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

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Abstract: The combination of bis(bipyridine)copper(II) $[Cu^{11}(bpy)_2^{2+}]$ and 2 equiv of base [HO⁻ or HOC(O)O⁻] with excess alcohol (e.g., PhCH₂OH) in an O₂-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 O₂ concentration with an apparent rate constant, k, for PhCH₂OH of 68 \pm 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 study¹ has demonstrated that the bis(bipyridine)cobalt(II) complex activates dioxygen (O₂) 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 groundstate triplet dioxygen (O_2), 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., $Cu^{11}(py)_4^{2+}$ in $H_2O_4^4$ Cu¹¹-(Salen)2⁺ in DMF with a large NaOH/alcohol ratio,^{5,6} and other complexes in alkaline media⁷] 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 ROadducts with the copper(II) centers prior to their interaction with O₂ and subsequent dehydrogenation.

On the basis of these reports and the ability of $Co^{11}(bpy)_2^{2+}$ to activate O_2 for the dehydrogenation of PhCH₂OH,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.

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 Table I. Cu¹¹(bpy)₂(OH)₂ (5 mM) Induced Activation of O₂ (8 mM, 1 atm) for the Dehydrogenation of Alcohols and PhCH(O) in MeCN

substrate		product yield (mM \pm 5%)				
$(ROH, 1 M) \rightarrow product(s)$	1 h	4 h	8 h	24 h		
$PhCH_2OH \rightarrow PhCH(O)$	298	360	371			
$n-C_6H_{13}OH \rightarrow n-C_6H_{12}(O)$	49	86	96			
2-butanol → butanone	0	12	20	29		
$c-C_6H_{11}OH \rightarrow c-C_6H_{10}(O)$	9	35	46			
CH ₃ CH = CHCH ₂ OH → CH ₃ CH = 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				
$2-ClPhCH_2OH \rightarrow 2-ClPhCH(O)$	218	262				
$2-CH_3PhCH_2OH \rightarrow 2-CH_3PhCH(O)$	150	210				
$2-MeOPhCH_2OH \rightarrow 2-MeOPhCH(O)$	84	156				
$4-ClPhCH_2OH \rightarrow 4-ClPhCH(O)$	301	329				
$4-MeOPhCH_2OH \rightarrow 4-MeOPhCH(O)$	263	379				
$3,4-(MeO)_2PhCH_2OH \rightarrow$	293	330				
$3,4-(MeO)_2PhCH(O)$						
$PhCH_2CH_2OH \rightarrow PhCH(O)$	9	15	17			
$PhCH(O) \rightarrow PhC(O)OH^{\mu}$	940					
→ PhH	66					

^a 1 mM Cu^{II}(bpy)₂(OH)₂.

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 cm²), 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% H₂O), dimethylformamide (DMF, 0.011% H₂O), pyridine (py, 0.014% H₂O), and dimethyl sulfoxide (Me₂-SO) were used as solvents. High-purity argon gas was used to deaerate the solutions. All compounds were dried in vacuo over CaSO₄ for 24 h prior to use. Cu¹¹(ClO₄)_{2'}6H₂O was obtained from GFS Chemicals, and 2,2'-bipyridine (bpy, 99+%) and benzyl alcohol (PhCH2OH) were obtained from Aldrich.

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Table II. Rates of Production of PhCH(O) from PhCH₂OH for Various Cu^{II}(bpy)₂(OCH₂Ph)₂/PhCH₂OH/O₂ Systems in MeCN

	PhCH(O) product yield (mM \pm 5%)				initial rate ^a				
$Cu^{ }(bpy)_2(OCH_2Ph)_2/PhCH_2OH/O_2$	1 min	2 min	3 min	5 min	7 min	10 min	15 min	(mM/min)	$k_{\rm obsd}^{b} ({\rm M}^{-2}{\rm s}^{-1})$
$1 \text{ mM/1 M/O}_2 (1 \text{ atm, 8.1 mM})$ 1 mM/1 M/air (1.7 mM)	30	48 18	56 25	68 39	76 51	84 58	93	30	62 88
1 mM/0.5 M/air		10	2.5	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)₂Cu¹¹(OCH₂Ph)₂ (5 mM)/O₂ (1 atm) System

	PhCH(O) product yield (mM ± 5%)			
solvent (1 atm of O_2)	 h	4 h	8 h	24 h
MeCN (8.1 mM)	298	360	371	
DMF (4.8 mM)	150	224		
$Me_2SO(2.1 \text{ mM})$	137	206		
(MeCN) ₃ py (4.3 mM)	122		247	
pyridine (py) (4.9 mM)	17	51		88
$H_2O(1 \text{ mM})$		163	172	

 $[Cu^{II}(MeCN)_4](ClO_4)_2$. 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 Cu¹¹(bpy)₂²⁺ complex [prepared in situ by the addition of 2 equiv of bipyridine (bpy) to Cu¹¹(MeCN)₄-(ClO₄)₂] were combined in the solvent (total volume 3 mL), followed by the addition of (a) 1 atm of O₂ 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, Et₃N, or py). The reaction mixtures were constantly stirred and maintained at ambient temperature ($24 \pm 2 \, ^{\circ}$ 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 Cu¹¹L_n²⁺/**O**₂/**Base Systems with Alcohols.** When base is added to a solution that contains Cu¹¹L_n²⁺, O₂ 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 Cu¹¹(bpy)₂²⁺, 10 mM HO⁻, and O₂ (1 atm, 8.1 mM). Benzyl alcohol (PhCH₂OH) 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 PhCH₂OH, 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 Cu¹¹-(bpy)₂²⁺/2HO⁻/PhCH₂OH/O₂ 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 O₂ 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 PhCH₂OH (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 PhCH₂OH/O₂ process. On the basis of the results, the Cu^{II}(bpy)₂²⁺ 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 Cu¹¹(bpy)₂²⁺, 1 M PhCH₂OH, and 1 atm of O₂, the initial rate is 150 mM min⁻¹). However, for all conditions, the process essentially stops after

Table IV. Effects of Ligand and Base on the Rate and Extent of Dehydrogenation of PhCH₂OH (1 M) with the $Cu^{11}(MeCN)_4^{2+}$ (5 mM)/O₂ (1 atm, 8 mM) System in MeCN

	PhCH(O) product yield $(mM \pm 5\%)$			
ligand + base	1 h	4 h	8 h	24 h
10 mM bpy + 10 mM HO 15 mM bpy + 10 mM HO 5 mM bpy + 10 mM HO	298 280 287	360 324 347	371 332 372	344
10 mM bpy + 5 mM HO ⁻ 10 mM bpy + 15 mM HO ⁻ 10 mM bpy + 15 mM HO ⁻	207	2	4 229 316	6
$10 \text{ mM bpy} + 10 \text{ mM HOC}(0)0^{-10}$ 10 mM bpy + 15 mM HOC(0)0^{-10} mM bpy + 10 mM PbO ⁻¹⁰	149	173	176	83
$10 \text{ mM bpy} + 10 \text{ mM rm}^{10}$ $10 \text{ mM bpy} + 10 \text{ mM Et}_3\text{N}$ 10 mM bpy + 10 mM py	5	9	13	26
10 mM bpy + 10 mM $CH_3C(O)O^-$ 5 mM terpy + 10 mM HO^-	4 34	3 72	3	124
10 mM terpy + 10 mM HO 10 mM DPA ²⁻ + 10 mM HO 10 mM PA ⁻ + 10 mM HO ⁻	82	154 171 129	173 130	213



Figure 1. Absorption spectra for the combination of 1 mM $(bpy)_2Cu^{11}[OC(O)OH]_2$, 1 M PhCH₂OH, and 8.1 mM O₂ (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.

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)₂Cu¹OH(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)₂Cu¹OH(bpyH)⁺, one-third is present in (bpy)₂Cu¹¹[OC(O)Ph]₂, and one-third has precipitated as Cu¹¹O(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 $Cu^{1}(MeCN)_{4}^{+}$ in the presence of various mole ratios of bipyridine (0.05-cm cell length). Inset: absorbance at 438 nm vs bpy/Cu¹ mole ratio.



Figure 3. Cyclic voltammograms for the $Cu^{11}(bpy)_2^{2+}/Ph-CH_2OH/O_2/HO^-$ system in air-saturated MeCN [0.1 M Et₄N(ClO₄)]: scan rate, 0.1 V s⁻¹; GCE, 0.009 cm²; 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)-OCH₂Ph, 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 $Cu^{[1]}(bpy)_2^{2+}$ (a) in the presence of PhCH₂OH and O₂ 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 $Cu^{1}(MeCN)_{4}^{+}$ in combination with bipyridine (bpy) and O_{2} (1 atm, 8.1 mM) in MeCN [0.1 M Et₄N(ClO₄)]: scan rate, 0.1 V s⁻¹; GCE, 0.09 cm²; SCE vs NHE, +0.242 V.

Figure 4 illustrates the cyclic voltammetry for $Cu^{1}(MeCN)_{4}^{+}$ in MeCN, including the effect of increasing amounts of bipyridine on the reductive and oxidative processes for Cu(I) and the effect of O₂ on the 1:10 Cu(I)/bpy system. Initially, the Cu¹(bpy)_n⁺ complex undergoes a synergistic reduction via O₂ at -0.6 V vs SCE to give (bpy)₂Cu¹OO[•] and in turn (bpy)₂Cu¹OOCu¹(bpy)₂. The latter apparently is oxidized to Cu¹¹(bpy)₂²⁺ and O₂ 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⁺Cu¹¹OH (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., PhCH₂OH) catalyzes the dehydrogenation of the alcohol by O₂. Figure 3 confirms that the reaction is not initiated until the base is added, which indicates an initial formation of the bis(alkoxide) of $Cu^{II}(bpy)_2^{2+}$

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

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

$$2PhCH_2OH + O_2 \rightarrow 2PhCH(O) + 2H_2O$$
(2)

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

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

Species 2 can complete the catalytic cycle via reaction with two



substrate molecules

 $\mathbf{2} + 2\mathbf{PhCH}_{2}\mathbf{OH} \rightarrow \mathbf{1} + 2\mathbf{PhCH}(\mathbf{O}) + 2\mathbf{H}_{2}\mathbf{O}$ (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 $(bpy)_2Cu^{\dagger}OCH_2Ph$ (Figure 1), one-third is transformed to give $L_2Cu^{\dagger\dagger}[OC(O)Ph]_2$, and one-third precipitates as $Cu^{\dagger\dagger}O$ -(s). This appears to result from the buildup of water (eq 4) to an extent that it becomes a competitive substrate

$$4(1) + O_2 \xrightarrow{H_2O} 4(bpy)_2Cu^{I}OCH_2Ph + 2PhCH_2OH + 2PhC(O)OH (5)$$
7

[this accounts for 80–90% of the Cu(II) reduction and the production of PhC(O)OH]. The appearance of PhC(O)OCH₂-Ph (~0.5–1.0 mM) in the product profile accounts for the remaining 10–20% of the Cu(II) reduction

$$4(1) + O_2 \rightarrow$$

$$4(bpy)_2Cu^{I}OCH_2Ph + 2PhC(O)OCH_2Ph + 2H_2O \quad (6)$$
7

Over extended periods of time, the reduced copper is autoxidized

$$4(bpy)_{2}Cu^{I}OCH_{2}Ph + O_{2} \xrightarrow{slow} 2(1) + (Cu^{II}O)_{2}(s) + 4bpy$$
7
(7a)

$$2(7) + O_2 + 2PhCH_2OH \xrightarrow{slow} 2(1) + HOOH$$
 (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 $Co^{11}(bpy)_2^{2+}/HO^-/O_2/ROH$ 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 PhCH₂OH 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 O₂ with 1,4-cyclohexadiene ($\Delta H_{DBE} = 73$ 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 PhCH₂OH, 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)₂Cu¹OCH₂Ph (7) via paths B, C, and E or converted to Cu¹¹O(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 PhCH₂OH via path C and 6 to yield the reduced copper complex and PhC(O)OH. With sufficient buildup of PhC(O)OH, the Cu¹¹O(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)OCH₂Ph.

As in the case of the $(bpy)_2+Co^{11}OH/O_2$ system,¹ the $(bpy)_2Cu^{11}(OH)_2$ 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 [Ph-C(O)OO[•]] 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)_2Cu¹⁰OH, and O₂ in the product solution leads to the autoxidation of the reduced copper complex to give (bpy)_2Cu¹¹[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+Cu¹¹OH 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 O₂ 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.

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