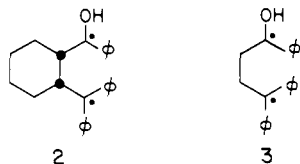


guarantees that all intersections are thermally accessible at room temperature or above.

If structural flexibility is sufficient for easy access to S-T intersections, is it also necessary? Recent work of Caldwell<sup>24</sup> shows that **2**, with  $\gamma$  fixed at ca.  $60^\circ$  and  $\alpha$  and  $\beta$  hindered, has an isc rate constant of  $1.45 \times 10^7 \text{ s}^{-1}$  at  $25^\circ \text{C}$  in heptane, compared to the flexible analog **3**, with an isc rate constant of  $1.19 \times 10^7 \text{ s}^{-1}$  in heptane.<sup>24</sup> Thus partial removal of flexibility does not prevent access to S-T intersections needed for efficient isc.



Another important question is the structural dependence of the spin orbit coupling (SOC) matrix element. SOC in biradicals is strongly dependent on the relative angular orientation of the termini and decreases approximately exponentially with increasing end-to-end distance.<sup>25</sup> Recent experiments on 1,7- to 1,15-biradicals containing an acyl terminus have shown that SOC is the dominant isc mechanism<sup>26</sup> and that isc occurs mainly in geometries with small end-to-end distances.<sup>26c</sup> An accurate knowledge of SOC

is obviously required to understand isc in biradicals. Preliminary SOC calculations on trimethylene (based on the Breit-Pauli spin-orbit interaction<sup>27</sup>) have already appeared from this laboratory.<sup>28</sup> Further SOC calculations are in progress.<sup>29</sup>

In conclusion, 2-configuration MCSCF 3-21G calculations of the S-T energy gap  $E_{ST}$  were performed as a function of the three internal rotations and the pyramidalization of the terminal methylenes. Through-bond coupling is found to dominate the structural dependence of  $E_{ST}$ . We<sup>15</sup> and Dougherty<sup>20</sup> have found the same effect in trimethylene. The importance of through-bond coupling in larger biradicals is unknown since the effect is expected to attenuate with increasing chain length. For the isc process, our most important result is that at room temperature or above, a thermally equilibrated triplet tetramethylene cannot avoid encountering S-T intersections. However, the calculations are not sufficient to predict the product distribution. This contrasts with triplet trimethylene, for which we showed<sup>15</sup> that knowledge of the S and T surfaces are sufficient by themselves to correctly predict nearly exclusive cyclization. For triplet tetramethylene, a prediction of the product distribution as well as the isc rate constant would require a knowledge of SOC plus a dynamical treatment of the S-T crossing.

**Acknowledgment.** The authors thank Richard A. Caldwell, Gerhard L. Closs, and J. C. Scaiano for communicating their results prior to publication. We acknowledge the National Science Foundation for support.

(24) Caldwell, R. A.; Dawan, S.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 6454.

(25) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(26) (a) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 4543. (b) Zimmt, M.; Doubleday, C.; Gould, I.; Turro, N. J. *J. Am. Chem. Soc.*, in press. (c) Zimmt, M.; Doubleday, C.; Turro, N. J. *J. Am. Chem. Soc.*, in press.

(27) Bethe, H.; Salpeter, E.; "Quantum Mechanics of One- and Two-Electron Atoms"; Springer: New York, 1957.

(28) Furlani, T.; King, H. *J. Chem. Phys.* **1985**, *82*, 5577.

(29) Carlacci, L.; Doubleday, C.; Furlani, T.; King, H.; McIver, J., to be published.

## Oxidation of 2,6-Di-*tert*-butylphenol by Molecular Oxygen. 2. Catalysis by Cobaltous Polyamine Chelates through Their ( $\mu$ -Peroxo)- and ( $\mu$ -Peroxo)( $\mu$ -hydroxo)dicobalt(III) Complexes

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**Abstract:** The oxidation of 2,6-di-*tert*-butylphenol by molecular oxygen is catalyzed by the cobaltous chelates of tetraethylenepentamine (TETREN), dipicolyl-diethylenetriamine (PYDIEN), and 1,4,10,13-tetraaza-7-thia-tridecane (TATTD), through their ( $\mu$ -peroxo)dicobalt(III) complexes and by those of dipicolylethylenediamine (PYEN), tris(aminoethyl)amine (TREN), and triethylenetetramine (TRIE) through their ( $\mu$ -hydroxo)( $\mu$ -peroxo)dicobalt(III) complexes. Reaction products are identified as the oxidative coupling product 3,3',5,5'-tetra-*tert*-butyldiphenoquinone and the partial oxygen insertion product, 2,6-di-*tert*-butylbenzoquinone. The rates of reaction of the substrate as well as the formation of products are shown to be first order with respect to the concentrations of both the cobalt-dioxygen complex and the substrate. The reaction with  $[\text{Co}_2(\text{TETREN})_2\text{O}_2]^{4+}$  does not occur in the absence of free molecular oxygen in solution and occurs at a reduced rate under air relative to oxygen.

The role of cobalt-dioxygen complexes in the oxidation of organic substrates, most notably hindered phenols, is the objective of several recent reports.<sup>1-3</sup> Following pioneering work by Van Dort and Geurson<sup>4</sup> on the salcomine ([bis(salicylaldehyde)

ethylenimine]cobalt(II))-catalyzed oxidation of 2,6-substituted phenols to produce substituted benzoquinones and diphenoquinones, Nishinaga carried out extensive studies on such systems,<sup>5,6</sup> demonstrating the role of the phenoxy radical, which is the first intermediate in the formation of the oxidized coupled product. A significant contribution to the cobalt Schiff-base-

(1) Nishinaga, A.; Tomita, H.; Nishizawa, K.; Matsuura, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1504.

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

(3) Wang, X. Y.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1984**, *23*, 271.

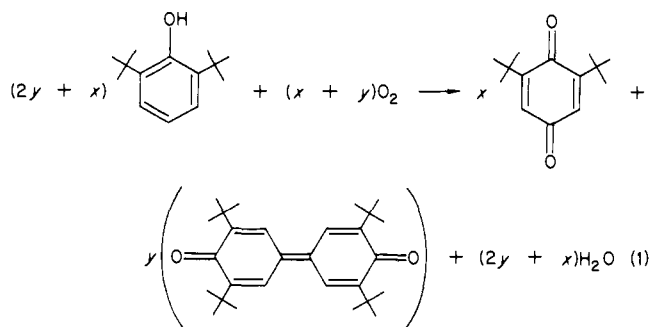
(4) Van Dort, H. M.; Geurson, H. J. *Recl. Trav. Chim. Pays-Bas.* **1967**, *86*, 520.

(5) Nishinaga, A. "Biochemical and Medical Aspects of Active Oxygen"; Hayaishi, O., Asada, K., Eds.; University Park Press: Baltimore, MD, 1977; p 13.

(6) Nishinaga, A.; Tomita, H.; Shimizu, T.; Matsuura, T. *Fundam. Res. Homogeneous Catal.* **1978**, *2*, 241.

catalyzed oxidation of phenols has been the isolation and crystal structure determination of (quinolato-*p*-peroxy)cobalt(III) complexes.<sup>1</sup> Nishinaga proposed this type of intermediate as the benzoquinone precursor, formed by insertion of free dioxygen directly into a coordinated cobalt(III) phenoxide complex (Kochi<sup>7</sup> has suggested the possibility that this complex could involve a cobalt-carbon bond).

Drago<sup>8</sup> in a more detailed study showed reaction pathways involving direct coupling of the cobalt(III) superoxo complex with the phenoxyl radical (through the carbon para to the oxygen). A similar mechanism with a fundamentally different catalytic system, involving the ( $\mu$ -peroxy)( $\mu$ -hydroxo)tetrakis(bipyridyl)-dicobalt(III) complex was proposed in the oxidation of DBP<sup>9</sup> to produce BQ and DPQ<sup>2-</sup> (eq 1). The possibility that the reaction



intermediate for oxygen activation is the mononuclear superoxo cobalt(III) complex formed by equilibrium-controlled dissociation was suggested.<sup>2</sup>

The present paper demonstrates the use of ( $\mu$ -peroxy)dicobalt(III) complexes of TETREN, PYDIEN, PYDIEN, and TATFD, as well as the ( $\mu$ -hydroxo)( $\mu$ -peroxy)dicobalt(III) complexes formed by PYEN, TREN, and TRIEN, to bring about the same reaction, while raising new questions concerning the mechanistic aspects.

## Experimental Section

**Reagents and Materials. Preparation of Ligands.** The synthesis of compounds TAOTD, PYDAE, TATFD, and SPYDAE has been previously described.<sup>10</sup> TREN was obtained as the free base and purified through repeated crystallization of the trihydrochloride salt. TETREN was prepared as the pentahydrochloride salt after repeated crystallization in aqueous HCl from the twice-distilled commercially available product. PYEN was prepared as the tetrahydrochloride salt by the methods of Gruenwedel.<sup>11</sup> PYDIEN was synthesized by formation of the Schiff base as described previously,<sup>12</sup> but reduction was performed with sodium bromohydrate instead of by catalytic hydrogenation. The trihydrochloride salt was isolated and recrystallized twice from ethanol/water. SDTMA was prepared by a previously published method.<sup>13</sup> TRIEN and SEDDA were obtained in pure form from commercial sources and used without further purification.

**Other Materials.** [Co(TETREN)(OH)](ClO<sub>4</sub>)<sub>2</sub> was prepared according to House and Garner.<sup>14</sup> The potassium hydroxide solution

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

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

(9) Abbreviations used in this paper are defined as follows: DBP, 2,6-di-*tert*-butylphenol; BQ, 2,6-di-*tert*-butylbenzoquinone; DPQ, 3,3',5,5'-tetra-*tert*-butylphenylquinone; TETREN, tetraethylenepentamine; PYDIEN, dipicolylidethylenetriamine; TATFD, 1,4,10,13-tetraaza-7-thiatridecane; PYEN, dipicolylethylenediamine; TREN, tris(aminoethyl)amine; TRIEN, triethylenetetramine; TAOTD, 1,4,10,13-tetraaza-7-oxatridecane tetrahydrobromide; PYDAE, 1,9-bis(2-pyridyl)-2,8-diaza-5-oxanonane tetrahydrobromide; SPYDAE, 1,9-di-2-pyridyl-2,8-diaza-5-thianonane tetrakis(benzenesulfonate) monohydrate; SDTMA, *N,N*-bis(2-aminoethyl)glycine; SEDDA, *N,N'*-ethylenediaminediacetic acid; EDTA, ethylenediaminetetraacetic acid.

(10) Bedell, S. A.; Timmons, J. H.; Martell, A. E.; Murase, I. *Inorg. Chem.* **1982**, *21*, 874.

(11) Gruenwedel, D. W. *Inorg. Chem.* **1968**, *7*, 495.

(12) Harris, W. R.; Murase, I.; Timmons, J. H.; Martell, A. E. *Inorg. Chem.* **1978**, *17*, 889.

(13) McLendon, G.; MacMillan, D. T.; Hariharan, M.; Martell, A. E. *Inorg. Chem.* **1974**, *14*, 2322.

employed in the potentiometric studies was prepared from J. T. Baker "Dilut-It" potassium hydroxide concentrate under CO<sub>2</sub>-free conditions and was standardized with potassium hydrogen phthalate. The cobalt nitrate solution used for potentiometric measurements was standardized by titration with EDTA. Cobalt(II) solutions for kinetic studies were prepared from CoCl<sub>2</sub>·6H<sub>2</sub>O. The ligand solutions in these studies were readied by neutralization of the ligand hydrohalide salts (except for SEDDA) with KOH in methanol, and the corresponding potassium salts were filtered off. Care was taken to prevent carbon dioxide from entering these solutions. All other chemicals used were of reagent quality.

**Equilibrium Measurements.** For the ligand PYEN, the acid form of the ligand was treated with standard carbonate-free potassium hydroxide solution, and the hydrogen ion concentrations were recorded after addition of each increment of base. The cobaltous chelate formation equilibria (under nitrogen and oxygen) were determined with 1:1 molar ratios of the ligand to Co<sup>2+</sup> at a concentration of 2.50 × 10<sup>-3</sup> M. Hydrogen ion concentrations were determined with a Corning Model 130 pH meter equipped with glass and calomel electrodes calibrated with standard HCl and NaOH to read -log [H<sup>+</sup>] rather than activity. For the purposes of this paper, -log [H<sup>+</sup>] is expressed by the term p[H]. Solutions were adjusted to 0.10 M ionic strength by the addition of KNO<sub>3</sub> and maintained at 25.00 ± 0.05 °C with constant temperature water circulated through a sealed, jacketed cell. A smooth and uniform stream of nitrogen gas, which was prepurified by passing through two alkaline pyrogallol scrubbers and then through 0.10 M KNO<sub>3</sub> solution, was allowed to pass over the reaction solution in order to maintain an inert atmosphere. For the equilibrium measurements under an oxygen atmosphere, pure oxygen was passed through an Ascarite column to remove traces of CO<sub>2</sub> and then through a 0.100 M KNO<sub>3</sub> solution. Methods employed for the evaluation of equilibrium constants have been discussed in a previous paper.<sup>10</sup>

**Visible Spectra.** Electronic spectra were recorded on a Cary Model 14 double-beam spectrophotometer in matched 1.000-cm cells.

**Kinetic Measurements.** The dioxygen complex was formed by adding aliquots of standard cobalt and ligand solutions to methanol. The reaction mixtures were adjusted to 95 wt % methanol-water. In the case of the dibridged dioxygen adducts, 0.5 equiv of potassium hydroxide was added to the solution. Elapsed time of oxygenation prior to substrate addition was recorded in order to account for any decomposition of the catalyst that might occur in the course of the reaction. The reaction vessel was maintained at 35.00 ± 0.05 °C by a continuous supply of thermostated water through the jacketed cell. Inlet and outlet tubes assured a steady supply of oxygen, which was first passed through an Ascarite absorption tube and then through a 95% methanol-water scrubber. After complete oxygenation of the cobaltous complex, an aliquot of the substrate, 2,6-di-*tert*-butylphenol, was added to the reaction mixture. During the reaction, samples were withdrawn through a septum with a microliter syringe and injected into a Hewlett-Packard 5830A gas chromatograph, fitted with a 6 ft × 1/8 in. 80-100 WAS column with 10% UCW-982. Temperature programming from 180 to 200 °C at 10 °C/min was employed. To provide an internal standard, 1,2,4,5-tetramethylbenzene was added to the reaction vessel. Reactions were followed by the disappearance of the chromatographic peak for 2,6-di-*tert*-butylphenol.

During the course of the reactions, a precipitate formed which was identified by elemental analysis, NMR, and mass spectrum as 3,3',5,5'-tetra-*tert*-butyldiphenylquinone. The oxygen insertion product 2,6-*tert*-butylbenzoquinone was also formed and identified by gas chromatography and mass spectrometry. Product analysis by 90- and 200-MHz NMR was carried out on chloroform solutions prepared by evaporating the reaction mixture and dissolving the residue in chloroform, followed by extraction of the cobalt complex in water.

In separate experiments, the degradation rates of the dioxygen complexes in a 95 wt % methanol-water mixture were monitored by the change in their visible absorption spectra.

## Results and Discussion

**PYEN Dioxygen Complex Formation.** The oxygenation equilibrium constants and the phenol oxidation rate constants for the monobridged ( $\mu$ -peroxy) and dibridged ( $\mu$ -peroxy)( $\mu$ -hydroxo) dioxygen complexes involved in this study are listed in Table I.

For the monobridged complexes,  $K_{O_2}$  is defined by eq 2.

The pH-dependent equilibrium for the dibridged species is defined by eq 3. Although the ligand protonation ( $K_H^n =$

$$K_{O_2} = \frac{[M_2L_2O_2]}{[ML]^2[O_2]} \quad (2)$$

(14) House, D. A.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 272.

**Table I.** Oxygenation Constants and Oxidation Constants of 2,6-Di-*tert*-butylphenol for Monobridged and Dibridged Cobalt-Dioxygen Complexes

ligand <sup>a</sup>	log $K_{O_2}$ <sup>b</sup>	$10^3 k_{\text{obsd}}$ , M <sup>-1</sup> s <sup>-1</sup>	$10^3 k_1$ , <sup>c</sup> M <sup>-1</sup> s <sup>-1</sup>	$10^3 k_2$ , <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>	$R$ ( $k_1/k_2$ )
Monobridged ( <i>m</i> -Peroxo)					
TETREN	15.8 <sup>e</sup>	0.67	0.24	0.22	1.1
PYDIEN	11.4 <sup>e</sup>	3.7	1.6	1.0	1.6
TATTD	8.4 <sup>f</sup>	1.1	0.65	0.24	2.7
SPYDAE	5.0 <sup>f</sup>	g			
TAOTD	2.2 <sup>f</sup>	g			
Dibridged [( $\mu$ -Peroxo)( $\mu$ -hydroxo)]					
TRIEN	6.1	0.17	0.0008	0.083	0.001
TREN	4.4	0.086	0.002	0.042	0.047
PYEN	3.8	4.6	0.11	2.2	0.05
BIPY	-2.6 <sup>h</sup>	4.6	0.60	2.0	0.30
SDTMA	2.3 <sup>i</sup>	g			
SEDDA	-4.1 <sup>i</sup>	g			

<sup>a</sup> BIPY, 2,2'-bipyridyl; other ligands defined in ref 9. <sup>b</sup> Defined by equation  $K_{O_2} = [M_2L_2O_2]/[ML]^2[O_2]$  for monobridged and  $K_{O_2}' = [M_2L_2(OH)O_2][H^+]/[ML]^2[O_2]$  for dibridged (coupling). <sup>c</sup> Quinone formation (oxygenation). <sup>d</sup> Diphenoquinone formation (coupling). <sup>e</sup> Values from ref 12. <sup>f</sup> Values from ref 10. <sup>g</sup> The dioxygen complex reversibly oxidized before appreciable amount of substrate could be oxidized. <sup>h</sup> Value for 2:1 complex from ref 17. <sup>i</sup> Values from ref 16 and references therein.

$[H_nL]/[H^+][H_{n-1}L]$  and cobaltous chelate equilibrium constants ( $K_{ML} = [ML]/[M][L]$ ) for the ligand PYEN have been reported,<sup>15</sup> the value of  $K_{O_2}'$  has not. The other constants deter-

$$K_{O_2}' = \frac{[M_2L_2(OH)O_2][H^+]}{[ML]^2[O_2]} \quad (3)$$

mined for this ligand in this study ( $\log K_H^1 = 8.22$ ,  $\log K_H^2 = 5.37$ ,  $\log K_H^3 = 1.5$ ,  $\log K_H^4 = 1.4$ ,  $\log K_{ML} = 12.48$ ) are in good agreement with the earlier results. The value of 3.83 for  $\log K_{O_2}'$  is much higher than predicted from the correlation of McLendon and Martell,<sup>16</sup> who found a linear relationship between  $\log K_{O_2}'$  and the sum of the  $pK_a$ 's for a series of aliphatic ligands. Since that report, values for other ligands containing pyridyl groups have appeared that also reflect unexpected stability of the dioxygen complexes. The values for  $\log K_{O_2}'$  for the dibridged oxygen complexes formed by the cobaltous chelates of bis(bipyridine),<sup>17</sup> PYEN, and 1,4,7-triaza-8-(2-pyridyl)octane,<sup>18</sup> when plotted against the sum of the  $pK_a$ 's, form a line parallel to that found for aliphatic ligands but with higher correlation. For the aliphatic ligands, total basicities are well represented by protonation equilibrium constants since electron donation to both a proton or a metal center is primarily of a  $\sigma$  nature. In the case of pyridyl-containing ligands,  $\pi$ -bonding contributions may have considerable influence on the stability of the peroxo-bridged Co(III) complexes.<sup>19</sup>

**Phenol Oxidation Kinetics.** Experimentally, the same rate law as described for the bipyridine system was found to apply to the present systems, as represented by eq 4 where  $x = 0$  for the

$$-\frac{d[\text{substrate}]}{dt} = k_{\text{obsd}}[Co_2L_2O_2(OH)_x]^{(4-x)+}[\text{substrate}] = k_{\text{obsd}}[\text{comp}][\text{substrate}] \quad (4)$$

monobridged complexes of TETREN, PYDIEN, TAOTD, and TATTD, and  $x = 1$  for the dibridged adducts of PYEN, TREN, and TRIEN; comp represents the binuclear dioxygen complex.

If the observed reaction rate for the consumption of the phenol is first order with respect to both substrate and dioxygen complex, then formation of the two products should also obey that rate law

since both are produced in significant amounts, and the following relationships can be written

$$\frac{d[BQ]}{dt} = k_1[\text{comp}][DBP]_i \quad (5)$$

$$\frac{d[DPQ]}{dt} = k_2[\text{comp}][DBP]_i \quad (6)$$

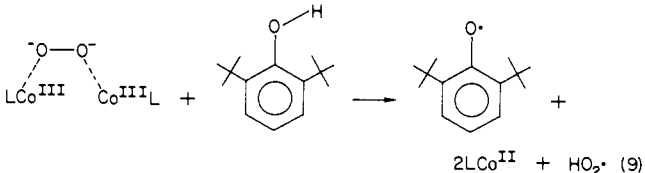
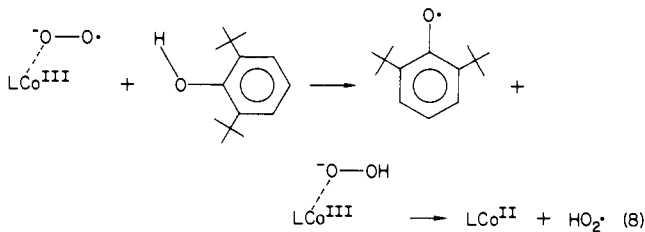
$$[DBP]_i = [DBP]_t + [BQ]_t + 2[DPQ]_t \quad (7)$$

where  $[DBP]_i$  represents the initial concentration of the substrate and  $[DBP]_t$ ,  $[BQ]_t$ , and  $[DPQ]_t$  are the concentrations of phenol, benzoquinone, and diphenoquinone at time  $t$ , and [comp] is the concentration of the binuclear dioxygen complex. Since gas-chromatographic measurements provide direct determinations of  $[DBP]_t$  and  $[BQ]_t$ , and final product analysis shows only BQ and DPQ to be formed;  $[DPQ]_t$  is determined by difference.

Values of  $k_1$  and  $k_2$  as well as  $k_{\text{obsd}}$  were found to remain constant as initial substrate and dioxygen complex concentrations were varied. Shown in Table I are the values for  $k_{\text{obsd}}$ ,  $k_1$ , and  $k_2$ .  $R = [DPQ]_t/[BQ]_t$  was found to remain constant throughout each run, as was reported by previous investigators.<sup>20</sup>

**Mechanism of Phenol Oxidation.** Since the disappearance of phenol is first order in both substrate and dioxygen complex, and if the rate-determining step involves formation of a (quinolato-*p*-peroxo)cobalt(III) complex enroute to BQ formation, then the competing reaction to form DPQ must also involve the same dependence since both BQ and DPQ are formed in appreciable amounts. While oxidation of the phenoxide dimer could certainly involve catalysis by the dioxygen complex, the dimerization process itself may be expected to be dependent on the square of the phenol concentration.

Another alternative is that the slow step of the reaction is the initial one to form the phenoxide radical. Drago reported no deuterium kinetic isotope effect upon substitution of the acidic proton of the phenol with deuterium. However, since the polyamine cobalt chelate dioxygen complexes investigated in this study tend to form almost exclusively binuclear dioxygen adducts, and the Schiff base systems investigated by Drago are known to involve more substantial amounts of the mononuclear superoxo complexes,<sup>21</sup> it is not unreasonable to expect different reactivities for the two types of complexes. Hydrogen abstraction by the mononuclear and binuclear complexes is shown in eq 8 and 9.



If the complexes involved in the present study reacted by eq 9, one might expect a lessened reactivity (compared to Schiff base systems) due to the extremely small equilibrium amounts of the superoxo complex. This would also explain why the values of  $k_{\text{obsd}}$  in Table I decrease as the degree of binuclear complex formation (as measured by  $k_{O_2}$  and  $k_{O_2}'$ ) increases. More peroxo-bridged complex in solution represents a decrease in the mononuclear superoxo complex. On the other hand, if eq 9 were to be the case, steric reasons could make the hydrogen abstraction more difficult,

(15) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1975, Vol. 2.

(16) McLendon, G.; Martell, A. E. *J. Chem. Soc., Chem. Commun.* **1975**, 223.

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

(18) Ng, C. Y. Ph.D. Dissertation, Texas A&M University, Dec 1982.

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

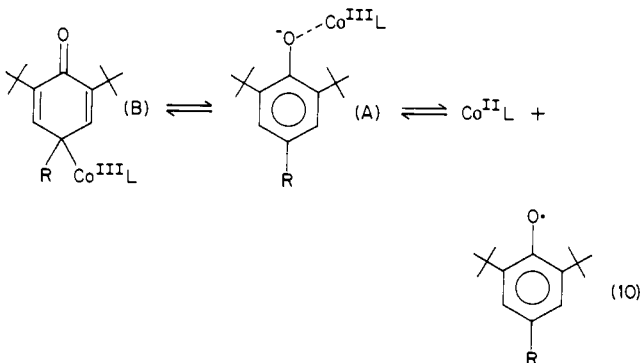
(20) Vogt, L. H.; Wirth, J. G.; Finkbeiner, H. L. *J. Org. Chem.* **1969**, *34*, 273.

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

since the hindered phenol must now attack an oxygen that is blocked by coordination at both ends. Here again, one might expect the highly stable dioxygen complexes to be slower to react because of the needed reduction of one of the cobalt centers, which have been shown to have more negative reduction potentials as the thermodynamic stability is increased.

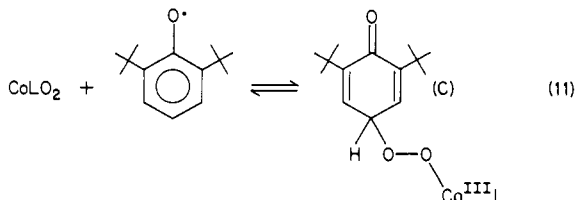
There is currently a disagreement between several workers over the role of dioxygen complexes in the oxidation of substituted phenols, particularly concerning the source of the oxygen that ends up in the benzoquinone. One mechanism involves coupling of coordinated dioxygen to the phenoxide radical, while another utilizes free dioxygen in solution as the reactant.

As mentioned earlier, Nishinaga<sup>5,6</sup> has suggested a mechanism for benzoquinone production involving the insertion of free dioxygen directly into a coordinated Co(III)-phenoxide complex A. Kochi<sup>7</sup> has suggested a facile interconversion between this type of phenolate complex and a cobalt-to-carbon bonded species B and the phenoxide radical with the cobaltous complex as shown in eq 10. He has drawn a parallel between the insertion of

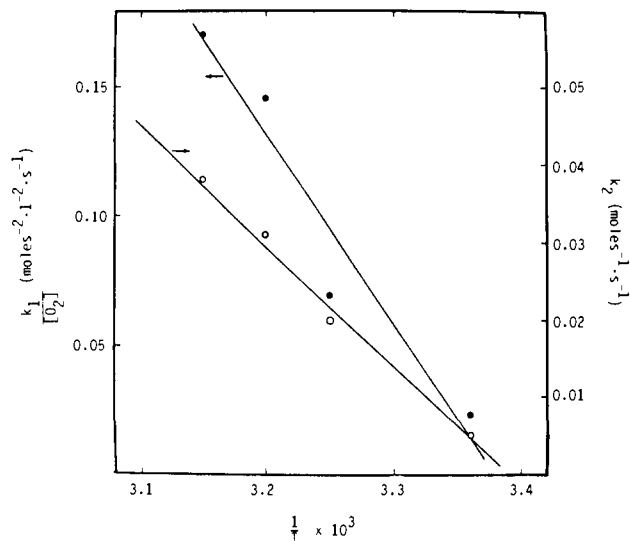


dioxygen into B and the autoxidation of alkylcobalt(III) complexes, including vitamin B<sub>12</sub>. Considering the unique nature<sup>22</sup> of vitamin B<sub>12</sub> chemistry, one must question the stability of the Co(III)-to-carbon bond with respect to resistance to solvolysis in a protic solvent such as that employed in the present study.

On the other hand, Drago<sup>8</sup> suggested reaction pathways involving direct coupling to the cobalt(III) superoxo complex with the phenoxide radical (through the carbon para to the phenoxide oxygen). While not demonstrating independence of the reaction toward free dioxygen, he reported an ESR spectrum of a (quinolate-*p*-peroxo)cobalt(III) complex C, which according to his interpretation, is in equilibrium with a small amount of phenoxide radical and superoxo cobalt(II) complex as indicated by eq 11. All of the previous work described by Drago<sup>8</sup> and Nishinaga<sup>5,6</sup> involves Schiff base systems.



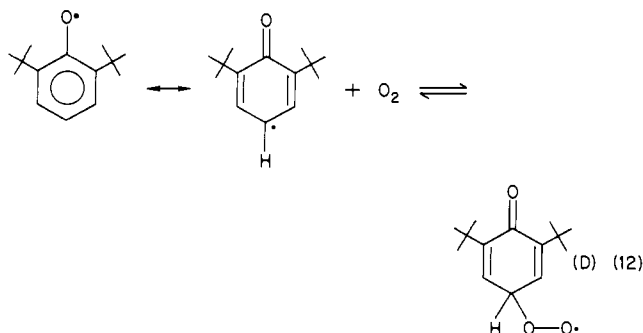
The dioxygen adduct of TETREN is the most thermodynamically stable of any thus far reported ( $\log K_{O_2} = 15.8$ ).<sup>12</sup> Because of the magnitude of this equilibrium constant, the Co(TETREN) system should provide virtually 100%  $\mu$ -peroxo-dioxygen complex formation over a wide range (i.e., to very low) of oxygen pressures. In the case of cobalt(II) Schiff base complexes with equilibrium oxygenation constants several orders of magnitude smaller, reductions in oxygen pressure should be accompanied by decreased concentrations of the dioxygen adduct. By this reasoning, a phenol oxidation rate dependence on oxygen concentration in the salcomine case may correspond to a decrease in active species concentration. The measured rate constant,  $k_1$ , for BQ formation with  $[\text{Co}(\text{TETREN})]^{2+}$  was found to differ under atmospheres



**Figure 1.** Plot of  $k_1/[\text{O}_2]$  and  $k_2$  vs.  $1/T \times 10^3$ . Conditions:  $[\text{Co}_2(\text{BIPY})_4(\text{OH})\text{O}_2]^{3+} = 0.04 \text{ M}$ ;  $[\text{substrate}] = 0.04 \text{ M}$ . ( $\bullet$ ,  $k_1/[\text{O}_2]$ ;  $\circ$ ,  $k_2$ ).

of oxygen and air by a factor of 3.9. Since in both cases the peroxo-bridged binuclear dioxygen complex concentration is the same, a role for free dioxygen in the mechanism involving the binuclear peroxo complexes as reactants or starting materials should be considered. Further substantiation of this role is demonstrated by the fact that when solutions of fully formed dioxygen complexes of cobaltous TETREN and PYDIEN are flushed with nitrogen to remove dissolved oxygen, added substrate will not react over the course of several hours (despite the presence of the fully formed peroxo-bridged binuclear dioxygen complex, as indicated by the intense brown color).

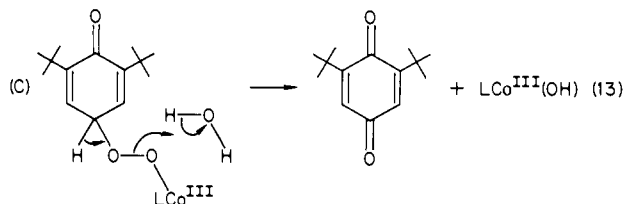
Dioxygen concentration dependence in the mechanism for BQ production involving a binuclear peroxo complex as a reaction intermediate can be further proved from the plot of  $k_1/[\text{O}_2]$  vs.  $1/T$  as shown in Figure 1. The division of  $k_1$ , the rate constant for formation of the oxygen insertion product, by dioxygen concentration is essential since it varies appreciably throughout the temperature range employed. The constant  $k_2$ , and therefore DPQ formation, does not show an oxygen concentration dependence in the Arrhenius plot. Bearing in mind that in solution the dioxygen concentration far exceeds the equilibrium controlled concentration of mononuclear superoxo complexes formed by the ligands involved in this study, it is possible for radical coupling of the dioxygen with the phenoxide radical to occur, followed by coordination to a cobaltous center. This is similar to a classical mechanism for hydrocarbon autoxidations.<sup>23</sup> In autoxidations of most hydrocarbons, this reaction is irreversible. It has been pointed out,<sup>24</sup> however, that with highly resonance stabilized radicals such as the di-*tert*-butylphenoxide, an equilibrium is possible as shown in eq 12.



(23) Reich, L.; Stivala, S. S. "Autoxidation of Hydrocarbons and Polyolefins"; Marcel-Dekker: New York, 1969.

(24) Gilbert, B. C.; Dobbs, A. J. "Organic Peroxides"; Swern, D., Ed.; Wiley Intersciences: New York, 1972; Vol. III, p 271.

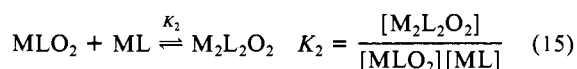
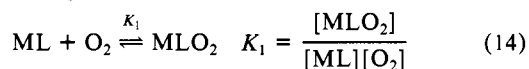
This equilibrium may explain the observed oxygen dependence. Intermediate D can then combine with the equilibrium controlled amounts of the unoxygenated metal chelate to assist in the degradation of D to produce Nishinaga's intermediate C. The formation of C with its formal electron transfer to the superoxide, should weaken the oxygen-oxygen bond, allowing it to form the benzoquinone as shown in eq 13. Without a complex capable



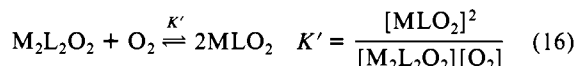
of stabilizing C, D is slower to react, allowing further formation of the diphenoxinone. The oxidative coupling reaction to produce DPQ may also be catalyzed by the dioxygen complex.

The ratio of  $k_1$  to  $k_2$  is found to increase as the formation constants of the binuclear oxygenated species decrease, which indicates that a higher percentage of mononuclear oxygen complex species favors the production of BQ according to the mechanistic scheme described earlier.<sup>2</sup>

Oxygen dependence of benzoquinone production may also be a result of the equilibrium-controlled concentration of the mononuclear superoxide. If one considers the equilibria defined by eq 14 and 15 as important steps in the formation of the binuclear complex, then  $K_{O_2} = K_1 K_2$ . Since the values of  $K_1$  and  $K_2$  have



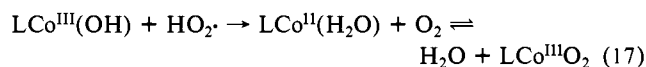
not been determined, it is possible to argue that these equilibria allow for reduced concentrations of the mononuclear superoxide ( $MO_2$ ) at lowered dioxygen pressures. Thus, increased dioxygen concentration would tend to increase the concentration of  $MLO_2$  relative to  $M_2L_2O_2$ . Thus,



In view of the observed increase in the rate of oxygen insertion with dioxygen concentration, eq 11 would seem to be favored as the reaction pathway for BQ formation.

The traditional role of the cobaltic species produced after benzoquinone is split out of the (quinolato-*p*-peroxy)cobalt(III) complex is to serve as the hydrogen abstractor, thereby regenerating the cobaltous species. One must then wonder why the complexes of ligands such as SPYDAE, TAOTD, SDTMA, and SEDDA do not function in this manner. As mentioned in Table I, these complexes were found to decompose to species irreversible to dioxygen adduct formation, and reaction of the DBP was not detected. If these complexes undergo oxidation to cobalt(III) species, then why do they not function to abstract hydrogen atoms

from the phenol? Most probably the form of the cobalt(III) complex is not the same as that formed by cleavage of the metal-organic peroxide. Some of these ligands are known to be degraded during the oxidation process. To test this theory,  $[Co(TETREN)(OH)](ClO_4)_2$  was reacted with the phenol (both reactants at 0.040 M) under oxygen. Due to the insolubility of this salt in methanol, it became necessary to perform the experiment in *N*-methylpyrrolidone, a coordinating solvent that could interfere with the expected reaction. Nevertheless, only a small amount of substrate was reacted after 1 day. Both BQ and DPQ were detected in the reaction mixture. UV-Visible spectra during the reaction failed to detect any  $\mu$ -peroxy species. Although the reduction of cobalt(III) by the phenol could not be proved in this experiment, it is considered a key step in the regeneration of the dioxygen complex. Copper(II) chelates have been shown to act in this way in the catalytic production of DPQ.<sup>25</sup> Another possible reductant produced in the reaction is the superoxide formed following decomposition of the cobalt hydroperoxide produced by the hydrogen abstraction from the phenol as shown in eq 17.



Reasons were given above to explain why the rates of phenol oxidation decrease for the very stable dioxygen complexes. Since cobaltous complexes that do not undergo oxygenation do not catalyze the oxidation,<sup>26</sup> one would expect to find an optimum stability where the factors contributing to increased reactivity are balanced out by those decreasing it. Unfortunately, as shown in Table I, the least thermodynamically stable dioxygen adducts are also less kinetically stable (i.e., they decompose before substrate reaction can occur), so that this optimum thermodynamic stability cannot be seen in the case of the dibridged complexes. With the monobridged complexes, this peak of reactivity is seen for the PYDIEN system.

## Conclusions

Although the reaction systems described above are complex, the following generalizations and conclusions which may be made at this stage would help guide future investigations: oxygen insertion does not take place in the absence of dioxygen complexes; free oxygen in solution strongly increases the rate of oxidation of the substrate; the ratio of the rate of insertion to the rate of coupling remains constant over the course of reaction under a given set of conditions; the rate of oxidation of the substrate is first order in concentrations of the dioxygen complex and first order in substrate concentration; the binuclear dioxygen complexes of very high stability are less reactive than those of intermediate stability; the dependence of rate of oxidation on free dioxygen in some systems points to the mononuclear dioxygen complex as an essential intermediate in the reaction pathway for oxygen insertion.

**Acknowledgment.** This research was supported by a grant, A-259, from The Robert A. Welch Foundation.

(25) Ochiai, E. *Tetrahedron* **1964**, *20*, 1831.

(26) Drago, R. S.; Corden, B. B.; Zombeck, A. *Comments Inorg. Chem.* **1982**, *1*, 53.