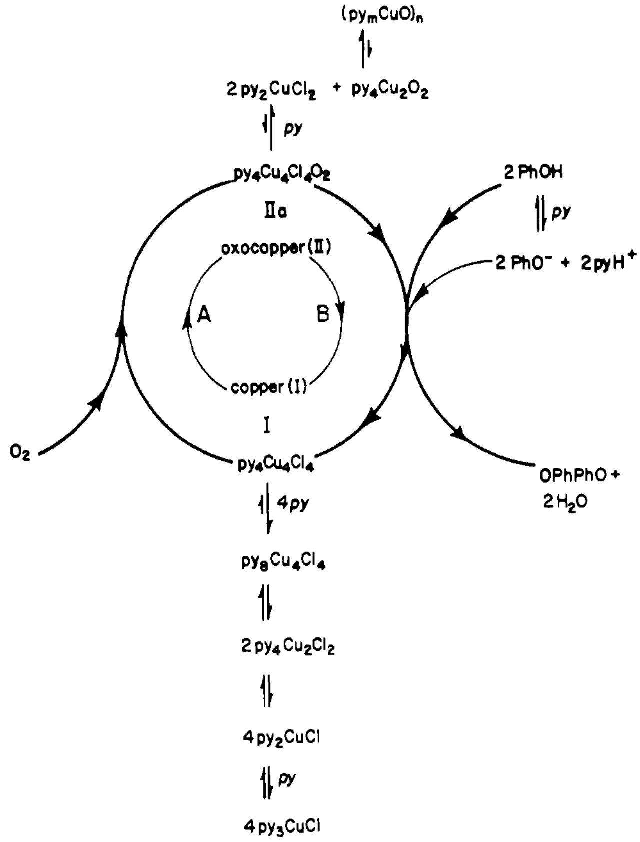
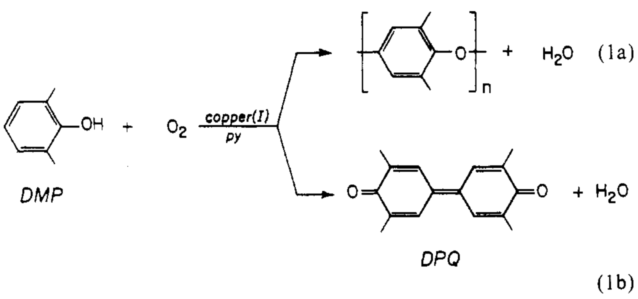
Scheme I



Simple mono- and bidentate amine ligands also promote many useful copper-catalyzed reactions of dioxygen, for example reaction 1a.[7,12] However, the actual forms of copper and dioxygen involved in the catalytic mechanisms are unknown,[8] largely because of difficulties in characterizing and distinguishing between labile copper initiators and catalysts.[10]



Copper(I) halide/pyridine mixtures, CuX/py, in aprotic solvents provide widely used initiators for eq 1 and a host of other important reactions of dioxygen with protic organic substrates.[6,10,12] Coordinated pyridine is cheap, effective, and oxidatively stable, which is often not the case with other ligands.[9]

Because of their historical and practical importance,[7-12] we have examined aprotic CuX/py/O$_2$ systems in detail.[9,10,13-16] As summarized in Scheme I, the tetranuclear copper(I) and oxocopper(II) components (py)$_4$Cu$_4$Cl$_4$ (I) and (py)$_4$Cu$_4$Cl$_4$O$_2$ (IIa) of the hypothetical[10] four-electron cycle are subject to breakdown[13] and disproportionation[15,16] with increasing proportions of py, which also could deprotonate the phenolic substrate. These factors would greatly complicate any attempt at detailed stoichiometric or kinetic explanation of why reaction 1a predominates over reaction 1b at high [py].[12,16-18] However, if an aprotic solvent could be found for I,[19] then the kinetics of components A and B of Scheme I could be studied independently.[10] In particular, if the phenolic substrate did not affect the rate of oxidation of I to IIa by dioxygen or alter the properties of IIa as a protic base and oxidant of phenolate, then components A and B would contain the rate-determining catalytic steps.[10]

In this paper we show kinetically that tetranuclear (py)$_3$Cu$_4$Cl$_4$O$_2$ (IIb) is the oxocopper(II) component responsible for the direct oxidative coupling of 2,6-dimethylphenol (DMP) to 3,3',5,5'-tetramethyl-1,4-diphenoquinone (DPQ) in nitrobenzene (eq 1b).

Experimental Section

Materials. Copper(I) chloride synthesized by the literature method[20] was used throughout this work. Pyridine (Aldrich or American Burdick and Jackson) was fractionally distilled from BaO. Nitrobenzene (Aldrich) was purified as previously described.[13] The substrate DMP (different batches from Aldrich) was used as received. An authentic sample of DPQ was synthesized as previously described.[13]

Synthesis of (py)$_4$Cu$_4$Cl$_4$ (I). Solutions of the yellow tetranuclear copper(I) complex (py)$_4$Cu$_4$Cl$_4$ (I) were obtained by adding solid CuCl to a stirred, equimolar solution of py in nitrobenzene under dinitrogen at room temperature. These solutions are highly air sensitive, as were solids precipitated by addition of deoxygenated hexane. Since precipitated solids gave very irreproducible analytical data and were only partly redissolvable[21] in deoxygenated methylene chloride or nitrobenzene, we established that I is indeed tetranuclear (py)$_4$Cu$_4$Cl$_4$ by cryoscopic measurements[13] of freshly prepared solutions of I in deoxygenated nitrobenzene at the (1–5) × 10^{-2} m level. M_r: found, 740 ± 20; calcd for I, 712.

Synthesis of (py)$_4$Cu$_4$Cl$_4$O$_2$ (IIa). Manometric measurements[13] of dioxygen uptake by solutions of I in nitrobenzene at 25 °C established the stoichiometry $\Delta[O_2]/\Delta[I] = 1.00 \pm 0.03$ over the concentration range [I] = (5.00–50.00) × 10^{-3} M. Cryoscopic examination of the brown product solutions indicated formation of the tetranuclear oxocopper(II) complex (py)$_4$Cu$_4$Cl$_4$O$_2$ (IIa). M_r: found, 760 ± 20; calcd for IIa, 744. Attempted precipitation of IIa by addition of anhydrous diethyl ether or hexane gave insoluble solids with copper contents approaching that of CuO, as previously observed.[13,15,16]

Synthesis of (py)$_3$Cu$_4$Cl$_4$O$_2$ (IIb). Slurry oxidation of CuCl with dioxygen at the molar ratio [py]/[CuCl] = 0.75 in ambient-temperature nitrobenzene gave solutions of the tetranuclear oxocopper(II) complex

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(4) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.

(5) Casella, L.; Silver, M. E.; Ibers, J. A. *Inorg. Chem.* **1984**, *23*, 1409. Ahmad, S.; McCullum, J. D.; Shiemke, A. K.; Appelman, E. H.; Loehr, T. M.; Sanders-Loehr, J. *Inorg. Chem.* **1988**, *27*, 2230 and references therein.

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(7) Hay, A. S. *Adv. Polym. Sci.* **1967**, *4*, 496; *Polym. Eng. Sci.* **1976**, *16*, 1.

(8) (a) Gampp, H.; Zuberbuhler, A. D. *Met. Ions Biol. Syst.* **1981**, *12*, 133. (b) Zuberbuhler, A. D. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J. A., Eds.; Adenine Press: Guilderland, NY, 1983; p 238.

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(11) Davies, G.; El-Sayed, M. A. *Comments Inorg. Chem.* **1985**, *5*, 155 and references therein.

(12) (a) Hay, A. S.; Shenian, P.; Gowan, A. C.; Erhardt, P. F.; Haaf, W. R.; Therberg, J. E. In *Encyclopedia of Polymer Science and Technology*; Interscience: New York, 1969; p 92. (b) Finkbeiner, H. L.; Hay, A. S.; White, D. M. Polymerization by Oxidative Coupling In *Polymerization Processes*; Schildnecht, C. E., Skeist, I., Eds.; Wiley-Interscience: New York, 1977; p 537, and references therein.

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(18) Endres, G. F.; Hay, A. S.; Eustance, J. W. *J. Org. Chem.* **1963**, *28*, 1300.

(19) Copper(I) halides are very insoluble in methylene chloride, a favored solvent for reactions 1,[12] at molar ratios $R < 1.0$.[10,13] As a result, kinetic measurements of their heterogeneous oxidation to freely soluble products II by dioxygen do not relate to the corresponding homogeneous catalytic reactions.

(20) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

(21) This behavior is expected for a labile copper(I) species that readily loses coordinated py on attempted precipitation.

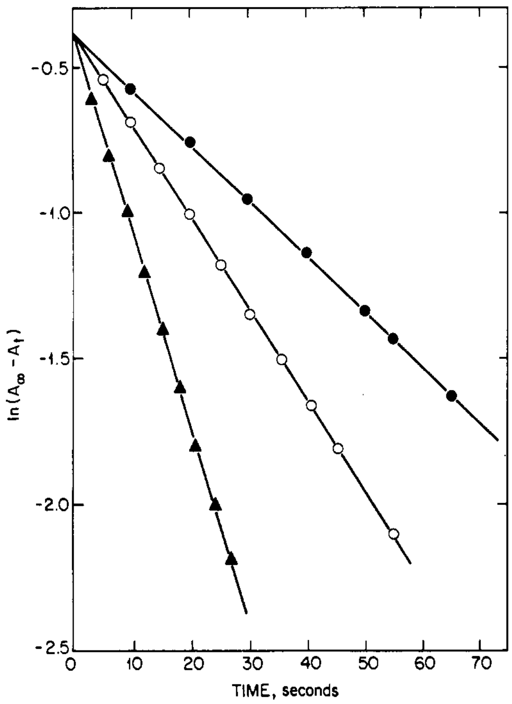

Figure 1. First-order kinetic plots for oxidation of excess I with dioxygen (4.4×10^{-4} M) in nitrobenzene at 25 °C. Initial reductant concentrations (mM) are (●) 5.0, (○) 7.5, and (▲) 11.3.

$(py)_3Cu_4Cl_4O_2$ (IIb), which was identified by cryoscopy.[13] Products IIa and IIb were found to behave identically as oxidants for DMP.

Spectral and Kinetic Measurements. All electronic spectra were recorded with a Perkin-Elmer Lambda 4B spectrophotometer at 25 °C with matched quartz cells. Kinetic measurements of reactions 1b and 2 were

$$I + O_2 \rightarrow IIa \qquad (2)$$

made by spectrophotometry in a Beckman DK-1A instrument whose cell housing was maintained to within ±0.1 °C of the desired temperature. All reactants were thermostated for at least 30 min before mixing. The monitoring wavelength was 431 or 850 nm for DPQ formation or IIa,b formation/consumption, respectively. Each reaction was monitored for at least 5 half-lives. Final absorbances at each set of fixed experimental conditions were used to calculate the stoichiometric yields of DPQ ($\epsilon = (5.06 \pm 0.05) \times 10^4$ M^{-1} cm^{-1} at 431 nm) in reaction 4 (with dioxygen present or absent) or of IIa in reaction 2.

Results and Discussion

Aprotic $CuX/py/O_2$ systems have received a great deal of attention because of their precedence,[17] practical simplicity, economy, and wide application as catalytic oxidants in synthetic organic and polymer chemistry.[7-18] The pyridine ligand is not oxidized,[9,10,15] and the choice of aprotic conditions greatly simplifies the products of copper(I) oxidation by dioxygen. This process results in the complete four-electron reduction of dioxygen to give oxocopper(II) products that initiate reactions 1 under ambient conditions.[7-18]

However, as outlined in the Introduction and Scheme I, aprotic $CuX/py/O_2$ systems are complicated functions of pyridine and copper concentrations even in the absence of substrates.[13,15,16] This is one of the penalties of employing a monodentate ligand to solubilize copper(I) halides and their oxocopper(II) oxidation products. Attempts to simplify the system by employing low molar ratios $R = [py]/[CuCl] \simeq 1.0$ lead to very low copper(I) solubility in methylene chloride, a very practical solvent for reactions 1. Although CuCl is much more soluble in methylene chloride at $R = 2$, cryoscopic determinations and kinetic measurements of copper(I) oxidation by dioxygen reveal a complicated mixture of mono-, di-, and tetranuclear metal species whose proportions depend on the total copper concentration.[13]

Our discovery that nitrobenzene is an excellent solvent for CuCl at $R = 1.0$ is important because it eliminates intractable complications at higher R. Once this discovery was made, we immediately established the existence of tetranuclear I at $R = 1.0$ under all practical conditions by cryoscopy. We were then able to address fundamental questions regarding the catalytic mechanism of reaction 1b: Does 2,6-dimethylphenol intercept the complete reduction of dioxygen by copper(I) complex I to give oxocopper(II) species?[10] If not, do the latter initiate *and* catalyze DMP oxidation? We will show kinetically that this is the case in the following sections.

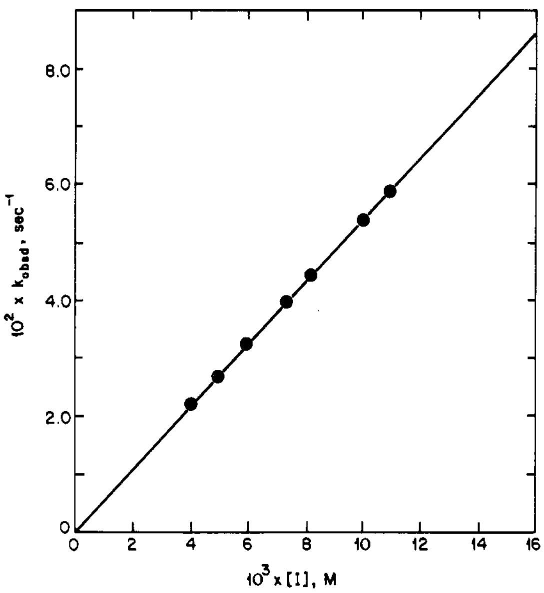

Figure 2. Plot of k_{obsd} vs [I] for oxidation of excess I with dioxygen in nitrobenzene at 25 °C. Linearity with no significant intercept indicates irreversible rate law 3.

Table I. Kinetic Data for Oxidation of Tetranuclear Halo(pyridine)copper(I) Complexes by Dioxygen in Nitrobenzene[a]

complex	k_T[b]	$\Delta H_T^{\ddagger}$[c]	$\Delta S_T^{\ddagger}$[d]
$(py)_4Cu_4Cl_4$	110	2.1 ± 0.3	−58 ± 3
$(py)_8Cu_4Cl_4$	770	2.9 ± 0.2	−36 ± 1
$N_4Cu_4Cl_4$[e]	15	3.9 ± 0.3	−40 ± 3
$N_4Cu_4Cl_4$[f]	28	4.4 ± 0.3	−37 ± 3
$N_8Cu_4Cl_4$[f]	110	4.3 ± 0.3	−35 ± 2
$N_4Cu_4Br_4$[e]	0.58	5.9 ± 0.2	−40 ± 3
$N_8Cu_4Br_4$[f]	1.2	5.7 ± 0.3	−40 ± 2

[a] Data from ref 13 except for first entry. [b] Units are M^{-1} s^{-1} at 25 °C. [c] Units are kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1} at 25 °C. [e] N = DENC. [f] N = ENCA.

Kinetics of Oxidation of I by Dioxygen in Nitrobenzene. The kinetics of oxidation of excess I to IIa by dioxygen in nitrobenzene (eq 2) were easily monitored by conventional spectrophotometry in the wavelength range 700–900 nm, where large absorbance changes were observed. Plots of ln $(A_\infty - A_t)$ vs time, where A_t is the absorbance at fixed wavelength and time t, were linear for at least 5 half-lives and gave no evidence for reaction precursors or intermediates (Figure 1). This indicates that reaction 2 is first order in $[O_2]$, as expected for aprotic oxidation of a tetranuclear halo pyridine complex containing at least two copper(I) centers by dioxygen.[13,22,23] Plots of the pseudo-first-order rate constant k_{obsd} vs [I] were accurately linear and passed through the origin (Figure 2), indicating that the rate law for irreversible reaction 2 is given by eq 3, where k_T is the experimental second-order rate

$$d[IIa]/dt = k_T[I][O_2] \qquad (3)$$

constant. A plot of ln k_T vs $1/T$ was linear over the temperature range 23.2–49.3 °C, indicating that there is no change in the

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(22) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Gilbert, T. R.; Nabih, K. *Inorg. Chem.* **1986**, *25*, 1929.

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(24) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Martin, C. A. *Inorg. Chem.* **1986**, *25*, 4479 and references therein.

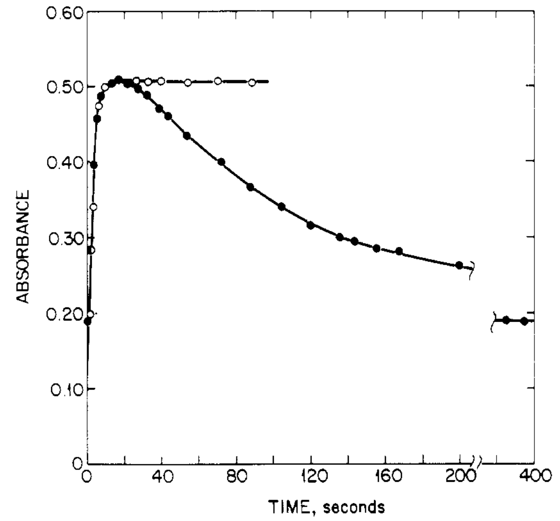
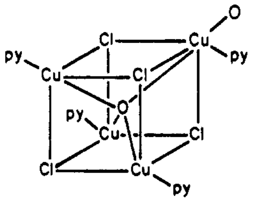


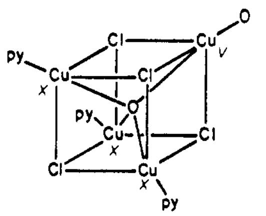
Figure 3. Absorbance–time changes at 850 nm for the reaction of dioxygen (4.4×10^{-4} M) with I (4.25×10^{-3} M, ○) and as a result of the presence of DMP (5.4×10^{-3} M, ●) in nitrobenzene at 25 °C.

molecularity of the tetranuclear copper(I) reductant I under these conditions.[13]

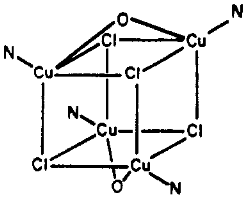
Kinetic parameters for rate law 3 are compared with data for corresponding oxidation of a variety of tetranuclear halo(pyridine)copper(I) complexes to tetranuclear oxocopper(II) products in nitrobenzene in Table I. The characteristic feature of these data is a simple second-order rate law with a very negative activation entropy and a low activation enthalpy. The latter is increased by changing X from Cl to Br.[13,22,23] These reactions are not subject to large kinetic solvent effects, which would otherwise indicate polar intermediates.[13] The accumulated data are quite consistent with insertion of dioxygen through one of the equivalent six faces of a "cubane" structure[13,25] of I as the rate-determining step.[13,22,23] We observe that increasing the number of pyridine ligands on each copper(I) center from 1 to 2 increases the insertion rate,[26] with the largest increase due to py. A plot of $\Delta H_{\mathrm{T}}^{*}$ vs $\Delta S_{\mathrm{T}}^{*}$ (not shown) correlates the data in Table I quite well and further supports a common insertion mechanism. The point of great relevance to this study is that the bis(μ-oxo) core structures III of the tetranuclear oxocopper(II) products of oxidation of $N_4Cu_4X_4$ complexes that contain monodentate N ligands *N,N*-diethylnicotinamide (DENC) and ethyl nicotinate (ENCA) instead of py have no especially basic terminal oxo group and no ability to initiate or catalyze reaction 1.[10,13,22-24]



IIa



IIb



III

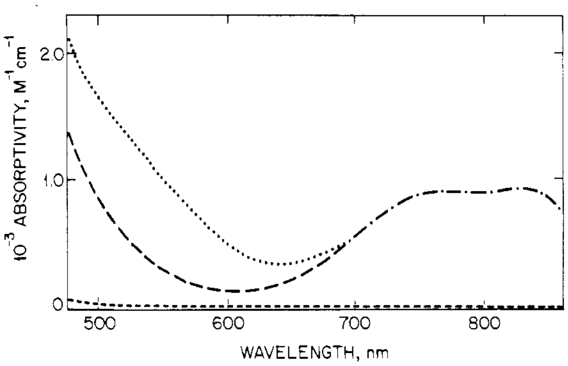


Figure 4. Electronic spectra of I (---), IIa (– –), and IIb·2DMP (···) in nitrobenzene at 25 °C.

No measurements were made of the rates of slurry oxidation of CuCl by dioxygen at $R = 0.75$ because these systems are heterogeneous and the measured dioxygen-uptake data are not relevant to homogeneous catalytic systems.[27]

Reaction 2 in the Presence of DMP. Figure 3 shows the absorbance–time changes at 850 nm resulting from the addition of dioxygen in nitrobenzene to large excesses of I and DMP in deoxygenated nitrobenzene. Also shown is the effect of omitting DMP from the system.

Two events are observed in the presence of DMP. The first is an absorbance increase corresponding to reaction 2. It is apparent that DMP has no effect on the rate of oxidation of I or the yield of IIa. This very important observation conclusively shows that DMP does not intercept the complete reduction of dioxygen by I to give an oxocopper(II) product.[28] A fast spectral scan at the time of maximum absorbance gave the data in Figure 4, which also shows the spectra of I and IIa. We observe that formation of an oxocopper(II) species in the presence of DMP results in higher absorptivity at wavelengths less than 695 nm, with evidence for a slight shoulder at 530 nm. However, there is negligible change at 750 or 850 nm, which are characteristic wavelengths for tetranuclear oxohalo(pyridine)copper(II) complexes with three halo ligands per copper center.[29] Subsequent measurements showed that the absorptivities of the phenol-containing product in Figure 4 are independent of $[I]_0$ and $[DMP]_0 > 2.0 \times 10^{-3}$ M provided that $[DMP]_0/[I]_0 > 2.0$ in nitrobenzene. This indicates formation of a strong, reactive complex of gross stoichiometry II·2DMP (see below).

The second event in Figure 3 is an absorbance decrease corresponding to the consumption of copper(II). Of great significance is the fact that the absorbances at the beginning and end of the absorbance–time sequence are small and essentially the same, indicating total copper(II) consumption. This particular system cannot be catalytic since no O_2 remains after the first step because I is present in excess.

It is also obvious from Figure 3 that phenol oxidation is the rate-determining catalytic step in Scheme I, a conclusion that is valid up to saturated dioxygen concentrations (4.4×10^{-3} M)[13] in nitrobenzene (see below).

Stoichiometry of Oxidation of DMP by II. There are no previously reported measurements of the stoichiometry of the direct aprotic oxidation of a phenolic substrate by a characterized oxocopper(II) species.

The diphenoquinone product DPQ of eq 1b dissolves in nitrobenzene to give red solutions with a pronounced absorbance

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[25] Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1982**, *21*, 995.

[26] From this observation we might expect phenol coordination by copper(I) to increase its rate of oxidation by dioxygen, which is not observed (Figure 3).

[27] Hopf, F. R.; Rogic, M. M.; Wolf, J. F. *J. Phys. Chem.* **1983**, *87*, 4681.

[28] The same maximum absorbance in the presence or absence of DMP in Figure 3 is consistent with the insensitivity of the 750–850-nm spectrum of IIb to coordination of 1 mol of py[13] or 2 mol of phenolate (Figure 4). By contrast, coordination of py at the X sites of IIa causes substantial changes in this region.[16]

[29] This observation is a very strong indication that IIb is tetranuclear in the catalytic cycle. See ref 13, 16, and 24 and: Davies, G.; El-Toukhy, A.; Onan, K. D.; Veidis, M. *Inorg. Chim. Acta* **1985**, *98*, 85.

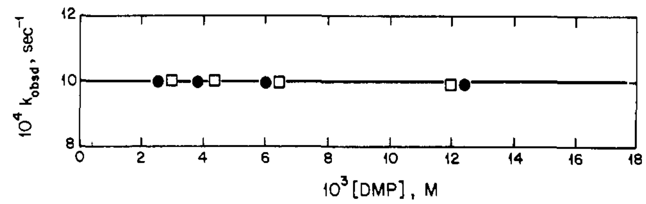

Figure 5. Plot of the first-order rate constants for oxidation of excess DMP by IIa (●) and IIb (□) in nitrobenzene at 21.0 °C.

maximum at 431 nm ($\epsilon = (5.06 \pm 0.05) \times 10^4$ M^{-1} cm^{-1}).[30] Equation 4 represents the *stoichiometric* oxidation of DMP to

$$\mathrm{IIa} + 2\mathrm{DMP} \rightarrow \mathrm{I} + \mathrm{DPQ} + 2\mathrm{H_2O} \qquad (4)$$

DPQ by IIa. If copper(I) reoxidation reaction 2 is inhibited, e.g. by water from eq 4, then the stoichiometry $S = \Delta[\mathrm{DPQ}]/\Delta[\mathrm{IIa}]$ is 1.0, whereas if reaction 2 occurs, then $S > 1.0$ and the system is catalytic, as in Scheme I.

Nitrobenzene solutions of IIa or IIb (9.45×10^{-5} M) were completely reacted with DMP up to the concentration 12.2×10^{-3} M. Each reaction was continuously monitored by spectrophotometry at 431 or 850 nm, and final absorbances at 431 nm were used to calculate S. The results showed that S is 0.97 ± 0.03 if the molar ratio [DMP]/[IIa] is at least 4.0 and 12.2×10^{-3} M $\geq$ [DMP] $\geq 2 \times 10^{-3}$ M (see below). Of particular significance is the same value of S in the presence of dioxygen, which can only be explained by very efficient inhibition of the reoxidation of I required to complete the catalytic cycle of Scheme I. We found in separate experiments that reaction 2 is indeed very strongly inhibited by water.[31] Work detailed below shows that S increases sharply above 1 at [DMP] $> 2 \times 10^{-2}$ M or when [IIa,b] is lowered from 9.45×10^{-5} to 1.5×10^{-5} M at [DMP] = 5.4×10^{-3} M. The simplest explanation of catalytic activity at high [DMP] or low [IIa,b] is hydrogen-bonded interaction of DMP with coproduct water, which prevents inhibition of reoxidation reaction 2.[32]

Complications Caused by Coproduct Water. It has long been known that preparative catalytic CuX/py/O_2/phenol systems are most effective under dry, aprotic conditions.[7-16,18] This requirement is best approached by employing an aprotic solvent in which water has low solubility, by continuously distilling water from the system or by adding a strong dehydrating agent. We have already noted that coproduct water strongly inhibits reaction 2[31] and that this inhibition is all but eliminated by employing high phenol and low copper concentrations. Buildup of water can also destroy a catalytic CuX/py/O_2/phenol system by reacting with oxocopper(II) components to give species that will not oxidize phenols.

One important property of species II is their basic terminal oxo group.[10,15,24] Species created by proton transfer from water to II would be weaker oxidants for phenols because they are already protonated.[33] The highest possible concentration of water in a stoichiometric system (eq 4) is equal to twice the initial concentration of I. Decreasing $[\mathrm{I}]_0$ at constant $[\mathrm{DMP}]_0$ or increasing $[\mathrm{DMP}]_0$ at constant $[\mathrm{I}]_0$ should both increase S if interaction of water with DMP[32] reduces or eliminates protonation of II or inhibition of reaction 2.

For these reasons our description of the results of the next section very carefully specifies the experimental conditions.

Kinetics of Oxidation of DMP to DPQ by II. The kinetics of eq 4 were investigated spectrophotometrically at 431 and 850 nm over a range of concentrations of II and DMP and of temperature in nitrobenzene. We first employed $[\mathrm{IIa}]_0 = 9.45 \times 10^{-5}$ M and $[\mathrm{DMP}]_0 = (2.2\text{–}12.2) \times 10^{-3}$ M at 21 °C in eq 4 and found that the first-order[34] rate at fixed temperature was independent of monitoring wavelength and the concentrations of dioxygen and DMP. Very significantly, use of IIa or IIb as oxidant gave the same rate data (Figure 5). Those data indicate $k_4 = (9.8 \pm 0.3) \times 10^{-4}$ s^{-1} at 21.0 °C. Studies at temperatures in the range 21.0–46.9 °C gave $\Delta H_4^* = 20.2 \pm 0.3$ kcal mol^{-1} with $\Delta S_4^* = -7 \pm 2$ cal deg^{-1} mol^{-1} at 25 °C in nitrobenzene.

Wavelength independence of the DMP oxidation rate is consistent with the strict stoichiometric requirements of eq 4. The lack of dioxygen dependence confirms very effective inhibition of reaction 2 under conditions that give $S = 1.0$. Independence of the rate from $[\mathrm{DMP}]_0$ indicates a saturated kinetic condition where all the copper(II) in the system is in one reacting form. Identical behavior with either IIa or IIb as oxidant indicates that the active oxocopper(II) component contains three coordinated pyridine ligands and is not especially sensitive to deactivation by accumulating water.[34,35]

Further investigation showed that the saturated kinetic condition of Figure 5 breaks down to give lower rates and $S < 1.0$ if $[\mathrm{DMP}]_0 < 5 \times 10^{-4}$ M at $[\mathrm{IIa,b}]_0 = 9.45 \times 10^{-5}$ M and 32 °C. Under these conditions we found that the initial rates[35] of DPQ formation, IR, were accounted for by eq 5.

$$[\mathrm{IIa,b}]_0/\mathrm{IR} = a/[\mathrm{DMP}]_0^2 + b \qquad (5)$$

This equation is consistent with the following stoichiometric mechanism with $a = 1/K_pk_p$ and $b = 1/k_p$:

$$\begin{array}{c} \mathrm{IIb} + 2\mathrm{DMP} \rightleftharpoons \mathrm{IIb{\cdot}2DMP}\ K_p \qquad (6a) \\ \Big\downarrow {\scriptstyle \mathrm{py}\ k_p} \\ \mathrm{I} + \mathrm{DPQ} + 2\mathrm{H_2O} \qquad (6b) \end{array}$$

A linear plot of $[\mathrm{IIa,b}]_0/\mathrm{IR}$ vs $1/[\mathrm{DMP}]_0^2$ gave a value of k_p that agreed with the data at higher [DMP], where the system is kinetically saturated (Figure 5). We also derived $K_p = (7 \pm 1) \times 10^7$ M^{-2} at 32 °C, which confirms that the reactive complex IIb·2DMP is thermodynamically stable enough to account for rate saturation at [DMP] $> 2 \times 10^{-3}$ M (Figure 5).

An indication of the importance of reactive coproduct water in this system is given by the following stoichiometric and kinetic experiments at 32 °C.

The first experiment had $[\mathrm{IIb}]_0 = 1.5 \times 10^{-5}$ M and $[\mathrm{DMP}]_0 = 5.4 \times 10^{-3}$ M with no added O_2. The system exhibited kinetic saturation (Figure 5), and the rate constant agreed with data at higher [IIb]; S was found to be 0.96 ± 0.03. However, introduction of O_2 gave a catalytic system with $S = 2.1$. This is a clear indication that lowering $[\mathrm{II}]_0$ at least partially[36] eliminates inhibition of reaction 2 by coproduct water.

The third experiment had $[\mathrm{IIb}]_0 = [\mathrm{DMP}]_0 = 4.4 \times 10^{-4}$ M in the presence of dioxygen (2.1×10^{-3} M). We found that the IR data did not fit eq 5, that the system was far from being catalytic ($S = 0.21$), and that inactive[33] copper(II) remained at the end of the reaction. These are clear indications that high molar ratios $[\mathrm{II}]_0/[\mathrm{DMP}]_0$ lead to coproduct water concentrations that seriously interfere with reaction 4 by deactivating the oxocopper(II) components.[33,34]

Characteristics of IIa, IIb, and Components of the Rate-Determining Catalytic Step. Tetranuclear oxocopper(II) complexes IIa and IIb are unusual, reactive species that cannot be isolated as intact solids.[13,24] They have very similar electronic spectra in nitrobenzene.[13] However, we know from the solvent dependence of their electronic spectra that they are asymmetric complexes; their other properties are consistent with previously proposed core structures.[13,24]

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(30) The Beer–Lambert law is obeyed by solutions of DPQ in nitrobenzene over the complete concentration range of this study.

(31) Strong inhibition of reaction 2 by traces of water can only be eliminated to give reproducible kinetic data by the employment of rigorously anhydrous conditions and highly purified solvents.[13,22,23] Dr. Maher Henary (personal communication) has made similar observations on the addition of acetone. We are continuing work to identify the inhibition mechanism.

(32) Any equilibrium interaction of water with DMP will be favored by increasing water or DMP concentrations.

(33) In separate experiments we found that deliberate addition of water to solutions of IIa in nitrobenzene gave unidentified products that reacted very slowly, if at all, with DMP.

(34) Very high quality first-order plots obtained under the specified conditions indicate that the reactive bis(phenolate) complex is much less sensitive to the presence of water than are IIa and IIb.[35]

(35) Initial rates IR were measured because first-order plots were linear only to 55–70% reaction under these comparatively "wet" conditions.

(36) S would, of course, be infinite in a perfect catalytic system.

Product IIb is ESR-silent and is believed to contain only five-coordinate copper(II). Addition of 1 mol of py to IIb gives IIa, which is ESR-active because it has six-coordinate copper(II) at distinguishable site V.[24] This site carries the terminal oxo group. The py ligand at site V is selectively replaced by 1 mol of a hard, bidentate ligand like *N,N,N',N'*-tetraethylethylenediamine,[24] which suggests that V would be the most likely coordination site for a phenolic ligand.[37]

Molecule IIa has a high affinity for py, addition of which results in marked electronic spectral changes in the 750–850-nm region due to py coordination at the X sites and reaction 7.[16] Although

$$\text{IIa} + 4\text{py} \rightarrow 2(\text{py})_2\text{CuCl}_2 + (\text{py})_4\text{Cu}_2\text{O}_2 \qquad (7)$$

we have purposefully used only IIa and IIb as oxidants for DMP in this study, we feel that any coordination of phenol at the X sites of IIb would cause major spectral changes in the 750–850-nm region, which are not observed (Figure 4). Thus, in the following discussion we presume that V is the only site of phenol coordination.

Our view of reaction 6a is then as follows. Rapid[38] deprotonation of 1 mol of DMP by the terminal oxo group of IIa gives the phenolate anion 2,6-$(\text{Me})_2\text{PhO}^-$, which displaces the py ligand at site V. This explains identical stoichiometric and kinetic results with IIb as the oxidant and little spectral change in the 750–850-nm region on reaction of IIa or IIb with DMP (Figure 4). The copper(II) center at site V now carries one phenolate and one hydroxo group and is six-coordinate. Since there is no evidence for a stoichiometrically significant monophenolate complex in this excess phenol system and seven-coordinate copper(II) seems very unlikely, we can assume that a second DMP molecule is rapidly[38] deprotonated by coordinated OH^- and that the second phenolate anion displaces the resulting water molecule from site V. This preserves six-coordination for copper(II) and positions both phenolate anions at the same site V.[39]

Tetranuclear molecules like IIa or IIb have the capacity to accept the four electrons transferred from 2 mol of DMP in eq 4. This would give $S = 1$ if reaction 2 is inhibited and deactivation of copper(II) by coproduct water is insignificant.[34] Electron transfer from phenolate at V to any of the three copper(II) centers of IIb at sites X should be facilitated by the bridging chloro ligands.[40] We would expect each copper(I) center created by electron transfer to have a lower affinity than copper(II) for the central μ_4-oxo group of IIb because of (a) lowered nuclear charge and (b) reluctance of copper(I) to be five-coordinate. The transfer of each electron to copper(II) thus frees a lone electron pair of the central oxo group, enabling it to complete the transfer of four protons from 2 mol of DMP. The second water molecule of eq 4 is expelled from the catalyst core when all the copper has been reduced to copper(I).

Conclusions. The results of this study give the most detailed picture so far obtained for a copper-catalyzed dioxygen reaction involving monodentate ligands. We have concluded that IIb is a very good multielectron catalyst for reaction 1b because it has the capacity to deprotonate and coordinate two phenol molecules at the same site while still in the copper(II) state (Figures 3 and 4). Quantitative yields of DPQ are consistent with close positioning of two phenol moieties at the same metal center while electron and proton transfer proceed to give efficient oxidative coupling. The key bis(phenolate) component appears to be much more resistant to water deactivation than are uncomplexed oxocopper(II) species II.[34]

A recent study from our laboratory[41] has shown that the commonly used oxocopper(II) initiator $\text{L}_2\text{Cu}_2\text{Cl}_2\text{O}$ (IV), where L is *N,N,N',N'*-tetraethylethylenediamine, rapidly gives very high yields of the alternative poly(phenylene oxide) product of catalytic reaction 1a and negligible DPQ. The simplest explanation for this different product and higher catalytic activity on changing the ligand from py to L would consist of the following.

(1) Dimers IV differ from tetramers II in having the capacity to accept only two electrons from DMP. Any DPQ production would thus require the involvement of 2 mol of IV·*n*(phenolate) in an intermolecular[37] reaction that seems far less likely than intramolecular reaction 6a,b.

(2) The bulky ethyl substituents of the strongly held bidentate ligand in IV apparently disfavor coordination of two phenolates by a single copper(II) center. Assuming that IV has the capacity to deprotonate two DMP molecules, this would put the resulting phenolates on different copper(II) centers. The resulting separation and the differences in (1) above apparently lead to reaction 1a. Higher catalytic activity with ligands L than with py suggests little sensitivity of IV·*n*(phenolate) or reoxidation of copper(I) component $\text{L}_2\text{Cu}_2\text{Cl}_2$ to the presence of coproduct water in catalytic system 1a.

Acknowledgment. This work was supported by Grants INT-8715384 and CHE-8717556 from the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, which are gratefully acknowledged. M.A.E.-S. and A.E.-T. thank Alexandria University for study leave. Finally, we thank Professor Allan Hay and Dr. Stephen Carter for valuable discussions.

Registry No. I, 104911-27-5; IIa, 104475-18-5; DMP, 576-26-1; O_2, 7782-44-7.

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(37) Coordination of phenolate at the site of deprotonation is intuitively reasonable, especially if phenolate is not mobile on the catalyst framework.

(38) Davies, G.; El-Shazly, M. F.; Rupich, M. W. *Inorg. Chem.* **1981**, *20*, 3757.

(39) Bis(phenolate) complexes of the type LCu(OPh)_2, where L is a bidentate amine, are well-known to be subject to thermal oxidative coupling. See ref 38 and: Harrod, J. F. *Can. J. Chem.* **1969**, *47*, 637. This coupling involves at least two molecules of LCu(OPh)_2 on the basis of the present work with tetranuclear copper catalysts.

(40) A variety of evidence indicates that bridging halo ligands in polynuclear copper(II) complexes are effective electron bridges. One example is the similar rate of transmetalation of the copper(I) and copper(II) sites in mixed-valence molecules $\text{N}_3\text{Cu}_3\text{Co(NS)}_2\text{X}_4$ by M(NS)_2, where N is DENC, NS is *S*-methyl isopropylidenehydrazinecarbodithioate, and M is Ni or Zn. See: Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Kasem, T. S.; Martin, C. A. *Inorg. Chem.* **1986**, *25*, 3904.

(41) Davies, G.; El-Sayed, M. A.; Henary, M. *Inorg. Chem.* **1987**, *26*, 3266.