J. Am. Chem. Soc. **1993,** *115,* 3239–3243

The Bis(bipyridine)copper(II)-Induced Activation of Dioxygen for the Catalytic Dehydrogenation of Alcohols

Xiu Liu, Aimin Qiu, and Donald T. Sawyer*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received November 10, 1992

Abstract: The combination of bis(bipyridine)copper(II) [$Cu^{II}(bpy)_2^{2+}$] and 2 equiv of base [HO^- or $HOC(O)O^-$] with excess alcohol (e.g., $PhCH_2OH$) in an O_2-saturated acetonitrile solution results in the rapid, catalytic transformation of the alcohol to its aldehyde (or ketone for secondary alcohols). The rate of the process is first-order each in substrate, catalyst, and O_2 concentration with an apparent rate constant, k, for $PhCH_2OH$ of 68 ± 9 $M^{-2}\ s^{-1}$. Aliphatic primary alcohols react 4–20 times slower, secondary alcohols react 2–10 times slower than primary alcohols, and α-allylic alcohols react 2–4 times slower than $PhCH_2OH$. The buildup of water (the coproduct) deactivates the catalyst via its reduction to the Cu(I) state. In the absence of alcohol, the catalyst initiates the auto-oxygenation of aldehydes to carboxylic acids.

A recent study[1] has demonstrated that the bis(bipyridine)-cobalt(II) complex activates dioxygen (O_2) for the catalytic dehydrogenation (oxidation) of *N*-methylanilines, benzyl alcohols, and aldehydes. Because copper(II) is similar to cobalt(II) with respect to having an unpaired electron to interact with ground-state triplet dioxygen ($^{\bullet}O_2^{\bullet}$), we anticipated that it could be effective for the constructive activation of O_2. Furthermore, copper(II) in *galactose oxidase* activates O_2 for the dehydrogenation of the primary alcohol group of galactose.[2] This cycle has been mimicked with a macrocyclic copper(II) complex, O_2, and primary alcohols.[3] However, the latter system requires alkaline conditions and accumulates HOOH, which inhibits the process.

Several copper(II) complexes [e.g., $Cu^{II}(py)_4^{2+}$ in H_2O,[4] $Cu^{II}(Salen)_2^+$ in DMF with a large NaOH/alcohol ratio,[5,6] and other complexes in alkaline media[7]] activate O_2 for the transformation of alcohols to aldehydes and carboxylic acids. The general view is that the basic matrix causes the alcohol substrates to form RO^- adducts with the copper(II) centers prior to their interaction with O_2 and subsequent dehydrogenation.

On the basis of these reports and the ability of $Co^{II}(bpy)_2^{2+}$ to activate O_2 for the dehydrogenation of $PhCH_2OH$,[1] we have undertaken a systematic investigation of the bis(bipyridine)-copper(II) complex as a catalyst to activate O_2 for the dehydrogenation of alcohols.

Table I. $Cu^{II}(bpy)_2(OH)_2$ (5 mM) Induced Activation of O_2 (8 mM, 1 atm) for the Dehydrogenation of Alcohols and PhCH(O) in MeCN

substrate (ROH, 1 M) → product(s)	product yield (mM ± 5%)			
	1 h	4 h	8 h	24 h
$PhCH_2OH \rightarrow PhCH(O)$	298	360	371	
$n\text{-}C_6H_{13}OH \rightarrow n\text{-}C_6H_{12}(O)$	49	86	96	
2-butanol → butanone	0	12	20	29
$c\text{-}C_6H_{11}OH \rightarrow c\text{-}C_6H_{10}(O)$	9	35	46	
$CH_3CH{=}CHCH_2OH \rightarrow CH_3CH{=}CHCH(O)$	141	196	242	
$PhCH{=}CHCH_2OH \rightarrow PhCH{=}CHCH(O)$	69	110	160	
$\rightarrow PhCH(O)$	4.6	5.4	6.8	
$C_2H_5OH \rightarrow CH_3CH(O)$	4.2	30	47	60
$PhCH(OH)CH_3 \rightarrow PhC(O)CH_3$	92	153		
$2\text{-}ClPhCH_2OH \rightarrow 2\text{-}ClPhCH(O)$	218	262		
$2\text{-}CH_3PhCH_2OH \rightarrow 2\text{-}CH_3PhCH(O)$	150	210		
$2\text{-}MeOPhCH_2OH \rightarrow 2\text{-}MeOPhCH(O)$	84	156		
$4\text{-}ClPhCH_2OH \rightarrow 4\text{-}ClPhCH(O)$	301	329		
$4\text{-}MeOPhCH_2OH \rightarrow 4\text{-}MeOPhCH(O)$	263	379		
$3,4\text{-}(MeO)_2PhCH_2OH \rightarrow 3,4\text{-}(MeO)_2PhCH(O)$	293	330		
$PhCH_2CH_2OH \rightarrow PhCH(O)$	9	15	17	
$PhCH(O) \rightarrow PhC(O)OH$[a]	940			
$\rightarrow PhH$	66			

[a] 1 mM $Cu^{II}(bpy)_2(OH)_2$.

Experimental Section

Equipment. The reaction products were separated and identified with a Hewlett-Packard 5880A Series gas chromatograph equipped with an HP-1 capillary column (cross-linked methyl silicone gum phase, 12 m × 0.2 mm i.d.) and by gas chromatography–mass spectrometry (Hewlett-Packard 5890A Series gas chromatograph with a mass-selective detector). A Vacuum Atmospheres inert-atmosphere glovebox was used for the storage, preparation, and addition of air-sensitive and water-sensitive reagents.

A three-electrode potentiostat (Bioanalytical Systems Model CV-27) with a Houston Instruments Model 200 X-Y recorder was used to record the voltammograms. The experiments were conducted in a 15-mL electrochemical cell with provision to control the presence of oxygen with an argon-purge system. The working electrode was a Bioanalytical Systems glassy-carbon inlay (area 0.09 cm^2), the auxiliary electrode a platinum wire, and the reference electrode a Ag/AgCl wire in an aqueous tetramethylammonium chloride solution that was adjusted to give a potential of 0.00 V vs SCE. The last was contained in a Pyrex tube with a cracked soft-glass tip, which was placed inside a luggin capillary.[8] A Hewlett-Packard Model 8450A diode-array spectrophotometer was used for the UV–visible measurements.

Chemical and Reagents. The reagents for the investigations and syntheses were the highest purity commercially available and were used without further purification. Burdick and Jackson "distilled in glass" grade acetonitrile (MeCN, 0.004% H_2O), dimethylformamide (DMF, 0.011% H_2O), pyridine (py, 0.014% H_2O), and dimethyl sulfoxide (Me_2SO) were used as solvents. High-purity argon gas was used to deaerate the solutions. All compounds were dried in vacuo over $CaSO_4$ for 24 h prior to use. $Cu^{II}(ClO_4)_2{\cdot}6H_2O$ was obtained from GFS Chemicals, and 2,2′-bipyridine (bpy, 99+%) and benzyl alcohol ($PhCH_2OH$) were obtained from Aldrich.

---

(1) Sobkowiak, A.; Sawyer, D. T. *J. Am. Chem. Soc.* **1991**, *113*, 9520.

(2) Whittaker, M. M.; Whittaker, J. M. *J. Biol. Chem.* **1988**, *263*, 6074.

(3) Groves, J. T.; Park, K.-T. In *The Role of Oxygen in Chemistry and Biochemistry*; Ando, M., Moro-oka, Y., Eds.; Elsevier: Amsterdam, 1988; pp 541–548.

(4) Driscoll, J. J.; Kosman, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 765.

(5) Huang, J.; Xi, Z. *Cuihua Xuebao* **1989**, *10*, 3261.

(6) Liu, W.; Xi, Z. *Cuihua Xuebao* **1990**, *11*, 152.

(7) Sakharove, A. M.; Skibida, I. P. *J. Mol. Catal.* **1988**, *48*, 157.

(8) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley-Interscience: New York, 1974; p 144.

0002-7863/93/1515-3239$04.00/0

Table II. Rates of Production of PhCH(O) from $PhCH_2OH$ for Various $Cu^{II}(bpy)_2(OCH_2Ph)_2/PhCH_2OH/O_2$ Systems in MeCN

$Cu^{II}(bpy)_2(OCH_2Ph)_2/PhCH_2OH/O_2$	PhCH(O) product yield (mM ± 5%) 1 min	2 min	3 min	5 min	7 min	10 min	15 min	initial rate[a] (mM/min)	k_{obsd}[b] ($M^{-2}\,s^{-1}$)
1 mM/1 M/O_2 (1 atm, 8.1 mM)	30	48	56	68	76	84	93	30	62
1 mM/1 M/air (1.7 mM)		18	25	39	51	58		9.0	88
1 mM/0.5 M/air				14	21	30	38	3.0	62
0.5 mM/1 M/air				15	22	30	42	3.0	62

[a] The initial rate of production of PhCH(O): $[d[PhCH(O)]/dt]_{t=0}$. [b] Rate law: $d[PhCH(O)]/dt = k_{obs}[PhCH_2OH][O_2][Cu^{II}(bpy)_2(OCH_2Ph)_2]$.

Table III. Effects of Solvent on the Rate of Dehydrogenation of $PhCH_2OH$ (1 M) by the $(bpy)_2Cu^{II}(OCH_2Ph)_2$ (5 mM)/O_2 (1 atm) System

solvent (1 atm of O_2)	PhCH(O) product yield (mM ± 5%) 1 h	4 h	8 h	24 h
MeCN (8.1 mM)	298	360	371	
DMF (4.8 mM)	150	224		
Me_2SO (2.1 mM)	137	206		
$(MeCN)_3py$ (4.3 mM)	122		247	
pyridine (py) (4.9 mM)	17	51		88
H_2O (1 mM)		163	172	

Table IV. Effects of Ligand and Base on the Rate and Extent of Dehydrogenation of $PhCH_2OH$ (1 M) with the $Cu^{II}(MeCN)_4^{2+}$ (5 mM)/O_2 (1 atm, 8 mM) System in MeCN

ligand + base	PhCH(O) product yield (mM ± 5%) 1 h	4 h	8 h	24 h
10 mM bpy + 10 mM HO^-	298	360	371	
15 mM bpy + 10 mM HO^-	280	324	332	344
5 mM bpy + 10 mM HO^-	287	347	372	
10 mM bpy + 5 mM HO^-		2	4	6
10 mM bpy + 15 mM HO^-			229	
10 mM bpy + 10 mM $HOC(O)O^-$	273	303	316	
10 mM bpy + 15 mM $HOC(O)O^-$	149	173	176	
10 mM bpy + 10 mM PhO^-	19	36	62	83
10 mM bpy + 10 mM Et_3N	5	9	13	26
10 mM bpy + 10 mM py	4	3	3	
10 mM bpy + 10 mM $CH_3C(O)O^-$	4	3	3	
5 mM terpy + 10 mM HO^-	34	72		124
10 mM terpy + 10 mM HO^-	82	154		213
10 mM DPA^{2-} + 10 mM HO^-		171	173	
10 mM PA^- + 10 mM HO^-		129	130	

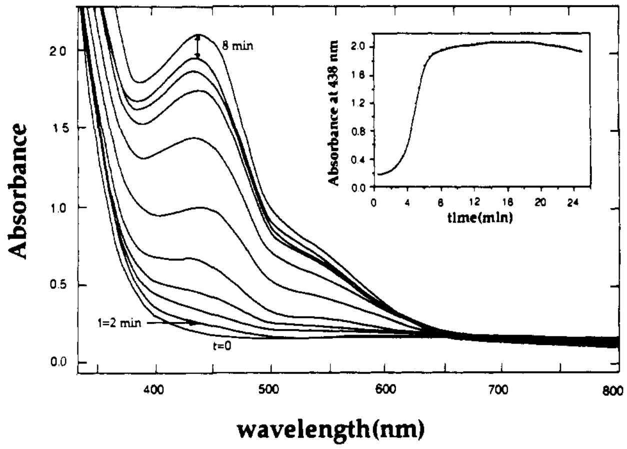


Figure 1. Absorption spectra for the combination of 1 mM $(bpy)_2Cu^{II}[OC(O)OH]_2$, 1 M $PhCH_2OH$, and 8.1 mM O_2 (1 atm) in MeCN (1.0-cm cell length) after various periods of reaction [0–24 min; at 40-s intervals except for the second (2-min interval) and the final spectrum (8-min interval)]. Inset: absorbance at 438 nm vs reaction time.

$[Cu^{II}(MeCN)_4](ClO_4)_2$. The $[Cu^{II}(MeCN)_4](ClO_4)_2$ complex was prepared by multiple recrystallizations of $[Cu^{II}(OH_2)_6](ClO_4)_2$ from MeCN.

Methods. The substrate and the $Cu^{II}(bpy)_2^{2+}$ complex [prepared in situ by the addition of 2 equiv of bipyridine (bpy) to $Cu^{II}(MeCN)_4(ClO_4)_2$] were combined in the solvent (total volume 3 mL), followed by the addition of (a) 1 atm of O_2 or air in a reaction cell (25-mL vial with cutout cap and Teflon-faced septum) and (b) base (HO^-, $HOC(O)O^-$, PhO^-, AcO^-, Et_3N, or py). The reaction mixtures were constantly stirred and maintained at ambient temperature (24 ± 2 °C). The progress of the reaction was monitored by withdrawing samples and injecting aliquots (0.2 μL) into a capillary-column gas chromatograph for analysis. The characterization of the products by GC–MS was done after the reaction was quenched with water and the products were extracted with diethyl ether.

Results

Reactivity of $Cu^{II}L_n^{2+}/O_2$/Base Systems with Alcohols. When base is added to a solution that contains $Cu^{II}L_n^{2+}$, O_2 and excess alcohol, the last is transformed to its aldehyde (primary alcohols) or ketone (secondary alcohols); tertiary alcohols are unreactive. Table I summarizes the product yields as a function of reaction time for a series of alcohols (1 M) in combination with 5 mM $Cu^{II}(bpy)_2^{2+}$, 10 mM HO^-, and O_2 (1 atm, 8.1 mM). Benzyl alcohol ($PhCH_2OH$) and its derivatives are much more reactive than aliphatic primary alcohols, and the latter are more reactive than secondary alcohols. α-Allylic alcohols (with their weak C–H bonds) are much more reactive than saturated substrates. With $PhCH_2OH$, the reaction reaches 80% completion in 1 h [Table I; 298 mM (1 h), 371 mM (8 h)].

Variation of the reactant concentrations for the $Cu^{II}(bpy)_2^{2+}/2HO^-/PhCH_2OH/O_2$ system in relation to the rate of formation of PhCH(O) (Table II) indicates that the dehydrogenation process is first-order each in catalyst, substrate, and O_2 concentration and has an apparent rate constant, k_{obs}, of 68 ± 9 $M^{-2}\,s^{-1}$ in MeCN. The effect of other solvents on the reaction rate is illustrated by the product yields for $PhCH_2OH$ (Table III). In water, the reaction rate is about half that in MeCN.

Table IV summarizes the effect of ligand, base, and their stoichiometry relative to Cu(II) upon the rate and extent of reaction for the $PhCH_2OH/O_2$ process. On the basis of the results, the $Cu^{II}(bpy)_2^{2+}$ complex is the most effective catalyst in combination with 2 equiv of HO^- or $HOC(O)O^-$. Excess base has a negative effect and usually induces precipitation of $Cu^{II}O$.

The results in Tables I and II indicate that the initial rate of PhCH(O) production is rapid (e.g., with 5 mM $Cu^{II}(bpy)_2^{2+}$, 1 M $PhCH_2OH$, and 1 atm of O_2, the initial rate is 150 mM min^{-1}). However, for all conditions, the process essentially stops after 20–80 catalyst turnovers. This dramatic decrease in reaction rate coincides with the reduction of the catalyst to the copper(I) state. Figure 1 illustrates the appearance of a copper(I) absorption band at 438 nm during the reaction history of a 1 mM $Cu^{II}(bpy)_2[OC(O)OH]_2$/1 M $PhCH_2OH/O_2$ (1 atm) system [the absorption of Cu(I) as a function of the bpy/Cu(I) ratio in MeCN (Figure 2) indicates formation of $(bpy)_2Cu^IOH(bpyH)^+$ (438 nm; ε 5900 $M^{-1}\,cm^{-1}$; $K_f = 1.6 \times 10^3\ M^{-1}$)]. Within 8 min, about one-third of the catalyst is reduced to its Cu(I) state, and the production of product [80 mM PhCH(O)] has essentially ceased (Table II). Spectrophotometric and electrochemical characterization of the product solution indicates that about one-third of the original copper is present in $(bpy)_2Cu^IOH(bpyH)^+$, one-third is present in $(bpy)_2Cu^{II}[OC(O)Ph]_2$, and one-third has precipitated as $Cu^{II}O(s)$. Authentic samples of the copper complexes have been used to confirm the analytical assay. Addition of more

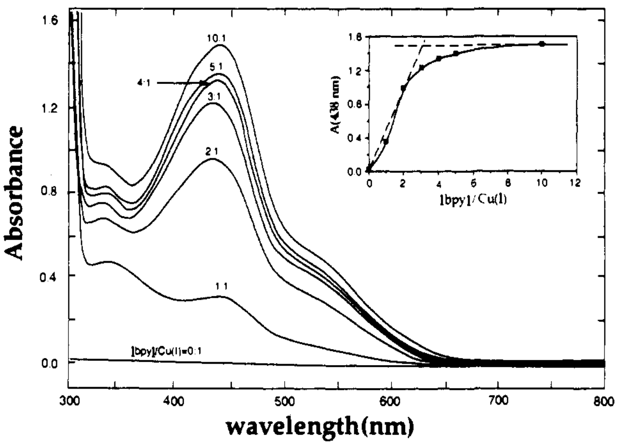


Figure 2. Absorption spectra in MeCN for 5.0 mM $Cu^I(MeCN)_4^+$ in the presence of various mole ratios of bipyridine (0.05-cm cell length). Inset: absorbance at 438 nm vs bpy/Cu^I mole ratio.

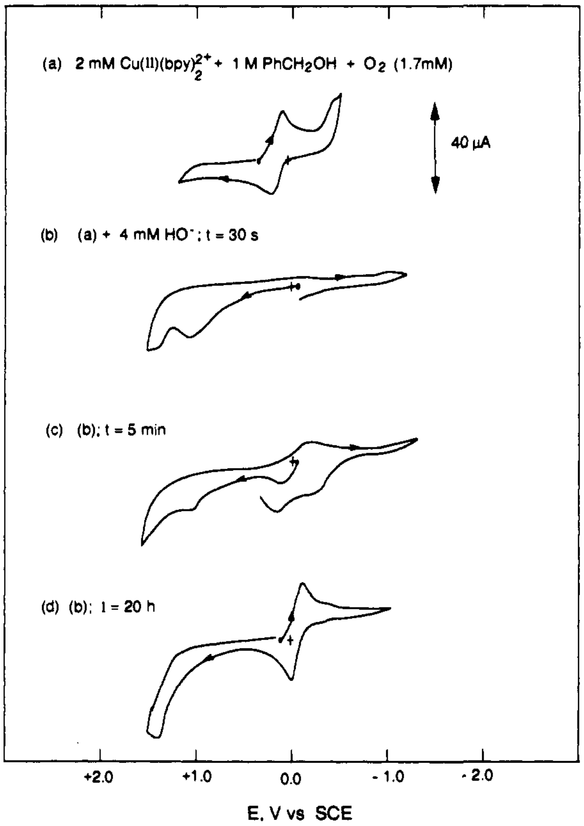


Figure 3. Cyclic voltammograms for the $Cu^{II}(bpy)_2^{2+}$/$PhCH_2OH$/O_2/HO^- system in air-saturated MeCN [0.1 M $Et_4N(ClO_4)$]: scan rate, 0.1 V s^{-1}; GCE, 0.009 cm^2; SCE vs NHE, +0.242 V.

base will induce additional reactivity that is proportional to the remaining soluble Cu(II).

When a spent reaction system for $PhCH_2OH$ is extracted with ether prior to analysis by GC-MS, a second product [PhC(O)-OCH_2Ph, the benzyl ester of benzoic acid] is found with a concentration that is about half that of Cu(I).

Characterization of the Reaction Complex. Figure 3 illustrates the cyclic voltammetry for $Cu^{II}(bpy)_2^{2+}$ (a) in the presence of $PhCH_2OH$ and O_2 and (b) after the addition of 2 equiv of HO^-/equiv of Cu(II). Initially, the only observed electrochemical process is broad oxidation at approximately +1.0 V vs SCE (curve b, Figure 3). Within 5 min about one-third of the Cu(II) in the original catalyst is present as Cu(I) (curve c), and after 20 h essentially all of the copper is again Cu(II) {mainly $(bpy)_2Cu^{II}[OC(O)Ph]_2$}, and there is a substantial oxidation peak at +1.4 V (consistent with the two-electron oxidation of HOOH).

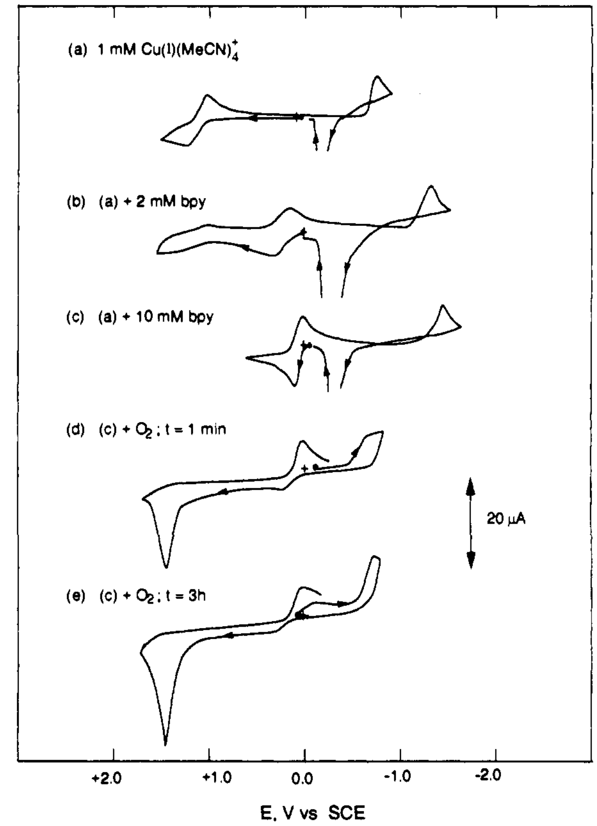


Figure 4. Cyclic voltammograms for $Cu^I(MeCN)_4^+$ in combination with bipyridine (bpy) and O_2 (1 atm, 8.1 mM) in MeCN [0.1 M $Et_4N(ClO_4)$]: scan rate, 0.1 V s^{-1}; GCE, 0.09 cm^2; SCE vs NHE, +0.242 V.

Figure 4 illustrates the cyclic voltammetry for $Cu^I(MeCN)_4^+$ in MeCN, including the effect of increasing amounts of bipyridine on the reductive and oxidative processes for Cu(I) and the effect of O_2 on the 1:10 Cu(I)/bpy system. Initially, the $Cu^I(bpy)_n^+$ complex undergoes a synergistic reduction via O_2 at −0.6 V vs SCE to give $(bpy)_2Cu^IOO^\cdot$ and in turn $(bpy)_2Cu^IOOCu^I(bpy)_2$. The latter apparently is oxidized to $Cu^{II}(bpy)_2^{2+}$ and O_2 at +1.5 V (curve d, Figure 4). After 3 h, about one-third of the original Cu(I) complex has been autoxidized to $(bpy)_2^+Cu^{II}OH$ (curve e, Figure 4).

Discussion and Conclusions

The results in Tables I–V provide compelling evidence that the combination of $Cu^{II}(bpy)_2^{2+}$ with 2 equiv of base [HO^- or $HOC(O)O^-$] in the presence of dioxygen and a primary alcohol (e.g., $PhCH_2OH$) catalyzes the dehydrogenation of the alcohol by O_2. Figure 3 confirms that the reaction is not initiated until the base is added, which indicates an initial formation of the bis(alkoxide) of $Cu^{II}(bpy)_2^{2+}$

$$Cu^{II}(bpy)_2^{2+} + 2PhCH_2OH + 2HO^- \rightarrow \underset{\mathbf{1}}{(bpy)_2Cu^{II}(OCH_2Ph)_2} + 2H_2O \quad (1)$$

The latter (**1**) appears to be the active catalyst for the autoxidation (dehydrogenation) of the alcohol substrate

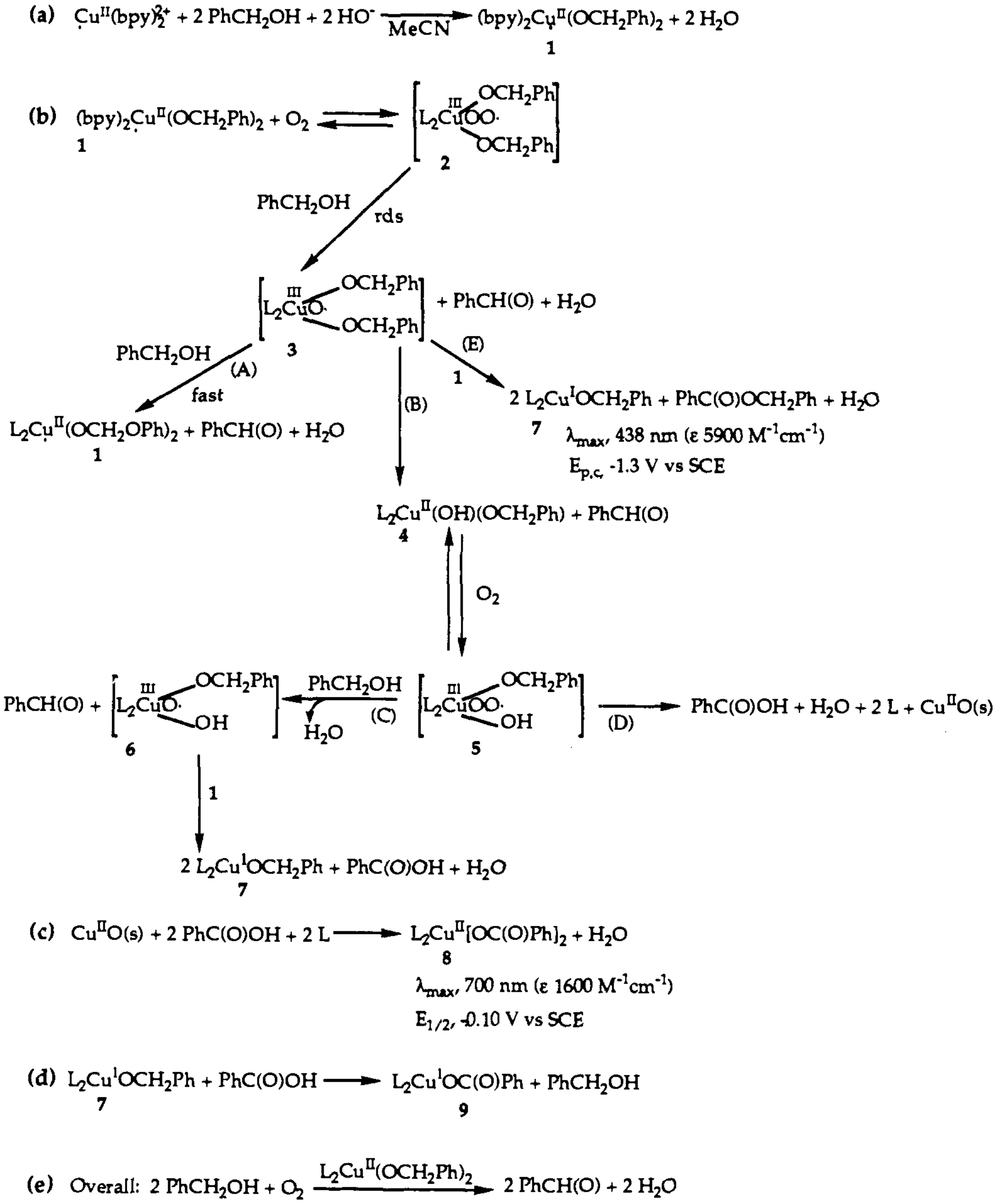
$$2PhCH_2OH + O_2 \xrightarrow{1} 2PhCH(O) + 2H_2O \quad (2)$$

Although the character of the reactive intermediate is unknown, a chemically reasonable species is a mononuclear dioxygen adduct

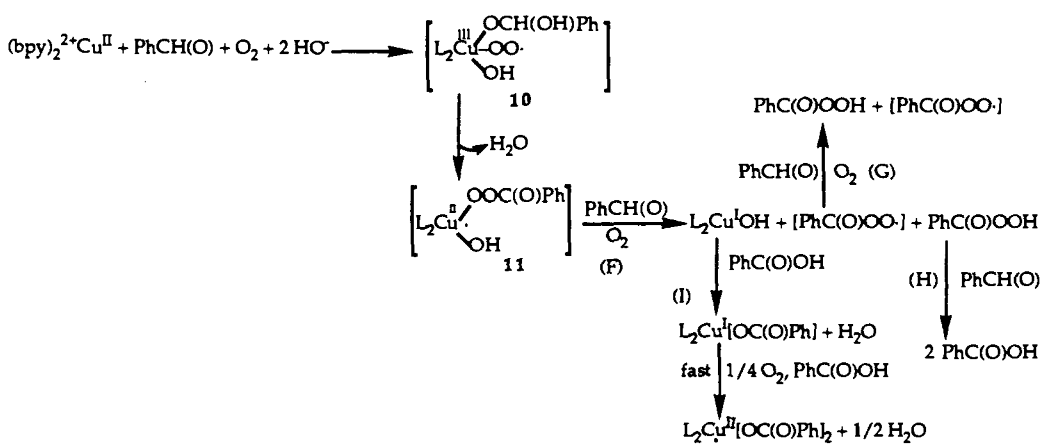
$$\mathbf{1} + O_2 \rightarrow \underset{\mathbf{2}}{[(bpy)_2(PhCH_2O)_2Cu^{III}(O_2)]} \quad (3)$$

Species **2** can complete the catalytic cycle via reaction with two

Scheme I. $(bpy)_2Cu^{II}(OH)_2$-Induced Autoxidation of Alcohols



Scheme II. $[Cu^{II}(bpy)_2{}^{2+}/\text{Base}]$-Induced Autoxidation of Aldehydes



substrate molecules

$$2 + 2\text{PhCH}_2\text{OH} \rightarrow 1 + 2\text{PhCH(O)} + 2\text{H}_2\text{O} \qquad (4)$$

Reference to Table I confirms that even for the most reactive substrates the autoxidation cycle (eqs 3 and 4) is severely slowed after 30–40% of the substrate has been dehydrogenated. Concurrent with the inhibition, about one-third of the copper is reduced to form $(bpy)_2Cu^IOCH_2Ph$ (Figure 1), one-third is transformed to give $L_2Cu^{II}[OC(O)Ph]_2$, and one-third precipitates as $Cu^{II}O(s)$. This appears to result from the buildup of water (eq 4) to an extent that it becomes a competitive substrate

$$4(\mathbf{1}) + O_2 \xrightarrow{H_2O} \underset{\mathbf{7}}{4(bpy)_2Cu^IOCH_2Ph} + 2PhCH_2OH + 2PhC(O)OH \quad (5)$$

[this accounts for 80–90% of the Cu(II) reduction and the production of PhC(O)OH]. The appearance of PhC(O)OCH$_2$Ph (~0.5–1.0 mM) in the product profile accounts for the remaining 10–20% of the Cu(II) reduction

$$4(\mathbf{1}) + O_2 \rightarrow \underset{\mathbf{7}}{4(bpy)_2Cu^IOCH_2Ph} + 2PhC(O)OCH_2Ph + 2H_2O \quad (6)$$

Over extended periods of time, the reduced copper is autoxidized

$$\underset{\mathbf{7}}{4(bpy)_2Cu^IOCH_2Ph} + O_2 \xrightarrow{\text{slow}} 2(\mathbf{1}) + (Cu^{II}O)_2(s) + 4bpy \quad (7a)$$

$$2(\mathbf{7}) + O_2 + 2PhCH_2OH \xrightarrow{\text{slow}} 2(\mathbf{1}) + HOOH \quad (7b)$$

which slowly extends the catalyzed dehydrogenation of alcohol substrates (Table I and Figure 3).

In many respects, the present copper system is similar to the $Co^{II}(bpy)_2{}^{2+}/HO^-/O_2/ROH$ system,[1] but is much more efficient [under comparable conditions, the Cu(II) system facilitates 60 catalyst turnovers in 1 h for the dehydrogenation of PhCH$_2$OH versus 4 for the Co(II) system]. The present results indicate that only bound substrates are reactive via formation of species **2** (eq 3), which also is the case for the Co(II) system [the reaction of O$_2$ with 1,4-cyclohexadiene (ΔH_{DBE} = 73 kcal mol^{-1})[9] is *not* catalyzed by $(bpy)_2Cu^{II}(OH)_2$ or $(bpy)_2{}^+Co^{II}(OH)$].[1]

On the basis of the results and the preceding discussion, a self-consistent set of reaction paths is outlined in Scheme I. After the initial formation of the substrate/dioxygen adduct (**2**), it facilitates the dehydrogenation of substrate via a catalytic cycle (path A, Scheme Ib). In the case of PhCH$_2$OH, this is the dominant pathway until 30–40% of the substrate is dehydrogenated, at which point the reaction is inhibited [most of the catalyst is reduced to $(bpy)_2Cu^IOCH_2Ph$ (**7**) via paths B, C, and E or converted to $Cu^{II}O(s)$ and PhC(O)OH via path D]. The buildup of water (coproduct from substrate dehydrogenation) apparently induces the formation of species **4** and **5** (path B, Scheme I); the latter reacts with PhCH$_2$OH via path C and **6** to yield the reduced copper complex and PhC(O)OH. With sufficient buildup of PhC(O)OH, the $Cu^{II}O(s)$ is dissolved (reaction c, Scheme I), and the alcohol ligands of Cu(II) (**1**) and Cu(I) (**7**) are replaced to give **8** and **9**, respectively. A second path for reduction of Cu(II) involves the collapse of intermediate **3** via path E of Scheme I to give **7** and PhC(O)OCH$_2$Ph.

As in the case of the $(bpy)_2{}^+Co^{II}OH/O_2$ system,[1] the $(bpy)_2Cu^{II}(OH)_2$ complex activates O$_2$/RCH(O) combinations to initiate the autoxidation of aldehydes (Table I). If alcohol is present, aldehyde is not an effective ligand and is unreactive. Scheme II outlines reaction paths for the ligand-induced formation of an O$_2$ adduct (**10**), which internally dehydrogenates the bound aldehyde (as the geminal diol)[10] to yield an initiator (**11**) for the autoxidation of aldehydes. The resultant peracid radical [PhC(O)OO$^\bullet$] becomes the metal-independent carrier for the autoxidation chain (path G).[11] The peracid product of path F does not accumulate because it reacts with excess aldehyde via a non-radical process to give two RC(O)OH molecules (path H, Scheme II). The combination of RC(O)OH, $(bpy)_2Cu^IOH$, and O$_2$ in the product solution leads to the autoxidation of the reduced copper complex to give $(bpy)_2Cu^{II}[OC(O)Ph]_2$ (path I).

In summary, the [base/substrate]-induced binding of O$_2$ to form species **2** (Scheme I) is the basis for the catalytic dehydrogenation of primary alcohols, amines, and aldehydes. The net process is similar to that for the galactose/galactose oxidase system,[2] but in contrast, the present system does not accumulate HOOH. However, HOOH in basic MeCN rapidly reduces $(bpy)_2{}^+Cu^{II}OH$ to its Cu(I) state.[12] This would be an alternative means to reduce and deactivate the Cu(II) catalyst in addition to those outlined in Scheme I. Although the catalyst is deactivated (via reduction) after 30–40% of the substrate alcohol is transformed to its aldehyde, it is slowly reoxidized by O$_2$ to become an active catalyst. Thus, the initial rapid catalytic cycle becomes a slow (rate decreased by a factor of 20–100) steady-state transformation of alcohols to aldehydes.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-9106742, the Welch Foundation under Grant No. 1042A, and the Monsanto Co. with a Grant-in-Aid. We thank the K. C. Wong Foundation Ltd. (Hong Kong) for its support of A.Q.

---

(9) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R.; Ed.; CRC Press: Boca Raton, FL, 1990; pp 9–85.

(10) Funderburk, L. H.; Aldwin, L.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 5444.

(11) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; pp 629–634.

(12) Sobkowiak, A.; Qiu, A.; Liu, X.; Llobet, A.; Sawyer, D. T. *J. Am. Chem. Soc.* **1993**, *115*, 609.