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pentacoordinate or, even more so, tricoordinate boron intermediates. In a sense the complex can be viewed as containing a "trapped" monohydroborato intermediate resulting from the "hydrolysis" of the starting borohydride.

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Registry No. $[Fe(NOX)_3(BF)_2]$, 66060-48-8; $[Fe(NOX)_3(BCl)_2]$, 97826-20-5; $[Fe(NOX)_3(BBr)_2]$, 97826-21-6; $[Fe(NOX)_3(BOH)_2]$, 66060-49-9; $[Fe(NOX)_3(BOCH_3)_2]$, 91837-84-2; $[Fe(NOX)_3(BH)_2]$, 84242-24-0; $[Fe(NOX)_3(BCH_3)_2]$, 97826-22-7; $[Fe(NOX)_3(B\text{-}n\text{-}C_4H_9)_2]$, 97826-23-8; $[Fe(NOX)_3(BC_6H_5)_2]$, 83356-87-0; $[Fe(DMG)_3(BH)_2]$, 97826-24-9; $[Fe(DMG)_3(BCH_3)_2]$, 97826-25-0; $[Fe(DPG)_3(BCH_3)_2]$, 97826-26-1; $[Fe(DMG)_3(BC_6H_5)_2]$, 97826-27-2; $[Fe(DMG)_3(BF)_2]$, 39060-38-3; $[Fe(DMG)_3(BOH)_2]$, 39060-43-0; $[Fe(DMG)_3(BOCH_3)_2]$, 39060-42-9; $[Fe(DMG)_3(BOC_2H_5)_2]$, 39060-41-8; BCl_3, 10294-34-5; BBr_3, 10294-33-4; H_3BO_3, 10043-35-3; $NaBH_4$, 16940-66-2; methylboronic acid, 13061-96-6; cyclohexanedione dioxime, 29256-75-5; methanol, 67-56-1; *n*-butylboronic acid, 4426-47-5; dimethylglyoxime, 95-45-4; phenylboronic acid, 98-80-6; diphenylglyoxime, 95-45-4.

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Stoichiometry and Kinetics of Oxidation of Dimeric Bis(μ-halo)bis((diamine)copper(I)) Complexes $L_2Cu_2X_2$ by Dioxygen in Aprotic Solvents

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Cryoscopic measurements show that the very soluble complexes formed from reaction of 1 mol of a tetraalkyl diamine L = $R_2N(CH_2)_nNR_2$ (R = methyl, ethyl, propyl, amyl; n = 2, 3) with 1 mol of a copper(I) halide (X = Cl, Br) in nitrobenzene are neutral dimeric species, $L_2Cu_2X_2$; solid-state evidence supports their assignment as bis(μ-halo)-bridged species in methylene chloride and nitrobenzene. The complexes rapidly react with dioxygen in these solvents with primary stoichiometry $2L_2Cu_2X_2 + O_2 \rightarrow 2L_2Cu_2X_2O$. Cryoscopic measurements on freshly prepared product solutions identified dimeric oxocopper(II) products, which polymerize and react with additional dioxygen at much lower rates than for copper(I) oxidation. Kinetic data for reduction of dioxygen by large excesses of $L_2Cu_2X_2$ complexes in nitrobenzene and methylene chloride obey the third-order rate law $d[L_2Cu_2X_2O]/dt = k_D[L_2Cu_2X_2]^2[O_2]$. Comparison of the kinetic data for oxidation of a range of $L_2Cu_2X_2$ complexes by dioxygen with corresponding data for tetrameric $N_nCu_4X_4$ and dimeric $N_4Cu_2Cl_2$ complexes (N = a monodentate pyridine; n = 4, 8) indicates steric restrictions to electron transfer due to interactions between alkyl substituents of the two $L_2Cu_2X_2$ dimers in the activated complexes for $L_2Cu_2X_2$ oxidation. It is suggested that these steric effects decrease donor–acceptor orbital overlap for electron transfer from copper(I) to dioxygen, but in no case is transfer of the third electron (necessary for breaking of the O–O bond) prevented.

Introduction

Copper(I) halides coordinated by monodentate pyridine ligands, N, can exist in monomeric, dimeric, or tetrameric forms at molar ratios $N/Cu^I{}_T$ = 1 and 2 in aprotic solvents.[1,2] The proportions of such molecular forms depend on the identity of L and the experimental conditions.[2] However, the products of aprotic oxidation of all these species by dioxygen are tetrameric dioxocopper(II) complexes, $L_nCu_4X_4O_2$; in fact, the rate law for oxidation of a halo(pyridine)copper(I) complex is a direct reflection of its molecularity because complete dioxygen reduction occurs in the presence of a large excess of copper(I).[1-3]

Our previous work with pyridine ligands established that a minimum of three electrons must be transferred from copper(I) for irreversible dioxygen reduction.[2] However, consideration of the narrow range of activation parameters for halo(monodentate pyridine)copper(I) oxidation (specifically a second-order rate law with $\Delta H_T{}^\ddagger$ = 2.1–5.9 kcal mol^{-1} and $\Delta S_T{}^\ddagger$ = –(35–48) cal deg^{-1} mol^{-1} for $N_nCu_4X_4$ oxidation (n = 4, 8; X = Cl, Br) and a third-order rate law with $\Delta H_D{}^\ddagger$ = 0–1.4 kcal mol^{-1} and $\Delta S_D{}^\ddagger$ = –(38–39) cal deg^{-1} mol^{-1} for $N_4Cu_2Cl_2$ oxidation)[1,2] strongly suggests that O–O bond breaking is not a significant factor in the activation process. Instead, we favor rate-determining insertion of O_2 into a Cu(X,X)Cu face of tetrameric $N_nCu_4X_4$ structures and have suggested that similar activated complexes are present in aprotic $N_nCu_4X_4$– and $N_4Cu_2X_2$–dioxygen systems when N is a monodentate pyridine ligand.[1-3]

Our recent data for the aprotic oxidation of the bis(μ-bromo)-bridged dimer $L_2Cu_2Br_2$[4] (L = TEED = *N,N,N′,N′*-tetraethylethylenediamine) by dioxygen stand in sharp contrast to the previous findings.[1-3] Although, as expected,[1,2] the rate law for oxidation of this complex in nitrobenzene is second-order in $[(TEED)_2Cu_2Br_2]$, the primary oxidation product is now dimeric, 5-coordinate $(TEED)_2Cu_2Br_2O$.[4] Formation of a dimeric rather than a tetrameric $L_4Cu_4X_4O_2$ product is the apparent result of a strong preference for 5-coordinate centers in oxocopper(II) complexes[1-3] (the symmetrical species $(LCuX)_4O_2$ would be 6-coordinate). This preference may be the origin of quite different activation parameters, $\Delta H_D{}^\ddagger$ = 12.9 kcal mol^{-1} and $\Delta S_D{}^\ddagger$ = –3 cal deg^{-1} mol^{-1}, for $(TEED)_2Cu_2Br_2$ oxidation.[4]

In this paper we report the stoichiometry and kinetics of oxidation of other $L_2Cu_2X_2$ complexes by dioxygen in methylene chloride and nitrobenzene. The molecularities of the reactants and products have been established by cryoscopy in nitrobenzene. The ligands, L = $R_2N(CH_2)_2NR_2$ (R = methyl, ethyl, propyl, amyl) and $R_2N(CH_2)_3NR_2$ (R = methyl),[5] and X = Cl or Br have been chosen for three principal reasons. First, we have found in previous work that it is necessary to alkylate primary amine ligands in order to obtain oxocopper(II) products with even moderate oxidative stability.[6] Second, all of the copper(II) products are

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[†] M.A.E.-S. and A.E.-T. were on leave of absence from the Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

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(5) Ligand abbreviations are as follows. (a) Ethylenediamine ligands L = $R_2N(CH_2)_2NR_2$: R = Me, TMED; R = Et, TEED; R = C_3H_7, TPED; R = C_5H_{11}, TAED. (b) $Me_2N(CH_2)_3NMe_2$ = TMPD.

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Table I. Cryoscopic and Electronic Spectral Data in Nitrobenzene

complex	M_r[a] found (calcd)	band max,[b] nm (ϵ, M^{-1} cm^{-1})	complex	M_r[a] found (calcd)	band max,[b] nm (ϵ, M^{-1} cm^{-1})
$[(TMED)CuCl]_2$	420 (430)		$[(TPED)CuBr]_2$	695 (743)	
$[(TMED)CuCl]_2O$	ppt[c]	690 (210)	$[(TPED)CuBr]_2O$	800 (759)	675 (260)
$[(TMED)CuBr]_2$	505 (519)		$[(TAED)CuCl]_2$[e]	830 (878)	
$[(TMED)CuBr]_2O$	570 (535)	675 (280)	$[(TAED)CuCl]_2O$	850 (894)	675 (185)
$[(TEED)CuCl]_2$	527 (542)		$[(TAED)CuBr]_2$	940 (967)	
$[(TEED)CuCl]_2O$	570 (558)	675 (228)	$[(TAED)CuBr]_2O$	1000 (983)	685 (220)
$[(TEED)CuBr]_2$[d]	620 (631)		$[(TMPD)CuCl]_2$	445 (458)	
$[(TEED)CuBr]_2O$[d]	630 (647)	700 (265)	$[(TMPD)CuCl]_2O$	505 (474)	675 (195)
$[(TPED)CuCl]_2$[e]	630 (654)		$[(TMPD)CuBr]_2$	510 (547)	
$[(TPED)CuCl]_2O$	650 (670)	675 (190)	$[(TMPD)CuBr]_2O$	550 (563)	675 (115), 975 (210)

[a] Typical error in found values is ±20. [b] Copper(I) reactants have no absorption maxima in the 400–700-nm region. [c] Product polymerization is rapid in this system,[10] and precipitation is generally observed in cryoscopic experiments at Cu_T concentrations that give dimeric species with the other ligands. [d] Data from ref 4. [e] Considerable time should be allowed to form these complexes from copper(I) halides and the ligands indicated. In other cases shown, formation is rapid in nitrobenzene and methylene chloride.

effective initiators for phenolic oxidative coupling.[7,8] Last, a range of ligands in a common, dimeric copper(I) reactant structure allows an assessment of steric and other effects on the rates of aprotic oxidation by dioxygen.

Experimental Section

Materials. The preparation and purification of copper(I) halides, diethyl ether, hexane, methylene chloride, and nitrobenzene were as previously described.[3] The alkyl diamine ligands L (Ames Laboratories, Aldrich, or Alfa) were dried over 4-Å molecular sieves and then distilled under reduced pressure immediately before use. Tetrabutylammonium perchlorate (TBAP) (Eastman) was recrystallized from ethanol and dried under vacuum.

Synthesis and Characterization of $L_2Cu_2X_2$ Complexes. Solutions of halo(diamine)copper(I) complexes were prepared by adding an equimolar amount of copper(I) halide to a stirred, deoxygenated solution of L in methylene chloride or nitrobenzene. The molecularities of the colorless or pale yellow, air-sensitive products were determined in nitrobenzene, as described previously,[2] at the midrange of total copper(I) concentrations, $[Cu^I_T]$, used for kinetic measurements.

Stoichiometry and Products of Aprotic Oxidation of Halo(diamine)copper(I) Complexes by Dioxygen. The stoichiometry of rapid oxidation of solutions of each halo(diamine)copper(I) complex by dioxygen in methylene chloride and nitrobenzene was determined manometrically.[2,4] Cryoscopic molecular weight data for reactant and primary product solutions in dinitrogen-saturated, dry nitrobenzene are listed in Table I.

Tests of Catalytic Activity. The catalytic activity of each oxidized product solution was confirmed as previously described[3] with a 100-fold excess of 2,6-dimethylphenol in methylene chloride.

Physical Measurements. Electronic spectra were recorded on Beckman DK-1A and Cary 2300 spectrophotometers at 25 °C. Kinetic measurements of copper(I) oxidation by dioxygen were made as previously described.[2,4] The reactant concentrations were $[Cu_T] = (3.3–20) \times 10^{-3}$ M and $[O_2]_0 = 3.5 \times 10^{-4}$ M over the temperature range 20.3–48.5 °C. The reactions were monitored at wavelengths between 500 and 700 nm. In each case the copper(I) reactant was in sufficient stoichiometric excess to ensure pseudo-first-order conditions, and the reactions always resulted in substantial absorbance increases at the monitoring wavelength.

Cyclic voltammetry was conducted with a CV-1A instrument connected to a Houston 2000 X-Y recorder. A Pt working electrode and a Pt-wire auxiliary electrode were employed in all measurements. All potentials were measured with respect to a saturated calomel electrode, SCE. Solutions to be electrolyzed were treated with methylene chloride saturated, dioxygen-free dinitrogen and were kept under the same atmosphere during electrochemical measurements.

Results and Discussion

Copper(I) Reactants. The cryoscopic data in Table I, which were made at the midrange of total copper(I) concentrations used for kinetic measurements of reactions with dioxygen (see below), indicate that all the halo(tetraalkyl diamine)copper(I) complexes of this study are dimeric in nitrobenzene near its freezing point (ca. 5 °C). Previous work[4] showed that the complex formed from 1 mol of TEED and 1 mol of copper(I) bromide crystallizes as a bis(μ-bromo)-bridged dimer from methylene chloride/ether at room temperature. Of the six possible complexes LCuX formed from L[5] = TMED or TEED and X = Cl, Br, or I, five crystallize as bis(μ-halo)-bridged dimers from acetonitrile at room temperature.[9] The exception is the complex with L = TMED and X = Cl, which crystallizes as the salt $[(TMED)_2Cu][CuCl_2]$ from acetonitrile.[9] Such a salt would be expected to be much less soluble in methylene chloride than the alternative neutral dimer $(TMED)_2Cu_2Cl_2$, but all the halo(diamine)copper(I) complexes of this study are highly soluble in methylene chloride. For this reason and in view of the cryoscopic (Table I) and kinetic evidence (see below), it is highly probable that all the halo(tetraalkyl diamine)copper(I) reactants are bis(μ-halo)-bridged dimers $L_2Cu_2X_2$ in methylene chloride and nitrobenzene under the conditions of the kinetic measurements.

Stoichiometry and Products of Reaction with Dioxygen. Exposure of a colorless or pale yellow solution of $L_2Cu_2X_2$ in methylene chloride or nitrobenzene to dioxygen causes a rapid color change to dark, greenish brown. Manometric dioxygen uptake and cryoscopic measurements (Table I) in nitrobenzene support the stoichiometry of eq 1, which indicates complete di-

$$2L_2Cu_2X_2 + O_2 \rightarrow 2L_2Cu_2X_2O \qquad (1)$$

oxygen reduction by dimeric copper(I) to produce dimeric oxocopper(II) products. The product solutions can be stabilized by treatment with excess carbon dioxide, which gives the corresponding (μ-carbonato)dicopper(II) dimers, many of which have been described previously.[10] If this precaution is not taken, the cryoscopic molecular weights of the products of eq 1 (measured under dinitrogen) increase with time, indicating polymerization,[11] and dark precipitates ultimately form. Precipitation of the polymerized product of oxidation of $(TMED)_2Cu_2Cl_2$ is the most rapid at 5 °C in nitrobenzene and precludes accurate crysocopic measurements for this system (Table I), but this phenomenon does not interfere with kinetic and spectral measurements of reaction 1 at higher temperatures and much lower product concentrations controlled by dioxygen as the limiting reagent.

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Table III. Kinetic Parameters for Oxidation of $[LCuX]_2$ (X = Cl, Br) by Dioxygen in Nitrobenzene

complex	$10^{-3}k_D$[a]	$\Delta H_D^{\ddagger}$[b]	$-\Delta S_D^{\ddagger}$[c]	complex	$10^{-3}k_D$[a]	$\Delta H_D^{\ddagger}$[b]	$-\Delta S_D^{\ddagger}$[c]
$[(TMED)CuCl]_2$	857	3.2	21	$[(TAED)CuCl]_2$	112	4.3	21
$[(TMED)CuBr]_2$	44	10.3	3	$[(TAED)CuBr]_2$	43.6	8.3	10
$[(TEED)CuCl]_2$	195	6.9	12	$[(TMPD)CuCl]_2$	1360	4.8	14
$[(TEED)CuBr]_2$[d]	0.55	12.9	3	$[(TMPD)CuBr]_2$	123	7.4	10
$[(TPED)CuCl]_2$	4.8	12.7	−1	$[(ENCA)_2CuCl]_2$[e]	3.1	1.4	38
$[(TPED)CuBr]_2$	0.48	15.2	−5	$[(py)_2CuCl]_2$[f]	15.7	0.0	39

[a] Units are $M^{-2}\ s^{-1}$ at 25 °C; typical error is ±5%. [b] Units are kcal mol^{-1}; typical error is ±0.4 kcal mol^{-1}. [c] Units are cal $deg^{-1}\ mol^{-1}$ at 25 °C; typical error is ±3 cal $deg^{-1}\ mol^{-1}$. [d] Data from ref 4. [e] ENCA = ethyl nicotinate; data from ref 2. [f] py = pyridine; data from ref 2.

Stored solutions of $L_2Cu_2X_2O$ products also slowly consume additional dioxygen, presumably due to oxidation of *N*-alkyl groups.[4,6] Although not investigated in detail, these reactions are much slower than reaction 1 and in no case do they interfere with kinetic measurements of copper(I) oxidation.

Cyclic Voltammetry. We have previously found that tetrameric $N_nCu_4X_4O_2$ complexes (N = a monodentate pyridine; n = 3, 4; X = Cl, Br) are electrochemically inactive at carbon, hanging mercury, and platinum electrodes in TBAP/methylene chloride. Our proposed structures for such complexes[1,2] contain tridentate, bridging halide. Since (μ-carbonato)halocopper(II) complexes, $L_2Cu_2X_2CO_3$, which contain terminal halide ligands, are electrochemically active,[10] it occurred to us that electrochemical activity could indicate terminal halide ligands in $L_2Cu_2X_2O$. This is not the case because both $L_2Cu_2X_2$ and $L_2Cu_2X_2O$ complexes give measurable but irreversible cyclic voltammograms in methylene chloride at Pt electrodes.[12] Since $L_2Cu_2X_2$ complexes contain 2-coordinate halo bridges (see above),[4,9] their oxidation products $L_2Cu_2X_2O$ may or may not,[4] based on this evidence alone.

Electronic Spectra. The room-temperature electronic spectra of the products in nitrobenzene are broad, unsymmetrical bands with maxima centered between 675 and 700 nm (Table I). Similar spectra for the corresponding μ-carbonato derivatives $L_2Cu_2X_2CO_3$ (maxima between 700 and 770 nm; see Figure 4 of ref 10a) are characteristic of 5-coordinate copper(II) centers in known dimeric structures.[10] The spectral evidence (ref 4 and present work) is consistent with a Cu(X,O,X)Cu bridging structure in $L_2Cu_2X_2O$ complexes.

Activity as Oxidative Coupling Initiators. All the $L_2Cu_2X_2O$ oxidation products are highly efficient initiators for the oxidative coupling of excess 2,6-dimethylphenol by dioxygen at room temperature to produce mixtures of the corresponding diphenoquinone and poly(phenylene oxide).[1,7,8] Under standard conditions (Experimental Section) the highest polymer yields were obtained with L = TMED and X = Cl.

Kinetics of Oxidation of $L_2Cu_2X_2$ Complexes by Dioxygen. Under conditions of $[L_2Cu_2X_2]$ in large excess, plots of ln ($A_\infty - A_t$) vs. time, where A_t is the absorbance at time t, were linear for at least 4 half-lives in their reactions with dioxygen (Figure 1), showing that the oxidations are first-order in $[O_2]$. The kinetic data provide no spectrophotometric evidence for any reaction precursors or intermediates under the conditions of this study. First-order rate constants, k_{obsd}, were found to be accurately linear in $[L_2Cu_2X_2]^2$ over a range of temperatures (Figure 2), showing that the overall rate law is eq 2, where k_D is the experimental

$$d[L_2Cu_2X_2O]/dt = k_D[L_2Cu_2X_2]^2[O_2] \qquad (2)$$

third-order rate constant. Plots of ln k_D vs. $1/T$ were accurately linear in each ligand system, showing that eq 2 is obeyed under all experimental conditions; thus, there is no evidence for changes in copper(I) reactant molecularity in any of the systems investigated.

Features of the Kinetic Data. The major features of the kinetic data for $L_2Cu_2X_2$ oxidation by dioxygen in aprotic solvents (Tables II[13]–IV) are as follows.

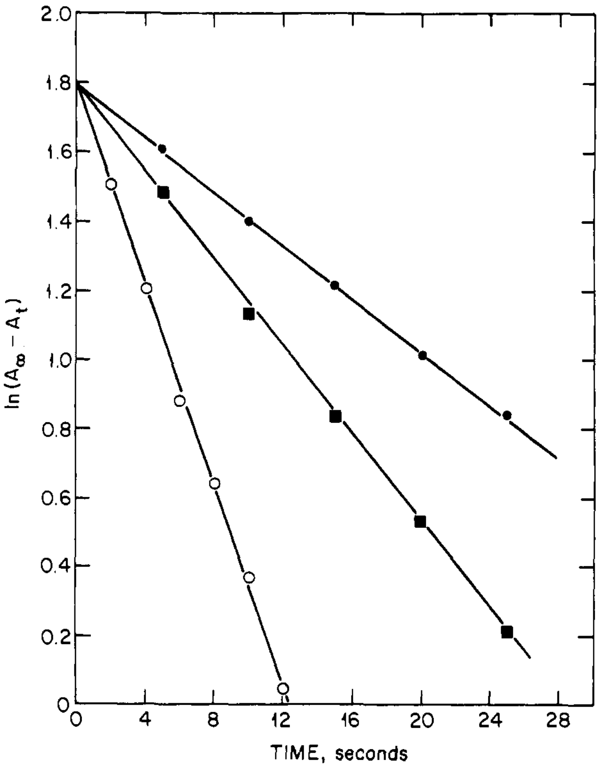

Figure 1. Typical first-order plots for $[(TPED)CuBr]_2O$ product formation in the oxidation of 6.6 × 10^{-3} M ($(TPED)CuBr)_2$ by 3.5 × 10^{-4} M dioxygen in nitrobenzene at (●) 31.8, (■) 39.4, and (○) 47.4 °C; reaction monitored at 700 nm.

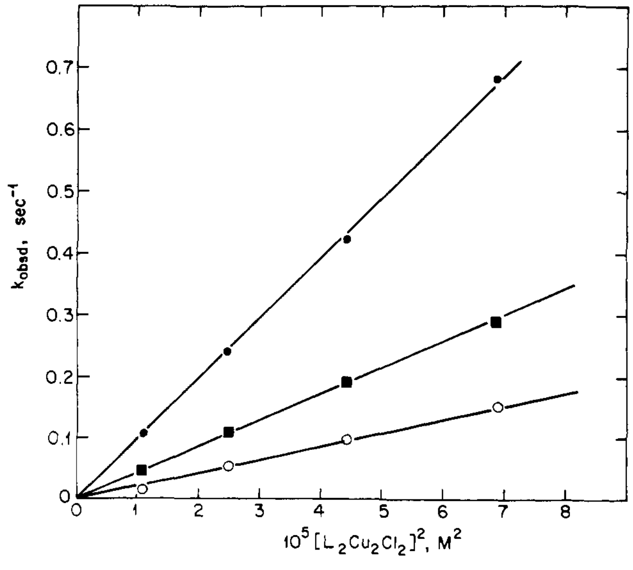

Figure 2. Dependence of the observed pseudo-first-order rate constant k_{obsd} on $[L_2Cu_2Cl_2]^2$ where L = TEED (●), TPED (○), and TAED (■) in methylene chloride at 21 °C.

(1) The third-order rate constant k_D at 25 °C varies by a factor of nearly 3000 as the ligands L and X are varied.

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(12) Typical $E_{1/2}$ values (V): $(TEED)_2Cu_2Cl_2$, 0.25 and 0.61; $(TEED)_2Cu_2Cl_2O$, −0.50; $(TEED)_2Cu_2Cl_2CO_3$, −0.29 and −0.73. These data indicate that $(TEED)_2Cu_2Cl_2$ is oxidized in two 1-electron steps and that copper(II) is more easily reduced in the carbonato derivative[10a] than in $(TEED)_2Cu_2Cl_2O$.

Table IV. Effect of Solvent on the Third-Order Rate Constant k_D for Oxidation of $[LCuCl]_2$ by Dioxygen at 21 °C

complex	solvent	$10^{-3}k_D$, M^{-2} s^{-1}	ratio[a]
$[(TMED)CuCl]_2$	nitrobenzene	820	1
	methylene chloride	810	
$[(TEED)CuCl]_2$	nitrobenzene	160	16
	methylene chloride	10	
$[(TPED)CuCl]_2$	nitrobenzene	3.7	1.5
	methylene chloride	2.2	
$[(TAED)CuCl]_2$	nitrobenzene	101	24
	methylene chloride	4.2	
$[(py)_2CuCl]_2$[b]	nitrobenzene	15.6	9
	methylene chloride	1.8	

[a] Ratio = k_D(nitrobenzene)/k_D(methylene chloride). [b] py = pyridine; k_D measured at 20.1 °C; data from ref 2.

(2) With fixed L, changing X = Cl to X = Br always causes k_D to decrease and $\Delta H_D^{\ddagger}$ and $\Delta S_D^{\ddagger}$ to increase.

(3) With fixed X, increasing the length of the alkyl substituents in L causes k_D to decrease and $\Delta H_D^{\ddagger}$ and $\Delta S_D^{\ddagger}$ to increase. The data for L = TAED do not fit this trend.

(4) Increasing the size of the chelate rings in $L_2Cu_2X_2$ from five to six members causes a minor increase in k_D with R = Me and with X = Cl and Br due to compensated changes in $\Delta H_D^{\ddagger}$ and $\Delta S_D^{\ddagger}$.

(5) A plot of $\Delta H_D^{\ddagger}$ vs. $\Delta S_D^{\ddagger}$ (not shown) is linear, within experimental error, for all diamine ligands (suggesting similar activation requirements[14]), but the data (Table III)[1,2] for the two pyridine ligand systems do not fit this plot: in both cases $\Delta S_D^{\ddagger}$ is more negative than is predicted by extrapolation of the other data to $\Delta H_D^{\ddagger}$ = 1.4 and 0.0 kcal mol^{-1}, respectively.

(6) The rate constants k_D at 21 °C are higher in nitrobenzene than in methylene chloride except for L = TMED (Table IV). The largest difference is observed with L = TAED.

Interpretation of the Kinetic Data. Overall, reaction 1 requires the transfer of 4 electrons from copper(I) to dioxygen and breaking of the O–O bond. The rate law, eq 2, indicates that there are two $L_2Cu_2X_2$ dimers and one dioxygen molecule in the activated complex. Possible rate-determining steps are (a) activated complex assembly, (b) electron transfer, and (c) O–O bond breaking.

Our previous work on the oxidation of tetrameric $N_nCu_4X_4$ complexes by dioxygen indicates, on the basis of low $\Delta H_T^{\ddagger}$, very negative $\Delta S_T^{\ddagger}$, and minimal solvent effects, that assembly of the activated complex is rate determining.[1,2] Comparison of $\Delta H_T^{\ddagger}$ with $\Delta H_D^{\ddagger}$ and $\Delta S_T^{\ddagger}$ with $\Delta S_D^{\ddagger}$ suggests rate-determining formation of similar activated complexes in the aprotic oxidation of $N_nCu_4X_4$ and $N_4Cu_2Cl_2$ complexes by dioxygen (Figure 3). Since assembly appears to be rate determining, it must result in effective donor–acceptor orbital overlap so that electron transfer and O–O bond breaking are very rapid.

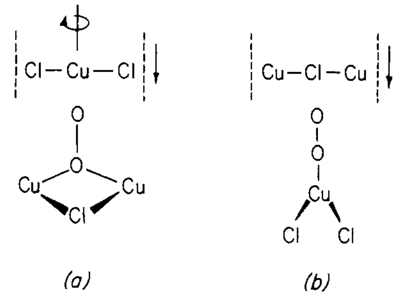

Figure 3. Hypothetical activated complex for dimer oxidation.[4] Ligands are omitted. The lower species is a very weak reaction precursor whose Cu–Cu axis is depicted orthogonal to that of a second dimer in view a. View b is along the Cu–Cu axis of the precursor. Steric repulsion is between ligated atoms of the separate dimers (see Figure 1 of ref 4 and text).

We feel that relatively high values of $\Delta H_D^{\ddagger}$ and $\Delta S_D^{\ddagger}$ for $L_2Cu_2X_2$ oxidation (Table III) are a reflection of less effective orbital overlap in the activated complexes with alkyl diamine ligands, despite the fact that such ligands allow the oxidation of copper(I) centers much more readily than do "softer" pyridines.[15] Because of progressively poorer orbital overlap, the barrier to electron transfer ($\Delta H_D^{\ddagger}$) and the disorder of the activated complex ($\Delta S_D^{\ddagger}$) increase with increasing length of the *N*-alkyl substituent in L (Table III); we assign these variations to increased alkyl substituent interactions between dimers in the activated complex. The increase in $\Delta H_D^{\ddagger}$ and $\Delta S_D^{\ddagger}$ in changing from X = Cl to X = Br in $L_2Cu_2X_2$ could be due to the influence of steric and electronic differences in the dimer bridging atoms.

On the basis of the above considerations, the least "compact" activated complex for dimer oxidation (Figure 3) is with L = TPED, but in this case the effect of solvent on k_D is very minor (Table IV). Extending the *N*-alkyl chain to five carbon atoms in TAED causes a sharp decrease in $\Delta H_D^{\ddagger}$ and $\Delta S_D^{\ddagger}$ (Table III) and the appearance of more marked solvent dependence of k_D (Table IV). We suggest that hydrophobic interactions between the two C_5H_{11} chains on each N atom of TAED are more substantial in nitrobenzene than in methylene chloride, lowering their effective steric volume so that k_D(TAED) > k_D(TPED) (Table IV).

Since steric effects obviously influence the rate of copper(I) oxidation by dioxygen, the stabilization of peroxodicopper(II) centers[16] requires much higher barriers to the transfer of the third electron[1,2] from a second dimer than are observed here.

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Registry No. $[(TMED)CuCl]_2$, 97731-69-6; $[(TMED)CuBr]_2$, 97731-70-9; $[(TEED)CuCl]_2$, 97731-71-0; $[(TPED)CuCl]_2$, 97731-72-1; $[(TPED)CuBr]_2$, 97731-73-2; $[(TAED)CuCl]_2$, 97731-74-3; $[(TAED)CuBr]_2$, 97731-75-4; $[(TMPD)CuCl]_2$, 97731-76-5; $[(TMPD)CuBr]_2$, 97731-77-6; $[(TEED)CuBr]_2$, 88510-91-2; $[(TMED)CuCl]_2O$, 97731-78-7; $[(TMED)CuBr]_2O$, 97731-79-8; $[(TEED)CuCl]_2O$, 97731-80-1; $[(TPED)CuCl]_2O$, 97731-81-2; $[(TPED)CuBr]_2O$, 97731-82-3; $[(TAED)CuCl]_2O$, 97731-83-4; $[(TAED)CuBr]_2O$, 97731-84-5; $[(TMPD)CuCl]_2O$, 97731-85-6; $[(TMPD)CuBr]_2O$, 97749-32-1.

Supplementary Material Available: Table II (kinetic data for oxidation of $L_2Cu_2X_2$ complexes (X = Cl, Br) by dioxygen in nitrobenzene) (2 pages). Ordering information is given on any current masthead page.

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(13) Supplementary data.

(14) $\Delta G_D^{\ddagger}$ for oxidation at 25 °C covers only a range of ca. 4 kcal mol^{-1} for the systems investigated, so $\Delta H_D^{\ddagger}$ should be proportional to $\Delta S_D^{\ddagger}$. However, copper(I) complexes $L_2Cu_2X_2$ with different L and X in nitrobenzene do give a linear relationship that includes all the data and suggests that all the reactions are subject to the same activation requirements. See: Wells, P. R. "Linear Free Energy Relationships"; Academic Press: London, 1968; p 21.

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