J. Am. Chem. Soc. **1991**, *113*, 9520-9523

Cobalt(II)-Induced Activation of Dioxygen for the Dehydrogenation of *N*-Methylanilines and Benzyl Alcohol

Andrzej Sobkowiak and Donald T. Sawyer*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received August 31, 1990. Revised Manuscript Received August 12, 1991*

Abstract: In acetonitrile the bis(pyridine)cobalt(II) complex [Co^{II}(bpy)$_2$](ClO$_4$)$_2$] activates dioxygen via the reversible formation of a μ-dioxygen complex. This complex dehydrogenates (oxidizes) *N*-methylanilines, benzyl alcohol, and aldehydes (with subsequent autoxidation). In the absence of substrate, the Co^{II}(bpy)$_2$$^{2+}$ complex reduces dioxygen via residual water in the solvent to generate HOOH. The complex does not activate O$_2$ for reaction with hydrocarbons [even 1,4-cyclohexadiene (ΔH_{DBE} 73 kcal mol^{-1}) is inert].

During the past decade there has been renewed interest in the selective oxygenation of hydrocarbons and other organic compounds via metal-catalyzed activation of dioxygen (O$_2$) and hydrogen peroxide (HOOH).[1-3] In nature, O$_2$ and HOOH are activated by metalloproteins to achieve selective oxidation and oxygenation of organic substrates. However, except for radical-chain autoxidations, there have been a limited number of reports of metal-catalyzed activation of O$_2$ in solution under mild conditions (these are summarized in several reviews).[1,2,4,5]

The Schiff base complexes of cobalt(II) reversibly bind dioxygen, and the oxygenated complexes have been used to oxidize hindered phenols,[6-22] stilbenes,[23] quinones,[24] quinone methides,[25] (*p*-nitrophenyl)hydrazones,[26] indoles,[27] flavonols,[28] sulfides,[29] N-substituted anilines,[30] and olefins.[31-33] Similarly, the bis(bipyridine)cobalt(II) complex[34] [Co^{II}(bpy)$_2$$^{2+}$] and cobalt(II)-polyamide chelates[35] activate O$_2$ for the oxidation of 2,6-di-*tert*-butylphenol. Although these reactions were carried out under different conditions (solvent, catalyst, substrate), the results conform to a general scheme whereby dioxygen binding by cobalt(II) activates it to abstract hydrogen atoms and to react with the radicals that are formed. However, hydrogen peroxide also can be formed via the cobalt complex/O$_2$/substrate system and thereby become the primary oxidant.[33]

Recent studies[36] have shown that bis(picolinato)iron(II) [Fe(PA$_2$)] and its μ-oxo dimer [(PA)$_2$Fe^{III}(PA)$_2$] activate HOOH [and KO$_2$(s) or electroreduced O$_2$] in a pyridine/acetic acid solvent system for the efficient and selective transformation of methylenic carbons to carbonyl groups and for the dioxygenation of acetylenes and aryl olefins. In the same solvent matrix, the combination of Fe^{II}(PA)$_2$, HOOH, diphenyl diselenide [PhSeSePh], and a hydrocarbon substrate (e.g., cyclohexane [c-C$_6$H$_{12}$]) (2:2:1:100 mol ratio) in py/HOAc reacts stoichiometrically (via Fenton chemistry) to give 2 equiv of the PhSe derivative of the substrate [e.g., two (c-C$_6$H$_{11}$)SePh].[37] In the presence of O$_2$ (1 atm, 3.4 mM) and excess substrate, the (2,6-dicarboxylatopyridine)iron(II) [Fe^{II}(DPAH)$_2$] complex is oxygenated to a reactive intermediate, (DPAH)$_2$Fe^{III}OOFe^{III}(DPAH)$_2$, which ketonizes methylenic carbons and dioxygenates acetylenes, aryl olefins, and catechols.[38] The presence of bromotrichloromethane (BrCCl$_3$) (equimolar to substrate, c-C$_2$H$_{12}$) causes the system to yield c-C$_6$H$_{11}$Br as the sole product (in the absence of BrCCl$_3$, the only product is cyclohexanone [c-C$_6$H$_{10}$(O)]). With equimolar 1-iodobutane (BuI) present, the yield of c-C$_6$H$_{10}$(O) is reduced and bipyridine is formed from oxidation of the solvent. When the 1.8:1 py/HOAc solvent is replaced with MeCN or 3:1 MeCN/py, the Fe^{II}(DPAH)$_2$/O$_2$ combination does not react with hydrocarbon substrates but undergoes oxygenation to give (DPAH)$_2$Fe^{III}OFe^{III}(DPAH)$_2$ via its μ-dioxygen adducts. However, the presence of 1,2-diphenylhydrazine (PhNHNHPh) causes the system to become a hydrocarbon monooxygenates mimic (c-C$_6$H$_{12}$ $\rightarrow$ c-C$_6$H$_{11}$OH).[39]

Recently, we have reported[40] that Co^{II}(bpy)$_2$$^{2+}$ activates HOOH for the selective ketonization of methylenic carbons, the dehy-

---

(1) *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980.

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

(3) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley-Interscience: New York, 1989.

(4) Matsuura, T. *Tetrahedron Lett.* **1977**, *33*, 2869.

(5) Meunier, B. *Bull. Soc. Chim. Fr.* **1983**, II-345.

(6) VanDort, H. M.; Guerson, H. J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 529.

(7) Vogt, L. H., Jr.; Wirth, J. G.; Finkbeiner, H. L. *J. Org. Chem.* **1969**, *34*, 273.

(8) Tomaja, D. L.; Vogt, L. H, Jr.; Wirth, J. G. *J. Org. Chem.* **1970**, *35*, 2029.

(9) Nishinaga, W.; Watanabe, Y.; Matsuura, T. *Tetrahedron Lett.* **1974**, 1291.

(10) Nishinaga, A.; Nishizawa, K.; Tomita, H.; Matsuura, T. *J. Am. Chem. Soc.* **1976**, *99*, 1287.

(11) Fullerton, T. J.; Ahern, S. P. *Tetrahedron Lett.* **1976**, 139.

(12) McKillop, A. M.; Ray, S. J. *Synthesis* **1977**, 847.

(13) Nishinaga, A.; Tomita, H.; Matsuura, T. *Tetrahedron Lett.* **1979**, 2893.

(14) Nishinaga, A.; Tomita, H.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 1261.

(15) Nishinaga, A.; Shimizu, T.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 1265.

(16) Nishinaga, A.; Tomita, H.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 2833.

(17) Nishinaga, A.; Tomita, H. *J. Mol. Catal.* **1980**, *7*, 179.

(18) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1981**, *22*, 4437.

(19) Nishinaga, A.; Shimizu, T.; Matsuura, T. *Tetrahedron Lett.* **1981**, *22*, 5293.

(20) Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7580.

(21) Corden, B. B.; Drago, R. S.; Perito, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2903.

(22) Ganeshpure, P. A.; Sudalai, A.; Satish, S. *Tetrahedron Lett.* **1989**, *30*, 5929.

(23) Ganeshpure, P. A.; Satish, S. *Tetrahedron Lett.* **1988**, *29*, 6629.

(24) Nishinaga, A.; Tomita, H.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 4853.

(25) Nishinaga, A.; Tomita, H.; Tarumi, Y.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 4849.

(26) Nishinaga, A.; Tomita, H.; Oda, M.; Matsuura, T. *Tetrahedron Lett.* **1982**, *23*, 339.

(27) Nishinaga, A. *Chem. Lett.* **1975**, 273.

(28) Nishinaga, A.; Tojo, T.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1974**, 896.

(29) Numata, T.; Watanabe, Y.; Oae, S. *Tetrahedron Lett.* **1978**, 4933.

(30) Benedini, F.; Galliani, G.; Nali, M.; Rindone, B.; Tollari, S. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1963.

(31) Zombeck, A.; Hamilton, D. E.; Drago, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 6782.

(32) Okamoto, T.; Oka, S. *J. Org. Chem.* **1984**, *49*, 1589.

(33) Hamilton, D. E.; Drago, R. S.; Zombeck, A. *J. Am. Chem. Soc.* **1987**, *109*, 374.

(34) Bedell, S. A.; Martell, A. E. *Inorg. Chem.* **1983**, *22*, 364.

(35) Bedell, S. A.; Martell, A. E. *J. Am. Chem. Soc.* **1985**, *107*, 7909.

(36) Sheu, C.; Richert, S. A.; Cofré, P.; Ross, B., Jr.; Sobkowiak, A.; Sawyer, D. T.; Kanofsky, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1936.

(37) Sheu, C.; Sobkowiak, A.; Zhang, L.; Ozbalik, N.; Barton, D. H. R.; Sawyer, D. T. *J. Am. Chem. Soc.* **1989**, *111*, 8030.

(38) Sheu, C.; Sobkowiak, A.; Jeon, A.; Sawyer, D. T. *J. Am. Chem. Soc.* **1990**, *112*, 879.

(39) Sheu, C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1990**, *112*, 8412.

(40) Tung, H.-C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1990**, *112*, 8214.

0002-7863/91/1513-9520$02.50/0

drogenation (oxidation) of alcohols and aldehydes, and the dioxygenation of aryl olefins and acetylenes. Dehydrogenase (or monooxygenase) chemistry is favored in pure MeCN solvent, but the ketonization of methylenic carbons and dioxygenase chemistry are dominant in MeCN/py (4:1 molar ratio). The selective ketonization of cyclohexene in MeCN/py contrasts with its enhanced monooxygenation in pure MeCN and is compelling evidence for two reactive intermediates. This cobalt(II)-induced activation of hydrogen peroxide has prompted a systematic investigation to characterize the bis(bipyridine)cobalt(II)/dioxygen system and its reactivity toward organic substrates.

Experimental Section

Equipment. Cyclic voltammetry was performed with a Bioanalytical Systems Model CV-27 voltammetric controller and a Houston Instruments Model 100 XY recorder. These measurements were made with a 10-mL microcell assembly that was adapted for the working electrode [a Bioanalytical Systems glassy-carbon electrode (area 0.09 cm^2)], a platinum wire auxiliary electrode (contained in a glass tube with a medium-porosity glass frit and filled with a solution of supporting electrolyte), and a Ag/AgCl reference electrode filled with aqueous tetramethylammonium chloride solution and adjusted to 0.00 V vs SCE)[41] with a solution junction via a Pyrex glass tube closed with a cracked soft-glass bead that was contained in a Luggin capillary. The cyclic voltammograms were initiated at the rest potential of the solution, and voltages are reported versus SCE. The solutions contained 0.1 M tetramethylammonium perchlorate (TEAP) as the supporting electrolyte.

The reaction products were separated and identified with a Hewlett-Packard 5880A series gas chromatograph equipped with a HP-1 capillary column (cross-linked methyl silicone gum phase, 12 m × 0.2 mm i.d.) and with a gas chromatography–mass spectrometry analyzer (Hewlett-Packard 5790A series gas chromatograph with mass-selective detector). Reference samples were used to confirm product identification. The quantities of products were calculated from standard curves for authentic samples. Direct injections of the product solutions were made. The UV–vis spectrophotometric measurements were made with a Hewlett-Packard Model HP 8450-A diode array rapid-scan spectrophotometer. All measurements, unless indicated otherwise, were made at 25 ± 1 °C.

Chemicals and Reagents. The reagents for the investigations and syntheses were the highest purity commerically available and were used without further purification. Burdick and Jackson "distilled-in-glass" grade acetonitrile (MeCN, 0.004% H_2O) and pyridine (py, 0.014% H_2O) were used as solvents. Tetraethylammonium perchlorate (TEAP, GFS Chemicals) was vacuum-dried for 24 h prior to use. Almost-dry HOOH (94%) was prepared from reagent-grade HOOH (50%, Fisher Scientific) via vacuum distillation.[42] This solution was dissolved in acetonitrile, and the concentration of HOOH was determined iodometrically.[43] Tetrabutylammonium hydroxide ($(Bu_4N)OH$) was obtained from Aldrich as a 1 M solution in methanol; its concentration was determined by acid–base titration. Anhydrous $[Co^{II}(MeCN)_4](ClO_4)_2$ was prepared by repeated recrystallization of $[Co^{II}(H_2O)_6](ClO_4)_2$ (reagent grade, GFS Chemicals) from acetonitrile. High-purity argon gas was used to deaerate the solutions.

Methods. The substrate and the $Co^{II}(bpy)_2^{2+}$ complex [prepared in situ by the addition of 2 equiv of bipyridine (bpy) to $Co^{II}(MeCN)_4(ClO_4)_2$] were combined in the solvent (total volume 3 mL) followed by the addition of 1 atm of O_2 or air in a reaction cell (25-mL vial with cut-out cap and Teflon-faced septum). The reaction mixtures were constantly stirred. The progress of the reaction was monitored by withdrawing samples and injecting an aliquot (0.2 μL) into the GC 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.

Hazard Warning: Special precautions are essential when working with concentrated hydrogen peroxide solutions in aprotic media. Such systems can undergo explosive decomposition in the presence of traces of metals or metal salts. Also, any source of ignition is dangerous with flammable organic solvents that are under an atmosphere of dioxygen.

Results

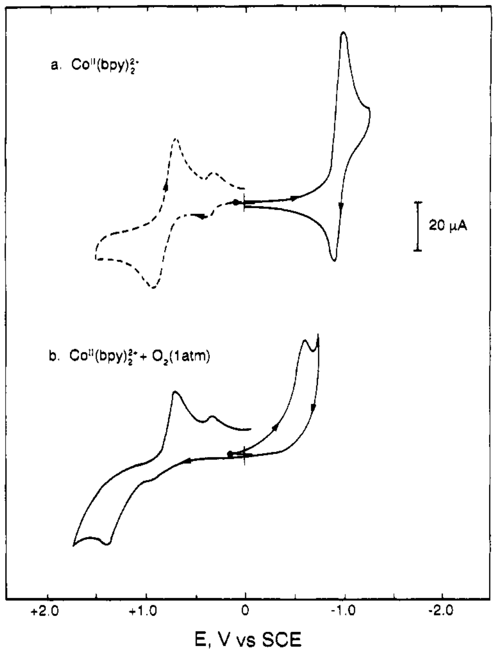


Figure 1. Cyclic voltammograms of 3 mM $Co(bpy)_2^{2+}$ in MeCN (0.1 M TEAP) (a) in the absence of dioxygen; (b) in the presence of O_2 (8.1 atm, 1 atm). Scan rate, 0.1 V s^{-1}; glassy-carbon working electrode (0.09 cm^2); SCE vs NHE, 0.242 V; (- - -), initial positive voltage scan.

Electrochemistry and Absorption Spectroscopy of $Co^{II}(bpy)_2^{2+}$ and Its O_2 Adduct. The cyclic voltammogram of the $Co^{II}(bpy)_2^{2+}$ complex in acetonitrile exhibits two reversible oxidation peaks (0.4 V vs SCE and 0.90 V) as well as an almost reversible reduction peak at −0.90 V (Figure 1a). When the molar ratio of cobalt(II) to bipyridine is 1, the couple at 0.4 V is not observed, and when it is 3 or greater, the anodic peak at 0.90 V is absent. Thus, the first small anodic couple (0.4 V) is due to the oxidation of $Co^{II}(bpy)_3^{2+}$ and the second 0.90 V) to the oxidation of $Co^{II}(bpy)_2^{2+}$.

In the presence of dioxygen, the $Co(bpy)_2^{2+}$ complex exhibits the same anodic voltammogram (potentials and height of the peaks) as in its absence. With an initial negative scan an irreversible reduction peak appears at −0.5 V prior to the reduction peaks for O_2 and $Co^{II}(bpy)_2^{2+}$. Reversal of the negative-voltage scan after this −0.5-V peak results in an anodic voltammogram without the peaks for free $Co^{II}(bpy)_2^{2+}$ and with a new peak at 1.4 V. Reversal of the positive scan at this point yields a reduction peak for $Co^{III}(OH)(bpy)_2^{2+}$ at 0.8 V [the same as in the absence of O_2 (Figure 1a)]. After the removal of dioxygen from the solution, the cyclic voltammograms are the same as before its introduction. Exactly the same behavior is observed when pyridine is used as a solvent. The height of the reduction peak for the $Co^{II}(bpy)_2^{2+}/O_2$ adduct as well as the height of the corresponding anodic peak decreases with time in acetonitrile and pyridine. The addition of 1 equiv of hydroxide ion (HO^-), phenoxide ion (PhO^-), triethylamine (Et_3N), pyridine (py), bicarbonate ($HOC(O)O^-$), or acetate ($MeC(O)O^-$) to $Co^{II}(bpy)_2^{2+}$ in acetonitrile causes an enhancement of the anodic peak current at 0.4 V and the disappearance of the second anodic peak at 0.95 V.

The UV–vis absorption spectrum for $Co^{II}(bpy)_2^{2+}$ in pyridine in the absence of O_2 exhibits a shoulder at 480 nm. Introduction of O_2 into the solution causes the appearance of a new absorption peak at 502 nm (Figure 2), which decays with time to give the original spectrum after about 2 h. The original spectrum is also observed after purging the O_2 from the solution with Ar. Similar changes occur in acetonitrile but are less distinctive.

The equilibrium constant of the $Co^{II}(bpy)_2^{2+}/O_2$ adduct in MeCN has been determined via UV–visible measurements of different concentrations of $Co(bpy)_2^{2+}$(B) (1, 8, 16, and 100 mM) in the presence of the various bases [B = py, Et_3N, $MeC(O)O^-$, $HOC(O)O^-$, PhO^-, and HO^-]. For each solution the UV spectrum has been measured (a) in the presence of argon, (b) after saturation of the solution with air (21% atm), and (c) after saturation with O_2 (1 atm). The results indicate that the $Co^{II}(bpy)_2^{2+}/O_2$

---

(41) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley-Interscience: New York, 1974; p. 199.

(42) *Handbook of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic Press: New York, 1963; pp 140–142.

(43) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; MacMillan: New York, 1969; p 854.

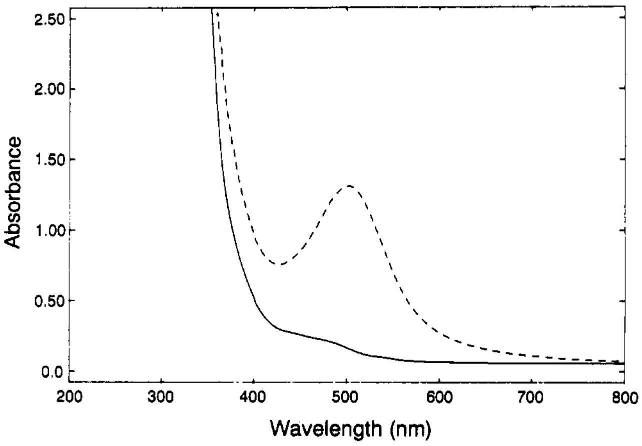


Figure 2. UV-visible spectrum of 3 mM $Co(bpy)_2^{2+}$ in pyirdine; (—), in the absence of dioxygen, and (- - -), in the presence of O_2 (5.1 mM, 1 atm) (1-cm cell path).

Table I. $Co^{II}(bpy)_2^{2+}$-Induced (16 mM) Activation of O_2 (1 atm, 8.1 mM) and HOOH (200 mM) in Acetonitrile for the Dehydrogenation of *N*-Methylanilines

substrate (1 M)	products (mM) (±10%) with O_2, 24-h reaction time	products (mM) (±10%) with HOOH, 12-h reaction time
$PhNH_2$	no products	no products
$PhNHCH_3$	$PhNH_2$ (16)	$PhNH_2$ (13), $PhN(CH_3)[CH(O)]$ (16)
PhNHPh	no products	no products
$PhN(CH_3)_2$	$PhNHCH_3$ (64), 4,4′-$[(CH_3)_2NPh]_2CH_2$ (34)	$PhNHCH_3$ (14), 4,4′-$[(CH_3)_2NPh]_2CH_2$ (15), $PhN(CH_3)[CH(O)]$ (31)

Table II. Activation of Dioxygen by $[(bpy)_2Co^{II}(B)]^{2+}$ for the Dehydrogenation (Oxidation) of Primary Alcohols and Aldehydes in Acetonitrile

A. $PhCH_2OH$ (1 M), $[(bpy)_2^{2+}Co^{II}(B)]$ (8 mM), O_2 (1 atm, 8 mM), 25 °C

	PhCH(O) product yields (mM) (±10%)				
base (8 mM)	1 h	4 h	10 h	50 h	pK_a of the base[a]
solvent (MeCN)	<1	<1	1	5	
HO^-	13	32	39	57	30.4
PhO^-		19	36	64	16.0
$HOC(O)O^-$	19	30	61	97	14[b]
$MeC(O)O^-$	1	2	4	9	8[b]
Et_3N	12	12	36	46	10
Py	<1	1	2	7	1.8

B. O_2 (1 atm, 8 mM), 25 °C

		product yields (mM) (±10%)			
substrate (1 M)	$[(bpy)_2^+Co^{II}(OH)]$ (mM)	1 h	4 h	9 h	22 h
(1) $RCH_2OH \rightarrow RCH(O)$					
$PhCH_2OH$	8	13	32	39	53
$PhCH_2OH$	16	21	50	59	91
$PhCH_2OH$	200	75	166	242	311
$PhCH_2OMe$	16		3		14
$PhCH_2OH$ (60 °C)	200	324	623	764	869
n-$C_6H_{13}OH$ (60 °C)	200	3	5	6	6
n-$C_6H_{13}OH$	16	<1	1	2	4
n-$C_6H_{13}OH$	200	4	4	5	5
(2) $RCH(O) \rightarrow RC(O)OH$					
PhCH(O)	16	562	887	953	982
n-$C_5H_{11}CH(O)$	16	459	755	892	974

[a] Reference 46. [b] Estimated by comparison with PhC(O)OH.

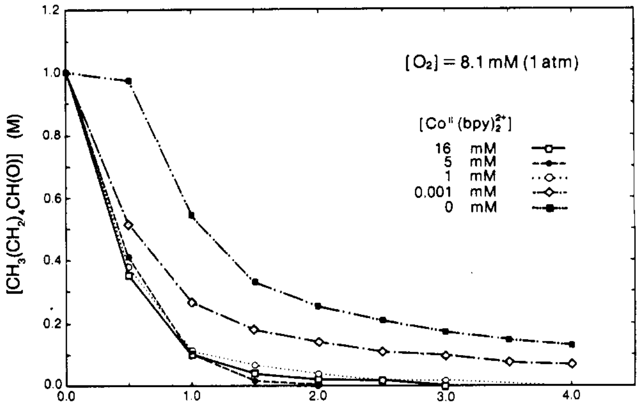


Figure 3. Decay of $CH_3(CH_2)_4CH(O)$ concentration via its Co^{II}-$(bpy)_2^{2+}$-induced autoxidation by O_2 to $CH_3(CH_2)C(O)OH$ in MeCN.

adduct (complex) has (a) a stoichiometry of 2:1 [probably $(bpy)_2^{2+}(B)Co^{III}OOCo^{III}(B)(bpy)_2^{2+}$] and (b) an approximate value for its formation constant (K_f) of 0.7 ± 0.3 mM^{-2} [the values for each of the bases (B) fall within the limits].

Reactivity of the $Co^{II}(bpy)_2^{2+}/O_2$ Adduct with Organic Substrates. The $Co^{II}(bpy)_2^{2+}/O_2$ complex (in the absence and the presence of a base) does not react with hydrocarbons [cyclohexane (c-C_6H_{12}), cyclohexane (c-C_6H_{10}), benzene (PhH), toluene ($PhCH_3$), ethylbenzene ($PhCH_2CH_3$), and 2-methylbutane (Me_2CHCH_2Me)]. Even 1,4-cyclohexadiene (1,4-CHD) (C-H bond energy, ΔH_{DBE} = 73 kcal mol^{-1})[44] remains unchanged in the reaction mixture after 72 h.

The addition of $Co^{II}(bpy)_2^{2+}$ to O_2-saturated (8.1 mM)[45] solutions of *N*-methylanilines catalyzes their dehydrogenation to give formaldehyde and the demethylated aniline (Table I). The reaction is first-order with respect to the concentrations of catalyst, O_2, and substrate. When HOOH is used as the oxidant, *N*-methyl amides are also present among the products.

In the presence of a base, $Co^{II}(bpy)_2^{2+}$ activates O_2 for the catalytic dehydrogenation of benzyl alcohol ($PhCH_2OH$). The results are summarized in Table II, which also includes the pK_a values for the various bases. Again, the reaction rate is first-order with respect to the concentrations of $Co^{II}(bpy)_2^{2+}$, O_2, and substrate. n-Hexanol (n-$C_6H_{13}OH$) reacts much more slowly than benzyl alcohol (Table IIB). The PhCH(O) from the oxidation of excess benzyl alcohol is unreactive because the $PhCH_2OH$ substrate is a stronger nucleophile.

The addition of trace levels (>10^{-6} M) of bis(bipyridine)cobalt(II) to O_2-saturated solutions of aldehydes in acetonitrile initiates their rapid autoxidation to carboxylic acids. Figure 3 illustrates the $Co^{II}(bpy)_2^{2+}$-induced autoxidation of hexanal $[CH_3(CH_2)_4CH(O)]$ for O_2-saturated acetonitrile. The same types of concentration profiles are observed for air-saturated solutions of $CH_3(CH_2)_4CH(O)$ and for O_2- and air-saturated solutions of PhCH(O). The initial reaction rates are first-order in catalyst, substrate, and O_2 concentrations. However, within 1 h the autoxidation process is almost independent of catalyst concentrations. Although the $Fe^{II}(bpy)_2^{2+}$ and $Mn^{II}(bpy)_2^{2+}$ complexes also induce the autoxidation of aldehydes, they are much less effective initiators and the propagation dynamics are much slower. The oxidation of benzaldehyde depends on the ratio of the concentrations of the substrate and catalyst. The reaction occurs if the ratio is greater than about 20.

Discussion and Conclusions

The electrochemical and spectroscopic results indicate that $Co^{II}(bpy)_2^{2+}$ interacts with base (B) and O_2 to form a 2:1 complex:

$$2Co^{II}(bpy)_2^{2+} + 2B + O_2 \rightleftarrows (bpy)_2^{2+}(B)Co^{III}OOCo^{III}(B)(bpy)_2^{2+}\ \mathbf{(1)} \qquad (1)$$

$$(K_f)_{py} = 0.7 \pm 0.3\ mM^{-2}\ \text{(pyridine solvent)}$$

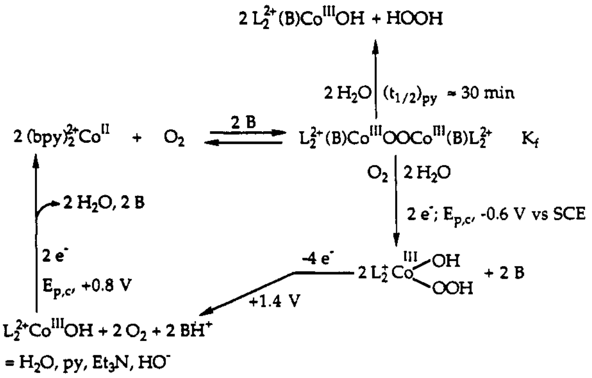
---

[44] *CRC Handbook of Chemistry and Physics* 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990; p 9-85.

[45] Sawyer, D. T.; Chiericato, G., Jr.; Angelis, C. T., Jr.; Tsuchiya, T. *Anal. Chem.* **1982**, *54*, 1720.

[46] Barrette, W. C., Jr.; Johnson, H. W., Jr.; Sawyer, D. T. *Anal. Chem.* **1984**, *56*, 1980.

Scheme I. Redox and Hydrolysis Reactions for the $(bpy)_2^{2+}Co^{II}(B)/O_2$ System



which is in accord with numerous other cobalt complexes with nitrogen-based ligands.[47-53] The constant, K_f, has been evaluated from the spectroscopic data.[54] In aqueous solutions, $Co^{II}(bpy)_2^{2+}$ combines with O_2 to form dibridged μ-peroxo-μ-hydroxo complexes.[55]

Although the μ-dioxygen complex (**1**) is reversibly formed, on the basis of the electrochemical and spectroscopic measurements it decomposes to $Co^{III}(OH)(bpy)_2^{2+}$ and HOOH within about 2 h. Again, this is consistent with previous studies of binuclear μ-dioxygen cobalt complexes[56-58] and with electrochemical studies of cobalt/dioxygen complexes in various base-containing aprotic solvents (MeCN, py, DMF, and Me_2SO).[59] Invariably the cobalt/dioxygen adducts decompose to $L_2Co^{III}OH$ and HOOH at rates that are dependent upon the basicity of the ligand/solvent matrix and the amount of residual water. Scheme I outlines a set of self-consistent pathways for the redox chemistry and hydrolysis of the $(bpy)_2Co^{II}(B)/O_2$ adduct (**1**).

The absence of any activation by $(bpy)_2^{2+}(B)Co^{II}$ for the oxidation of 1,4-CHD by dioxygen indicates that **1** and the probable $[(bpy)_2^{2+}(B)Co^{III}OO^{\bullet}]$ intermediate are unable to abstract even weakly bonded hydrogen atoms (ΔH_{DBE} for the C–H bond in 1,4-CHD is 73 kcal mol^{-1}).[44] In contrast, the oxidation of *N*-methylanilines (ΔH_{DBE} for the C–H and N–H bonds is about 90–95 kcal mol^{-1}) appears to occur by the removal of two hydrogen atoms in a single step. The first-order dependence of the reaction rate with respect to the catalyst, O_2, and substrate concentrations is consistent with substrate binding to $Co^{II}(bpy)_2^{2+}$ in an initial reversible step, which is followed by the formation of the μ-dioxygen reaction complex. The latter facilitates the almost concerted removal of two hydrogen atoms from each bound substrate to form water molecules and demethylated aniline.

$$2L_2^{2+}Co^{II} + O_2 + 2B \rightleftharpoons L_2^{+}(B^{+})Co^{II}OOCo^{III}(B^{+})L_2^{+}\ (\mathbf{1}) \qquad (2)$$

B = substrate; e.g., $PhN(CH_3)_2$

$$\downarrow$$

$$2PhNHCH_3 + 2L_2^{2+}Co^{II} + 2H_2O + 2H_2C(O)$$

The lack of reactivity for aniline ($PhNH_2$) and *N*-phenylaniline (PhNHPh) is consistent with this proposition. However, the secondary product from *N,N*-dimethylaniline indicates an alternative dehydrogenation pathway (Table I).

Although the base-induced formation of HOOH is possible in the *N*-methylaniline system (Scheme I), the generation of HOOH is a stoichiometric process that also produces $(bpy)_2^{2+}Co^{III}OH$. Thus, for such a path the concentration of the product would be less than one-half of the $Co^{II}(bpy)_2^{2+}$ concentration. Clearly, the product yields for $PhN(CH_3)_2$ are greatly in excess of the catalyst concentration (Table I) and must result from a process that is similar to that of eq 2, with the anilines acting as bases in the formation of **1**. If the adjacent C–H bonds of the substrate molecule (B) are sufficiently weak, then they are removed to give the observed products.

In contrast to anilines, alcohols are not basic enough to coordinate with $Co^{II}(bpy)_2^{2+}$ and thereby induce the formation of species **1**. However, the combination of HO^- [and other strong bases (Table II)] with the alcohol leads to its nucleophilic addition to the metal center.

$$Co^{II}(bpy)_2^{2+} + ROH + HO^- \rightarrow (bpy)_2^{+}Co^{II}(OR) + H_2O \quad (3)$$

The latter in turn reacts with O_2 to form species **1** (with RO^- the base, B). In the case of benzyl alcohol ($PhCH_2OH$), the α-C–H bonds are sufficiently weak ($\Delta H_{DBE} \approx 85$ kcal mol^{-1}) such that one is removed by the μ-dioxygen of species **1** followed by a rebound to give $PhCH(OH)_2/PhCH(O)$, H_2O. The difference in the α-C–H bond energy in $PhCH_2OH$ and $CH_3(CH_2)_4CH_2OH$ (85 vs 94 kcal mol^{-1})[44] accounts for the limited reactivity of the latter (Table II).

Although $Co^{II}(bpy)_2^{2+}$ does not activate O_2 for the oxidation of 1,4-cyclohexadiene (1,4-CHD) (ΔH_{DBE} = 73 kcal mol^{-1}), it initiates the autoxidation of benzaldehydes (ΔH_{DBE} = 87 kcal mol^{-1}).[44] This indicates that neither species **1** (Scheme I) nor its precursor $[(bpy)_2^{2+}(B)Co^{III}OO^{\bullet}]$ has sufficient radical character to abstract a hydrogen atom from 1,4-CHD. However, the system is able to produce sufficient $PhC(O)OO^{\bullet}$ radical from PhCH(O) to initiate its autoxidation. Because the autoxidation rates are independent of the catalyst concentration (Figure 3), the chain must be carried by the $R\dot{C}(O)$ and $RC(O)OO^{\bullet}$ radicals.[60-62] Clearly, given the respective bond energies, this must occur via an inner-sphere process within a PhCH(O) adduct of $Co^{II}(bpy)_2^{2+}$ (probably via the geminal diol of the aldehyde).[63,64] Because only trace levels of $Co^{II}(bpy)_2^{2+}$ are necessary for the initiation process (Figure 3), the reactive intermediate must be a 1:1:1 adduct [e.g., $(bpy)_2^{+}[PhCH(OH)O]Co^{III}OO^{\bullet}$] that yields $PhC(O)OO^{\bullet}$.

In summary, the base-induced binding of O_2 by $Co^{II}(bpy)_2^{2+}$ to form species **1** (Scheme I) is the basis for the oxidation (dehydrogenation) and oxygenation of susceptible basic substrates (substituted anilines and alkoxides). Likewise, the geminal diol form of aldehydes can serve as the base to induce formation with O_2 of an adduct to form $RC(O)OO^{\bullet}$ and thereby initiate their autoxidation.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-9106742 and the state of Texas under the Texas Advanced Research Program.

Registry No. $Co^{II}(bpy)_2(ClO_4)_2$, 78624-86-9; O_2, 7782-44-7; HOOH, 7722-84-1; $PhNHCH_3$, 100-61-8; $PhN(CH_3)_2$, 121-69-7; PhCH(O), 100-52-7; $PhCH_2OH$, 100-51-6; $PhCH_2OMe$, 538-86-3; n-$C_6H_{13}OH$, 111-27-3; n-$C_5H_{11}CH(O)$, 66-25-1; $PhNH_2$, 62-53-3; PhNHPh, 122-39-4; $PhN(CH_3)[CH(O)]$, 93-61-8; 4,4′-$[(CH_3)_2NPh]_2CH_2$, 101-61-1; $PhCO_2H$, 65-85-0; n-$C_5H_{11}CO_2H$, 142-62-1; HO^-, 14280-30-9; PhO^-, 3229-70-7; $HOC(O)O^-$, 71-52-3; $MeC(O)O^-$, 71-50-1; Et_3N, 121-44-8; py, 110-86-1.

---

(47) McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1.

(48) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(49) Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353.

(50) Drago, R. S.; Corden, B. B.; Zombeck, A. *Comments Inorg. Chem.* **1981**, *1*, 53.

(51) Martell, A. E. *Acc. Chem. Res.* **1982**, *15*, 155.

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

(53) Martell, A. E. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1988; p 87.

(54) Marzilli, L. G.; Marzilli, P. A.; Halpern, J. *J. Am. Chem. Soc.* **1971**, *93*, 1374.

(55) Bogucki, R. F.; McLendon, G.; Martell, A. E. *J. Am. Chem. Soc.* **1976**, *98*, 3202.

(56) Pignatello, J. J.; Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 5930.

(57) Ebihara, M.; Sasaki, Y.; Saito, K. *Inorg. Chem.* **1985**, *24*, 3831.

(58) Kikkawa, M.; Sasaki, Y.; Kawata, S.; Hatakeyama, Y.; Ueno, F. B.; Saito, K. *Inorg. Chem.* **1985**, *24*, 4096.

(59) Sobkowiak, *A*.; Sawyer, D. T. *Inorg. Chem.*, in press.

(60) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985.

(61) McNesby, J. R.; Heller, C. A., Jr. *Chem. Res.* **1954**, *54*, 325.

(62) Maslov, S. A.; Blyumberg, E. A. *Russ. Chem. Rev.* **1976**, *45*, 155 (*Usp. Khim.* **1976**, *45*, 303).

(63) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 183.

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