

Determination of 1-Hexene Isomerization. 1-Hexene and *cis*- and *trans*-2-hexene were identified by GLC with a 3-m, 1/8 in. o.d. stainless-steel column prepacked with 0.2% Carbowax on carbopack. A column temperature of 130 °C was used.

Catalytic Oxidations with H₂O₂. The experimental procedure used for these oxidations was as follows, using experiment 3 as a specific example: a solution of 0.0336 g of RhCl₃·3H₂O (0.128 mmol), 4.00 mL of ethanol, and 0.14 mmol of 2-heptanone or 2-octanone (GLC internal standard) was purged for 60 min with argon and heated to 40 °C for 7 min, and

0.63 mL of 0.63 M H₂O₂ (diluted in ethanol from aqueous 5 M H₂O₂) (0.398 mmol of H₂O₂) was added. This was immediately followed by the addition of 1.30 mL of alumina purged 1-hexene to initiate reaction.

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Registry No. RhCl₃, 10049-07-7; Cu, 15158-11-9; 1-hexene, 592-41-6.

Steric and Electronic Effects of Ligand Variation on Cobalt Dioxygen Catalysts

Barry B. Corden,[†] Russell S. Drago,*[‡] and Richard P. Perito[†]

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611, and the Department of Chemistry, Fred Stark Pearson Laboratory, Tufts University, Medford, Massachusetts 02155. Received March 5, 1984

Abstract: We report herein the observation that electronic and steric factors of cobalt dioxygen complexes with systematically derivatized pentadentate Schiff-base ligands affect their ability to catalyze the oxidation of substituted phenols and alter the rate of catalyst decomposition. The electronic and steric factors can be separated sufficiently to indicate that the activity of the cobalt dioxygen catalyst roughly parallels the trends in basicity of the bound O₂ suggested by EPR cobalt hyperfine coupling constants of the adducts and predicted from the electronic effects of substituents.

In recent work from this laboratory^{1,2} a spin-pairing (radical coupling) model has been proposed to account for the binding of O₂ to transition-metal complexes. One of the unique aspects of this model is the relationship of the negative charge on the bound O₂ (expressed as electron transfer) to the ligand field strength of the groups coordinated to cobalt(II). Interpretation of the EPR spectra of various Co-O₂ adducts indicates¹ a very substantial variation in the extent of electron transfer leading to semiquantitative estimates of 0.1 to 0.8 fractional negative charge on the bound O₂. These differences should lead to variations in the basicity,³ nucleophilicity, and radical reactivity of the coordinated O₂. Such variations should have significant implications for understanding the catalysis of certain biological^{4a-d} and industrial oxidations.^{4e-g}

The design of a system to probe variation in the reactivity of a bound O₂ is complicated. The metal-bound O₂ must be implicated in the reaction mechanism, and variation in its electronic properties must influence the rate or product distribution. One candidate for study involves the fairly well understood⁵⁻⁷ catalytic oxidation of 2,6-disubstituted phenols to the corresponding quinones by cobalt(II) Schiff base complexes. A recent study⁷ of the kinetics and mechanism of the oxidation of 2,6-dimethylphenol (DMP) by CoSMDPT (Figure 1) in the presence of molecular oxygen indicates that the active catalyst plays a role in two different steps in the reaction: first in initiating the reaction through hydrogen atom abstraction to form the phenoxy radical and then in the rate-determining step where the phenoxy radical combines with the cobalt-dioxygen complex which decomposes quickly to the quinone. This scheme is summarized in Figure 1.

The kinetic rate law determined for the oxidation of DMP by CoSMDPT in toluene at 25 °C with this mechanism is consistent and is given in eq 1. The value of k_T is $2.1 \times 10^{-3} \text{ (M}^2 \text{ s)}^{-1}$ if

$$d[\text{BQ}]/dt = k_T[\text{Co}][\text{O}_2][\text{DMP}] \quad (1)$$

it is assumed that the catalyst is completely oxygenated, and no

catalyst is decomposed during the period of initial rate data accumulation. Materials such as 2,2,2-trifluoroethanol that are more effective at hydrogen bonding to the bound O₂ than DMP inhibit the reaction. The phenoxy radicals couple to produce diphenoxyquinone via step e when step d is slowed, for example, by decreasing the cobalt-O₂ concentration.

In addition to reactivity trends, the influence of ligand variation on catalyst stability may provide insight into the nature of its decomposition. The CoSMDPT oxidation of DMP undergoes about 70 turnovers and slowly dies thereafter. Addition of a base (Na₂CO₃) slows the catalyst decomposition by about fourfold. The oxygen content of the spent catalyst is elevated to a 6:1 O/Co ratio compared to the 2:1 ratio present in the original catalyst, CoSMDPT.⁷ It is proposed that hydrogen peroxide formed from decomposition of HO₂ in step d oxidizes and cleaves the ligand leading to carboxylic acids.

According to the proposed mechanism,⁷ the metal complex plays two important roles in the catalysis of the oxidation: (1) coordination activates the O₂ molecule and enhances its basicity and

(1) Tovrog, B. S.; Kitko, D. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 5144.

(2) Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353 and references therein.

(3) Drago, R. S.; Cannady, J. P.; Leslie, K. A. *J. Am. Chem. Soc.* **1980**, *102*, 6014.

(4) (a) Eichhorn, G. L., Ed. "Inorganic Biochemistry"; Elsevier Scientific: New York, NY, 1973. (b) Ochiai, E. "Bioinorganic Chemistry"; Allyn and Bacon: Boston, MA 1977. (c) Spiro, T. G., Ed. "Metal Ion Activation of Dioxygen"; Wiley: New York, NY 1980. (d) Musso, H. "Oxidative Coupling of Phenols"; Taylor, W. I., Pattersby, A. R., Eds.; Marcel Dekker: New York, NY 1967. (e) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272. (f) Benson, D. "Mechanisms of Oxidations by Metal Ions"; Elsevier Scientific: New York, NY 1976. (g) Nishinaga, A. "Fundamental Research in Homogeneous Catalysis"; Ishi, Y., Tsutsui, M., Eds.; Plenum Press: New York, NY, 1978.

(5) (a) Nishinaga, A.; Tomia, H. *J. Mol. Catal.* **1980**, *7*, 179. (b) Hay, A. S. *J. Polym. Sci.* **1962**, *58*, 581.

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

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

[†]Tufts University.

[‡]University of Florida.

Table I. Elemental Analysis of Cobalt Complexes

complex ^a	found				calculated			
	C	H	N	M	C	H	N	M
Co(X-SMDPT)								
H	61.33	6.09	10.55	14.81	61.46	6.14	10.24	14.36
3MeO	58.36	6.28	8.87	12.19	58.72	6.21	8.13	12.53
4MeO ^b	57.52	6.34	9.12	12.29	57.62	6.31	8.76	12.29
5MeO ^b	58.32	6.41	8.91	12.27	57.62	6.31	8.76	12.29
4,6-(MeO) ₂	56.02	6.21	7.81	11.03	56.60	6.27	7.92	11.11
3EtO	60.26	6.46	8.27	12.07	60.24	6.67	8.43	11.82
5Br ^d	44.32	3.90	7.38	10.35	44.39	4.08	7.40	10.37
3,5-Br ₂ ^d	35.18	2.48	5.52	8.12	34.74	2.92	5.79	8.12
4OH ^e	56.18	5.87	8.49	12.39	56.18	5.81	9.32	13.06
4N(Et) ₂ ^b	61.21	8.07	12.12	9.93	61.04	7.95	12.27	10.38
5NO ₂	51.13	4.64	13.98	11.38	50.41	4.63	14.00	11.78
3,5- <i>t</i> -Bu	67.99	9.07	6.90	9.29	67.55	9.79	7.16	10.04
Co(X-SDAPE)								
H	59.51	5.49	6.98		60.46	5.58	7.05	14.83
5OMe	57.56	5.57	6.41		57.77	5.73	6.12	12.88
5Br ^c	43.67	3.43	5.01		43.27	3.63	5.05	10.62
CoSDAPPS	58.54	6.51	6.39	13.08	59.03	5.90	6.56	13.79
Co(5NO ₂ SDAES) ^e	43.90	4.42	9.91	11.02	44.53	4.48	10.39	10.93
Co(X-SDPT)								
H ^b	56.17	5.48	10.54	13.85	56.77	6.19	9.93	13.93
3MeO ^b	52.61	6.09	8.37	11.84	52.70	6.43	8.38	11.75
5NO ₂ ^b	47.40	4.33	13.32	11.78	47.63	4.60	13.89	11.68

^a Refer to Figure 2 for these abbreviations. ^b Water(s) of hydration. ^c 5Br is 29.67% Br found, 33.09% calcd; 3,5-Br₂ is 44.75% found, 49.88% calcd. ^d Br found is 27.61, 40.97, 29.27 and calcd 28.13, 40.97, 28.79 for 5BrSMDPT, 3-5Br₂SMDPT, and 5BrSDAPE, respectively. ^e This compound is abbreviated as Co(NSDAES) in this study.

PROPOSED MECHANISM

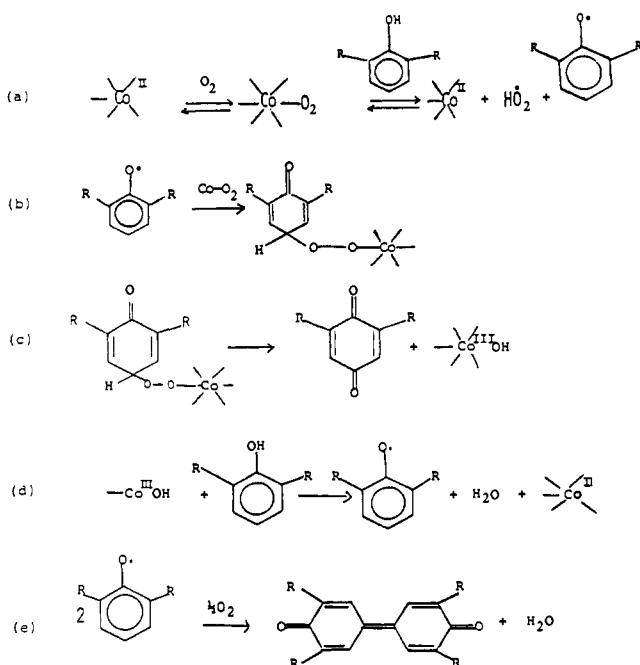


Figure 1. Proposed mechanism for the oxidation of 2,6-disubstituted phenols by cobalt dioxxygen catalysts.

ability to abstract hydrogen atoms; (2) coordination enhances the activity of the O₂ molecule in a free radical reaction with organic radicals. Initial rate variation and product distribution afford the means of determining the influence of ligand variation on bound O₂ reactivity.

Experimental Section

General. The EPR spectra were collected on a Varian Model E-9 spectrometer equipped with a Hewlett-Packard frequency counter. NMR spectra were obtained on a Varian 390 or an HR-220 MHz spectrometer. All elemental analyses were performed by the Microanalytical Laboratory at the University of Illinois (see Table I).

Kinetic Studies. The reaction progress was monitored by following O₂ consumption by using a gas buret filled with mercury fitted with a toluene

manometer connected to the buret as described previously.⁸

Oxidations performed at elevated pressures were conducted in a Parr pressure bottle (A. H. Thomas Co.) fitted with a pressure gauge and placed in a temperature-controlled oil bath. Typically, a 250-mL pressure bottle was charged with a 50-mL solution of the phenol (concentrations given in the text) and magnetic stir bar. The solid cobalt catalyst is floated on the solution in a plastic cap and the system purged several times with O₂ and then allowed to equilibrate at the appropriate temperature and pressure for 30 min. The reaction begins by stirring the solution and spilling the solid catalyst into the reaction medium. All reactions are stirred sufficiently to ensure that mass transfer of dioxygen in the solvent is not rate limiting. The O₂ consumption is found to correlate with product formation. Reported rates, reproducible to within 5%, are taken from the maximum slope of the oxygen uptake curve. A temperature-controlled oil bath maintained the reaction within ± 1.0 °C of the reported temperature.

Sampling of the reaction mixture in progress is accomplished through a modification of the high-pressure gas uptake apparatus that allows for the removal of the reaction mixture while under pressure. A rubber septum is attached to a three-way valve fitted directly above the pressure bottle. A luer-lock syringe with an 18 in. hypodermic needle is inserted into the reaction mixture, passing through the septum. Up to 1.0 mL of solution can be removed with negligible loss, less than 0.5 psi, of pressure.

The substrate and products of the 2,6-di-*tert*-butylphenol oxidation are analyzed conveniently by NMR integration of the *tert*-butyl resonances.^{9,10} A copious amount of CHCl₃ is added to the completed reaction mixture to ensure all products are in solution. The NMR measurements were performed within 1 h of the end of the reaction. The spent catalyst continues to produce phenoxy radicals, hence the coupled quinone, in air at STP at a slow rate.

When the spent reaction mixture of a bromo-substituted catalyst was extracted with water and titrated with silver nitrate, no AgBr precipitate was detected, indicating that bromide ion is not responsible for the observed catalysis.

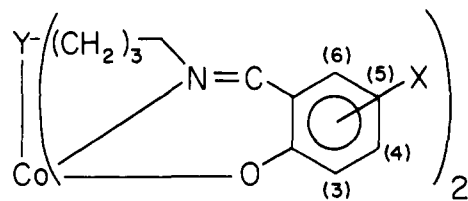
Purification of Materials. Specialty gases were obtained from Linde, Depke, or Matheson. All gases were passed through a drying column containing aqua-sorb, molecular 4 Å sieves (Linde) and Drierite unless used at high pressure. Solvents were purified according to standard procedure,¹¹ stored under molecular sieves, and freeze-pumped-thawed for four cycles prior to use.

(8) Drago, R. S.; Gaul, J. H.; Zombeck, Z.; Straub, D. *J. Am. Chem. Soc.* **1980**, *102*, 1033.

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

(10) Nishinaga, A.; Watanabe, K.; Matsuura, T. *Tetrahedron Lett.* **1974**, *14*, 1291.

(11) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, NY, 1974.



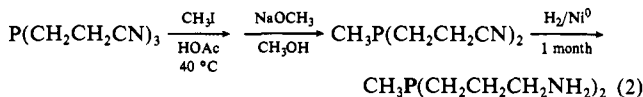
Co (SDAPE)	Y = O
Co (SMDPT)	Y = NCH ₃
Co (SDPT)	Y = NH
Co (SDAES)	Y = S
Co (SDAPPS)	Y = PCH ₃

Figure 2. Diagram of cobalt complexes used in this study.

All derivatized phenols as well as solid, unstabilized C₆H₅OH were purchased from Aldrich. All salicylaldehyde derivatives were obtained from Aldrich. Solids were used without further purification and liquids distilled prior to use. BF₃-THF (Aldrich) solution was refrigerated and used without further purification, and pyrophoric Raney Nickel catalyst was obtained as a gift from W. R. Grace.

Preparation of Ligands. The ligands X(CH₂CH₂CH₂NH₂)₂ were obtained in the following manner. Where X = NCH₃ (MeDPT) or NH (DPT), the ligands were purchased from Aldrich. Where X = O (DAPE) or S (DEAS), the ligands are obtained as the dicyano precursor (K&K or Pitzer.) The dicyano ether ligand is reduced to prepare the DAPE ligand by hydrogenation over a Raney Nickel catalyst at room temperature for 1 month according to the procedure of Israel et al.¹² Monitoring the 2000–2500 cm⁻¹ region in the IR indicates the extent of conversion to the diamine. This material can be used as the free base and need not be converted to the hydrochloride salt. The (DAES) ligand is prepared by reducing the dicyano precursor with a BF₃-THF complex.

The X = PCH₃ (DAPPS) can be synthesized by converting P(CH₂-CH₂CN)₃ according to eq 2. The first two steps proceed at greater than



90% overall yield to form a white powder, bis(2-cyanoethyl)methylphosphine.^{12a,b} The reduction to form the diamine is very sluggish at room temperature, and only 85% of the original cyano precursor is converted. The resultant mixture can be separated chromatographically on silica gel. The (X-SDAPPS) complex may be prepared by addition of CH₃P(CH₂CH₂CH₂NH₂)₂ to the appropriate Co(X-salen) complex in refluxing deoxygenated THF.¹⁴

Preparation of Cobalt Complexes. The cobalt complexes synthesized are listed in Table I and shown in Figure 2. The complexes Co(X-salen), Co(X-SMDPT), and Co(X-SDPT) (X = H, alkyl, halide, NO₂) were prepared according to the method of Bailes and Calvin^{12c} with the following modifications. The Schiff-base complexes require the combination of a 2:1 ratio of the appropriate salicylaldehyde derivative with the appropriate diamine in an ethanol solution. The ligand forms rapidly and is refluxed for 1 h in a deoxygenated solution prior to the addition of a stoichiometric amount of the metal acetate dissolved in a minimal amount of deoxygenated water. The solution is refluxed for 2 h, cooled to room temperature, filtered, and washed with cold, deoxygenated 1:1 hexane/absolute ethanol. The solid is dried in vacuo for 12 h prior to exposure to air. The yield in many of these reactions depends on the deprotonation of the Schiff-base which is facilitated by adding 0.5 g of KOH to 50 mL of the ethanolic solution of the ligand. The Co(X-SMDPT) complexes where X = OH, OC₂H₅, OCH₃, and N(C₂H₅)₂ were prepared in a basic medium. The SDPT ligand, however, has an acidic proton and is not base stable.

(12) (a) Isreal, M.; Rosenfield, J. S.; Modest, E. J. *J. Med. Chem.* **1964**, *m*, 710. (b) Niswander, R. H.; St. Clair, A. K.; Edmondson, S. R.; Taylor, L. T. *Inorg. Chem.* **1975**, *14*, 478. (c) Bailes, R. H.; Calvin, M. *J. Am. Chem. Soc.* **1947**, *69*, 1886.

(13) (a) Rauhut, A.; Hechenbleikner, I.; Currier, F. G.; Schaeffer, F. C.; Wyzrach, D. F. *J. Am. Chem. Soc.* **1959**, *81*, 1103. (b) Grayson, M.; Keough, P. T.; Johnson, G. A. *J. Am. Chem. Soc.* **1959**, *81*, 4803.

(14) Niswander, R. H.; Taylor, L. T. *Inorg. Chem.* **1976**, *15*, 2360.

Table II. Electron Transfer Numbers for Various Cobalt Dioxigen Complexes

complex	electron transfer (ET) ^b	complex	electron transfer (ET) ^b
Co(X-SMDPT)		Co(X-SDPT)	
H	0.5	H	0.4
3- <i>r</i> -Bu	0.5	3MeO	0.6
3MeO	0.7	5NO ₂	
4MeO	0.6	CoX-SDAPE	
5MeO	0.5	H	0.2
4,6-(MeO) ₂	0.5	OMe	0.3
5Br	0.4	Br	0.3
3,5-Br ₂	0.6	Co(DAPPS) ^a	~0.4
5NO ₂ ^a		Co(5NO ₂ SDAES) ^a	~0.6
4N(Et) ₂	0.5		

^a Poor spectral resolution; ET value has large uncertainty. ^b The procedure for calculating the electron transfer number from EPR hyperfine coupling constants is reported.¹

Table III. Oxidation of DMP by Cobalt Dioxigen Complexes^a

complex	initial rate ^b	turnovers ^c	τ _{1/2}	turnovers at τ _{1/2}
CoSMDPT ^f	3.5 × 10 ⁻²	98	210	58
Co(3- <i>r</i> -BuSMDPT)	3.6 × 10 ⁻³	94	150	46
Co(3,5-(<i>t</i> -Bu) ₂ SMDPT) ^f	3.5 × 10 ⁻³	65	240	32
Co(3MeOSMDPT)	9.3 × 10 ⁻³	117	145	41
Co(3EtOSMDPT) ^f	7.1 × 10 ⁻³	109	275	82
Co(5MeOSMDPT) ^f	2.7 × 10 ⁻³	81	465	41
Co(4,6-(MeO) ₂ SMDPT)	2.9 × 10 ⁻²	106	130	60
Co(5BrSMDPT)	3.7 × 10 ⁻³	92	360	65
Co(3,5-Br ₂ SMDPT) ^f	2.7 × 10 ⁻²	412	400	241
Co(3OHSMDPT) ^{d,e}	2.7 × 10 ⁻⁴	13		
Co(4OHSMDPT) ^e	no reaction			
Co(5NO ₂ SMDPT) ^{e,f}	1.4 × 10 ⁻⁴	34	700	19
Co(SDAPE)	2.4 × 10 ⁻⁴	14		
Co(SDPT)	4.3 × 10 ⁻³	91	120	71
Co(3MeOSDPT)	6.4 × 10 ⁻³	105	240	78
Co(5NO ₂ SDPT)	2.5 × 10 ⁻³	43	195	17
Co(NSDAES)	2.1 × 10 ⁻³	65		
Co(SDAPPS) ^e	8.1 × 10 ⁻⁴	6		

^a All reactions at room temperature, 75 psi initial O₂ pressure, 50 mL total volume of toluene solution, 0.1 g of catalyst, with 9.0 g of DMP. ^b Initial rate expressed as moles of O₂ consumed divided by moles of cobalt used per second. ^c After 20 h. Turnovers expressed as moles of O₂ observed divided by moles of cobalt used. ^d Induction period observed; rate measured after induction. ^e Catalyst is a slurry. ^f Reactions run in 50 mL of absolute MeOH, 75 psi initial O₂ pressure, 6.0 g of DMP at 25 °C, and 0.1 g of catalyst. For Co(X-SMDPT) complexes where X = H, 3,5-(*t*-Bu)₂, 3-EtO, 5-MeO, 3,5-Br₂, and 5-NO₂ the initial rates are 4.2, 9.2, 4.4, 3.0, 2.9, and 0.065 × 10⁻³ mol of O₂ consumed (per mol of cobalt), respectively. The turnovers are 31, 150, 56, 80, 63, and 4, respectively. The X = 5-NO₂ catalyst was not dissolved and exhibited a 250-min induction period after which the rate data were collected. τ_{1/2} (min) is defined as the time at which the reaction rate is half the initial rate.

EPR Spectra. Anisotropic EPR spectra were obtained in 1:1 toluene/dichloromethane glasses at 77 K. The *g* and *A* values were determined by computer simulation. Electron transfer into O₂ was calculated as described earlier.¹

Results

The cobalt(II) complexes used in this study exhibit characteristic cobalt dioxigen EPR spectra when examined as frozen solutions at 77 K. Electron transfer numbers¹ are presented in Table II. The results from oxidation of 2,6-dimethylphenol by a series of substituted tetradentate and pentadentate cobalt Schiff-base complexes in toluene or methanol solvent are reported in Table III.

The 2,6-dimethylphenol can be replaced by 2,6-di-*tert*-butylphenol (DtBP) without altering the salient features of the reaction while facilitating product analysis. The rate law for both substrates is first order in cobalt and dioxigen, and the reaction conditions were adjusted such that the rate is pseudo zero order in the phenol.

Table IV. Oxidation of 2,6-Di-*tert*-butylphenol by Cobalt Dioxxygen Complexes^a

substituent (X)	initial rate ^b	% DTBP ^c	% BQ ^c	turnovers ^d	$\tau_{1/2}$ ⁱ	turnover at $\tau_{1/2}$
Co(X-SMDPT)						
H	2.2×10^{-3}	<i>e</i>	100 ^e	(96 ^e)	330	46
H ^g	2.1×10^{-3}	57	43	167	700	85
3-MeO	2.4×10^{-3}	4	96	(110)	420	55
4-MeO	3.9×10^{-3}	<i>e</i>	100 ^e	(114 ^e)		
4-MeO ^g	3.0×10^{-3}	63	27	125	60	27
5-MeO	3.1×10^{-3}	11	87	99	260	48
4,6-(MeO) ₂	4.8×10^{-3}	<i>e</i>	100 ^e	(126 ^e)	185	37
4,6-(MeO) ₂ ^g	9.2×10^{-3}	72	28	143		
3,5-(<i>t</i> -Bu) ₂	1.9×10^{-3}	71 ^f	18 ^f	27	130	22
5-Br	9.6×10^{-3}	4	96	(144)	170	60
3,5-Br ₂	1.2×10^{-2}	<i>e</i>	100 ^e	(171 ^e)	130	93
3,5-Br ₂ ^g	1.1×10^{-2}	14	80 ^h	554		
5-NO ₂	2.9×10^{-4}	90	10	12		
4-diethylamino	5.4×10^{-3}	64	36	48	30	27

^a0.10 g of catalyst used, [DTBP] = 5×10^{-1} M at room temperature, $P_0 = 75$ psi of O₂, 50 mL total volume in toluene solution. ^bInitial rate expressed in moles of BQ formed per mole of Co per second. ^cConversion of DTBP to BQ based on NMR of reaction medium after 24 h. ^dTurnovers based on moles of BQ formed per mole of cobalt after 24 h. ^eTrace DTBP or BQ may not be detected by NMR if concentration is less than 3% due to width of *tert*-butyl resonances. Parentheses indicate that the turnover number is limited by exhausting the substrate. ^f11% DPQ was formed. ^gInitial [DTBP] = 2.0 M. ^h6% DPQ formed. ⁱ $\tau_{1/2}$ (min) is related to the half-life of the catalyst. It is the point where the reaction rate is half the initial rate.

The initial reaction rate, product distribution, and turnover number (moles of substrate consumed divided by the total number of moles of cobalt present, as indicated by the drop in oxygen pressure during the reaction for DMP or by oxygen pressure drop and NMR integration of reaction mixture resonances for the substrate DtBP) are listed in Table IV. The half-life ($\tau_{1/2}$) of the catalyst is defined as the time when the reaction rate drops to half the initial rate. The number of turnovers at this time is recorded.

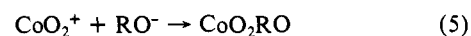
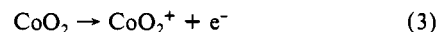
Discussion

Recent progress in our understanding of the nature of metal bound dioxygen indicates substantial variation in the extent of electron transfer from the metal into the coordinated O₂. Determining the effect of this variation in electron transfer on basicity and nucleophilicity is made difficult by the limited number and complex nature of the chemical reactions that have been shown to involve coordinated O₂. Accordingly, it was felt that the extensive work required to obtain precise rate constants would not provide any more relevant information than the following observations on systems that obey the rate law in eq 1: (a) the initial rate of O₂ consumption, (b) the ratio of BQ to DPQ, and (c) the number of catalyst turnovers. An increase in initial rate at constant BQ to DPQ ratio is evidence for enhanced radical generation and enhanced attack by the cobalt dioxygen catalyst on the phenoxy radical (i.e., an increase in the slow step b, Figure 1, of this proposed mechanism). A decrease in the ratio of BQ/DPQ without significant increase in the initial rate of oxygen uptake indicates decreased radical reactivity of CoO₂ with the phenoxy radical, while other combinations of O₂ uptake rate and BQ/DPQ ratio account for other observed changes in the reaction. In addition, by assuming that catalyst decomposition occurs by ligand oxidation some interesting observations regarding catalyst stability can be rationalized.

Of the systematic ligand variations employed in this study, altering the donor atoms about cobalt causes the most dramatic effect on the catalyst. Different donor atoms found at the central atom of the dipropylamino link of the Schiff-base ligand lead to a 100-fold variation in relative oxidation rates having a trend of NCH₃ > NH > S > PCH₃ > O. The ligands with only hydrogen substituents on the ring have initial rates of oxidation of 3.5×10^{-2} (NCH₃), 4.3×10^{-3} (NH), 2.1×10^{-3} (S), 8.1×10^{-4} (PCH₃), and 2.4×10^{-4} (O), respectively. The electron transfer values are 0.5 (NCH₃), 0.4 (NH), 0.4 (PCH₃), and 0.2 (O). Thus, we note increasing radical reactivity with increasing electron transfer onto O₂ in this series. The trend observed N > S > P > O indicates that both electron pair donation by a covalent donor and electrostatic interaction by a polar donor are important with the former making a larger contribution. This is consistent with quantitative studies of the binding of O₂ to a series of substituted porphyrins in which the axial base was varied. Covalency is more

important¹⁵ in binding of a base to Co-O₂ than to the analogous cobalt(II) complex.

Assuming that step b is the slow step, it is unclear why increasing negative charge on the bound O₂ should enhance the radical-coupling, rate-determining step when the bond formed has ^{δ+}C-O^{δ-} polarity. Radical coupling should have a low activation energy, and the energetic contributions can be summarized with the following thermodynamic cycle.



Increasing electron donation onto cobalt from the ligand favors step 3 but decreases the energetics of step 5. Step 3 is endothermic and step 5 exothermic. If the energy of step 3 were decreased more than the corresponding decrease in step 5 by more basic ligands, this would account for our observed trends. If step b is an equilibrium, as is the case when the hydrogen atom at the 4 position is replaced by an alkyl group, the resulting increase in steady-state concentration of the metalloperoxide would cause the rate to increase if step c were rate determining. Thus, increasing the negative charge on the bound O₂ merely parallels the expected stability in the metalloperoxide. Increasing the concentration of the peroxide increases the observed overall rate of the reaction by enhancing step c. Step c is preferred as the rate-determining step for it provides a consistent interpretation of all the available data.

Variation of the substituent on the phenyl ring leads to very minor variations in the rate of the reaction. Substituent variation at the 5 position (see Figure 2) yields expected results for group inductive effects in the oxidation of 2,6-di-*tert*-butylphenol: CH₃O > H > Br > NO₂. However, the electron transfer values in this series are 0.5, 0.5, and 0.4 which are all the same within experimental error. The results for the oxidation of dimethylphenol in methanol show no regular pattern with substituent change, indicating the existence of minor complicating solvation effects (Table III). Consequently, all of our conclusions regarding substituent effects will be drawn from the data in Table IV.

Substitutions in the 3 or the 4 position show nothing unusual leading again to very minor variations in the reaction rate. The most surprising result comes in the comparison of the 5-bromo with the 3,5-dibromo complexes. The initial rate of oxidation of both DMP and DTBP is greater for the latter derivative. This result correlates with a surprisingly larger value for the electron transfer into O₂ for this complex. Either a proper orientation of the C-Br dipole for the substituent in the three position¹⁶ (see

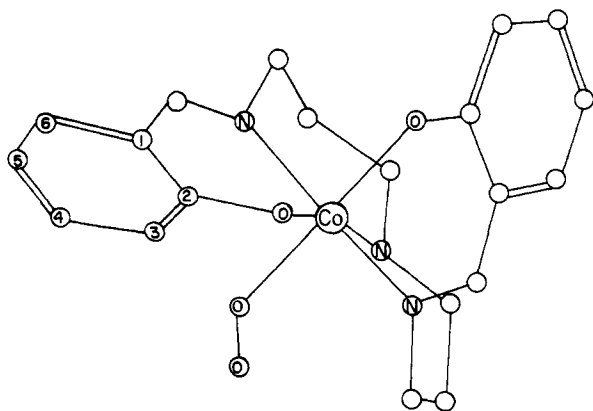


Figure 3. Proposed configuration of the cobalt dioxygen catalyst, CoSMDPT, based on the μ -peroxy dimer.^{16a}

Figure 3) or a geometric rearrangement^{16a,b} of the complex increases the binding of O₂ to the cobalt over that expected from the electron withdrawing substituent effect. Electron transfer and kinetic results from ligands with a *tert*-butyl group in the three positions suggest that the polar effect may be more significant.

The catalyst half-life ($\tau_{1/2}$) is obtained when the reaction rate has dropped to one-half of the initial rate. The number of turnovers recorded at the catalyst half-life ($\tau_{1/2}$) will be one-half of the total number of turnovers expected if the decomposition

(16) (a) Lindblom, L. A.; Schaefer, W. P.; Marsch, R. E. *Acta Crystallogr., Sect. B* 1971, 27B, 1461. (b) Cini, R.; Orioli, P. *J. Chem. Soc., Dalton Trans.* 1983, 2563. X-ray single-crystal studies on crystals of the μ -peroxy-dimer [$\text{CoSMDPT}_2\text{O}_2$] grown from either toluene^{16a} or benzene^{16b} solvent have resulted in two different isomers. Figure 2 represents the isomers found in ref 16b where the imine and phenolic donors are in the equatorial plane and the amine trans to the bound O₂, and Figure 3 represents the structure found in ref 16a. Clearly, both isomers may be present in solution, the relative amount determined by the solvent dielectric and the ring substituents.

pathway is first order in catalyst concentration. In most instances the number of turnovers recorded after 24 h (several half-lives) is significantly greater than expected for a first-order process. This indicates that decomposition due to dimerization of the cobalt complexes or hydrogen atom abstraction of the ligand by a proximal cobalt dioxygen complex could be contributing to catalyst degradation. Also, it has been shown that the product quinone can prevent decomposition of the catalyst presumably by serving as a trap for reactive species that may degrade the catalyst.⁷ The fact that high loading of the substrate phenol leads to an elevated number of turnovers and longer half-life suggests that the substrate itself is capable of protecting the catalyst, either by trapping small amounts of reactive products or by hydrogen bonding to the catalyst and blocking access to the cobalt complex. Finally, the catalyst stability does not manifest a meaningful trend in the SMDPT series. There is significant enhancement of stability for the 5-Br derivative.

The large number of turnovers attained with both the 4,6-dimethoxy and the 3,5-dibromo derivatives indicate that ring substitution stabilizes the catalyst. Attack of the ring by H₂O₂ can lead to ring cleavage and conversion to carboxylic acids. Thus, substituents leading to increased turnovers may block ring attack. The production of significant quantities of the coupled quinone with the *tert*-butyl-substituted CoSMDPT catalyst also suggests that the rate-determining step of the cobalt dioxygen attack on the phenoxy radical is becoming sterically restricted for these bulky substituents in the three position. The steric bulk of the *tert*-butyl groups is not great enough to prevent the initiation step involving the formation of the 2,6-di-*tert*-butyl phenoxy radical or its subsequent generation through the reduction of the cobalt catalyst (Figure 1, step d).

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Mechanistic Considerations in the Photodisproportionation of μ -Oxo-bis((tetraphenylporphinato)iron(III))

Mark W. Peterson, David S. Rivers, and Robert M. Richman*

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. Received September 20, 1984

Abstract: The photochemistry of μ -oxo-bis((tetraphenylporphinato)iron(III)) [(FeTPP)₂O] has been studied. Both continuous and flash photolysis establish a photochemical disproportionation to form the ferrous complex FeTPP and the ferryl complex FeOTTP. Using triphenylphosphine to trap the ferryl complex results in a net formation of FeTTP. This reaction is found to be intensity dependent at sufficiently high lamp intensities ($I_0 > 10^{-8}$ einstein), and these data have been computer fitted to the photodisproportionation mechanism. Olefins (cyclohexene and tetramethylethene) were found to react with the ferryl complex at high intensities to yield the ene-ol. Catalytic oxidation of cyclohexene was performed in the presence of dioxygen in sunlight to yield 2-cyclohexen-1-one with >1000 turnovers of the (FeTPP)₂O. There is no temperature dependence. The quantum yield increases with decreasing wavelength in the range λ 350–440 nm. This favors photochemistry from a highly distorted metal-to-metal charge-transfer state.

Several common elements emerge from a study of the most promising strategies for solar energy conversion. From semiconductor electrodes to photosynthesis, photon energy is initially converted to charge separation. Efficient mechanisms prevent immediate loss of this energy as heat in a back reaction. Whether by band bending¹ or subsequent electron transfer steps,² a small

amount of stored energy is sacrificed to further separate the charge pair. This charge can then do useful oxidation-reduction reactions. In solutions of synthetic compounds, epitomized by Ru(bpy)₃²⁺, exploitation utilizes these same elements.³ Photon energy is used to generate a charge-transfer excited state, and further separation of charge is achieved by bimolecular quenching which is fast with respect to back reaction. The oxidized and reduced species so generated are then capable of doing useful redox work. The search

(1) Wrighton, M. S.; Kaiser, S. W. *Adv. Chem. Ser.* 1977, 163, 71.

(2) Bolton, J. R. "Solar Energy: Chemical Conversion and Storage;" R. R. Hautala, R. B. King, and C. Kutal, Ed.; Humana, 1979, p 31.

(3) Sutin, N. *J. Photochem.* 1979, 10, 19.