Te(OH)$_4$Cl$^-$ anion. The Raman spectrum recorded at greater intensity showed seven bands (Table IV), which is more than that expected for the TeO$_2$Cl$^-$ ion, and four bands appear in the TeO single-bond region consistent with a species like Te(OH)$_4$Cl$^-$. If this is the third species present in these solutions, the position of the TeCl stretching vibration at 272 cm^{-1} indicates an equatorial rather than axial TeCl bond.[18] It was not possible to isolate a monochlorotellurate(IV) compound from these solutions to confirm this possibility; mixtures of Me$_4$NCl and TeO$_2$ in a minimum amount of water simply did not react.

Conclusion

The electronic and Raman spectra of solutions of TeO$_2$ in HCl indicate that three Te(IV) species (TeCl$_6^{2-}$, Te(OH)Cl$_4^-$, and a monochlorotellurate(IV) of uncertain degree of solvation, possibly Te(OH)$_4$Cl$^-$) are present. No evidence for species suggested by other authors such as TeCl$_5^-$,[3] Te(OH)$_2$Cl$_4^{2-}$,[4] or TeOCl$_3^-$,[5] among others, has been obtained although these may be present in very low concentration relative to the principal anions. The chlorotellurate(IV) species formed in solution parallel those known for the fluorotellurate(IV) system, Te(OH)F$_4^-$[7] and TeO$_2$F$^-$.[19] However, the highest fluoro coordination in aqueous HF solution is that of TeF$_5^-$, where the lone electron pair on Te is stereochemically active, while that in aqueous HCl is of the TeCl$_6^{2-}$ ion. It is interesting that the introduction of a single hydroxo group in the chlorotellurate(IV) system favors the formation of a square-pyramidal species rather than an octahedral species.

In the haloselenate(IV) systems that have been studied, the degree of halo coordination is lower than that observed for Te(IV) in hydrochloric acid of the same concentration.[6,21] Seleninyl chloride is the principal species in solutions of SeO$_2$ in 12 M hydrochloric acid.[6] The haloantimonate(III) system is similar to that for Te(IV), with the highest halo coordination being that of SbCl$_6^{3-}$, which dissociates to SbCl$_4^-$.[17] Investigation of the Raman spectra of the tetrachloroantimonate(III) solutions shows no evidence of an SbO stretching vibration, and Sb(OH)Cl$_4^-$ is apparently not formed.

The mixture used by Collins and Webster[8] for the preparation of the tetraphenylarsonium hydroxotetrachlorotellurate(IV) tetrahydrate was more acidic, due to excess HCl produced by hydrolysis, than that used for the tetramethylammonium compound reported here, and it appears likely therefore that, if this latter compound is protonated, the former compound is also a hydroxo- and not an oxotellurate(IV) compound, a conclusion that could not be arrived at from the X-ray study.[8] Further work concerning the preparation of oxohalotellurates is being pursued.

Acknowledgment. The Natural Sciences and Engineering Research Council of Canada is thanked for financial assistance.

Registry No. Me$_4$N[Te(OH)Cl$_4$], 88130-56-7; Te(OH)Cl$_4^-$, 88106-33-6; TeCl(OH)$_4^-$, 88106-34-7; TeO$_2$, 7446-07-3; HCl, 7647-01-0; TeCl$_6^{2-}$, 20057-66-3.

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Contribution from the Department of Chemistry,
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Metallotetraphenylporphyrin-Catalyzed Oxidation of 2,6-Di-*tert*-butylphenol

XIAN-YUAN WANG, RAMUNAS J. MOTEKAITIS, and ARTHUR E. MARTELL*

Received April 1, 1983

The rates of oxidation of 2,6-di-*tert*-butylphenol by molecular oxygen in DMF were investigated with CoTPP, Fe(TPP)Cl, Mn(TPP)Cl, VO(TPP), and CuTPP as catalysts (TPP = tetraphenylporphinato). The activities of the catalysts decrease in the order of CoTPP >> Fe(TPP)Cl > Mn(TPP)Cl > VO(TPP), while CuTPP is inactive. The order of selectivity for the formation of the quinone (oxygen insertion) relative to the coupling product is CoTPP >> VO(TPP) > Fe(TPP)Cl > Mn(TPP)Cl. The rate of oxygen insertion increases with temperature in the lower temperature range and decreases markedly at higher temperature, while the coupling reaction increases steadily with increasing temperature. The experimental results are interpreted with the aid of a proposed mechanism in which an intermediate dioxygen complex is required for the insertion reaction, but not for the formation of the coupling product.

Introduction

It is well-known[1] that molecular oxygen can be activated by many transition-metal complexes or chelates that can reversibly bind molecular oxygen. The study of the oxidation of hindered phenols with transition-metal (especially cobalt) dioxygen carriers is of interest because it involves metal-dioxygen adducts as intermediates in the oxidation process. Therefore, these systems serve as appropriate models for the reactions of oxygenase enzymes. Phenols may be oxidized to the corresponding quinones, coupled products (diphenoquinones), or polymers, depending on the choice of solvent, catalyst, or reagent. The oxidation of hindered phenols with the cobalt bis(salicylaldehyde) ethylenediimine (salen) dioxygen complex as catalyst was first reported in 1967 by Van Dort and Guerson.[2] A new synthetic procedure whereby salcomine was used as catalyst was employed by De Jonge and co-workers[3] for preparing 2,6-di-*tert*-butyl-*p*-benzoquinone from 2,6-di-*tert*-butylphenol. Several workers[4,5] have investigated the effects of various reaction conditions and the use of substituted derivatives of the substrate and the carrier ligand (salcomine) on the distribution of oxidation products and suggested that the benzoquinone (BQ) is produced from the mononuclear Co–O$_2$ species while diphenoquinone (DPQ) is produced from the μ-peroxo dimer. However, Kothari and Tazuma[6] indicated that the active species producing both BQ and DPQ is the mononuclear dioxygen adduct. Besides these cobalt complexes, metallophthalocyanines[6,7] have been found to be useful catalysts for the oxidation of hindered phenols.

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More recently Drago et al.[8] have suggested a possible mechanism for oxidation of hindered phenols with cobalt bis(3-(salicylideneamino)propyl)methylamine (CoSMDPT) by means of kinetic and EPR studies. This mechanism involves direct coupling of the mononuclear superoxo dioxygen complex with the para position of the phenoxide radical. Kochi[9] has suggested an intermediate having a direct metal–carbon bond.

Recently[10] a similar mechanism with an entirely different catalytic system, involving the (μ-peroxo)(μ-hydroxo)tetrakis(bipyridyl)dicobalt(III) complex was proposed in the oxidation of 2,6-di-*tert*-butylphenol (DBP) to produce BQ and DPQ. The possibility that the reactive intermediate for oxygen activation is the mononuclear superoxo cobalt(III) complex formed by equilibrium-controlled dissociation was suggested.

The purpose of the present investigation is to determine the catalytic activity of transition-metal porphyrin complexes as catalysts for the oxidation of hindered phenols by molecular oxygen. Attention is directed to the role of dioxygen complexes as intermediates and to selectivity of the oxidation process with respect to oxygen insertion vs. dehydrogenation of the substrate.

Experimental Section

Materials. 2,6-Di-*tert*-butylphenol (Aldrich) was of high quality and was used without further purification. The DMF, toluene, and pyridine (MCB) solvents used were of reagent grade quality. CoTPP,[12] CuTPP,[12] Fe(TPP)Cl,[13,14] Mn(TPP)Cl,[15] and VO(TPP)[16] were prepared by published methods. Purified oxygen was used without further purification.

Oxidation Procedure. The oxidation reaction was carried out in a 100-mL jacketed glass reactor, equipped with a Teflon stirrer and connected to an oxygen-containing gas buret, used for measuring directly the volume of oxygen absorbed in the course of the reaction. Samples for GC analysis were withdrawn with a syringe through a rubber septum. Constant reaction temperature was maintained by cycling water from a thermostated bath.

Product Identification and Analysis. Unreacted 2,6-di-*tert*-butylphenol and the di-*tert*-butyl-*p*-benzoquinone formed during the reaction were analyzed with a Hewlett-Packard 5830A GC using a 6-ft 10% UCW982 on 80-100 WAW $^1/_8$-in. column at 180–200 °C. The internal standard employed was 1,2,4,5-tetramethylbenzene (Aldrich). The coupling product 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone was identified in reaction mixtures by NMR and mass spectra and quantitatively measured spectrophotometrically and gravimetrically.

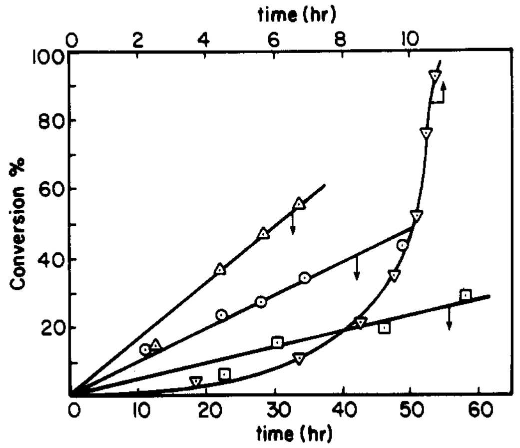

Figure 1. Conversion curves for the oxidation of 2,6-di-*tert*-butylphenol catalyzed by metallotetraphenylporphyrins (t = 55 °C; initial [phenol] = 500 mM DMF; [MTPP]/[phenol] = 0.010). Catalysts: ▽, CoTPP; △, Fe(TPP)Cl; ○, Mn(TPP)Cl; □, VO(TPP). Conversion % = % phenol oxidized.

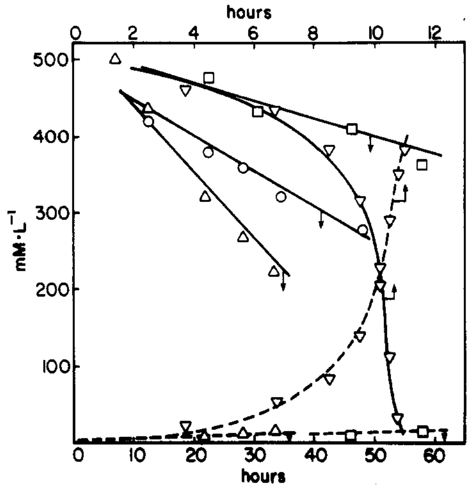

Figure 2. Concentration curves for the oxidation of 2,6-di-*tert*-butylphenol catalyzed by metallotetraphenylporphyrins (t = 55 °C; initial [phenol] = 500 mM DMF; [MTPP]/[phenol] = 0.010). Catalysts: ▽, CoTPP; △, Fe(TPP)Cl; ○, Mn(TPP)Cl; □, VO(TPP) (—, DTBP; ---, BQ).

Results and Discussion

Kinetic Results. Oxidations of 2,6-di-*tert*-butylphenol catalyzed by several metallotetraphenylporphyrins (CoTPP, Fe(TPP)Cl, Mn(TPP)Cl, VO(TTP), and CuTPP) were compared under the same reaction conditions (reaction temperature 55 °C; initial [phenol] = 500 mM in DMF; [MTPP]/[phenol] ~ 0.01). Oxygen uptake, conversion of starting material, and concentrations of phenol and the corresponding benzoquinone formed in the course of the reaction are shown in Figures 1 and 2, respectively. Experimental results indicate that the reaction rate of phenol oxidation with CoTPP is much faster than those of the reactions catalyzed by other metallotetraphenylporphins. The activity decreased in the following order: CoTPP >> Fe(TPP)Cl > Mn(TPP)Cl > VO(TPP), while CuTPP is inactive. When catalyzed by CoTPP, the oxidation reaction is complete in 12 h, and about 79% of reacted phenol is converted to the corresponding benzoquinone. With Fe(TPP)Cl as catalyst, no BQ was detected by GC until the reaction was carried out for about 21 h. Only about 5% of the reacted phenol was converted into BQ. For the VO(TPP)-catalyzed reaction, BQ was detected by GC when the reaction was carried out for 46 h and about 10% of reacted phenol was converted to BQ. When Mn(TPP)Cl was used as catalyst, no BQ was detected even when the reaction was carried out for 49 h. The order of selectivity toward BQ is CoTPP >> VO(TPP) > Fe(TPP)Cl > Mn(TPP)Cl. When the reaction was catalyzed by Fe(TPP)Cl, Mn(TPP)Cl, or VO(TPP), large amounts of red-brown precipitate (3,3′,5,5′-tetra-*tert*-butyldiphenoquinone, DPQ) were formed during the reaction. The precipitate was filtered out, washed with methanol, and dried. Its melting point was found to be 248–248.5 °C (lit. mp 243–244,[6] 246 °C[17]), and its NMR spectrum shows δ 1.4 (36 H), 7.7 (4 H). BQ is the main product of the CoTPP-catalyzed oxidation of the phenol, while

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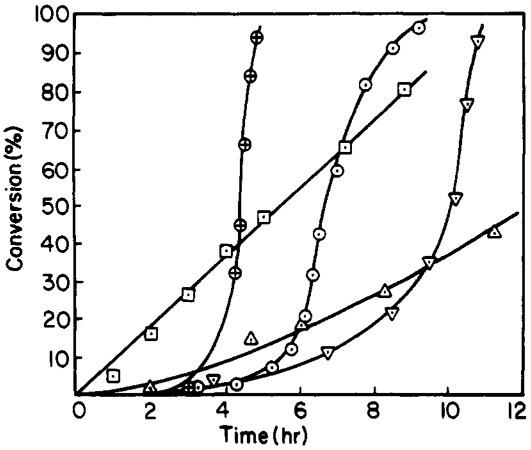


Figure 3. Conversion curves for the oxidation of 2,6-di-*tert*-butylphenol catalyzed by CoTPP at various temperatures (initial [phenol] = 500 mM DMF; [CoTPP]/[phenol] = 0.010): ○, 25 °C; ⊕, 40 °C; ▽, 55 °C; △, 70 °C; □, 85 °C.

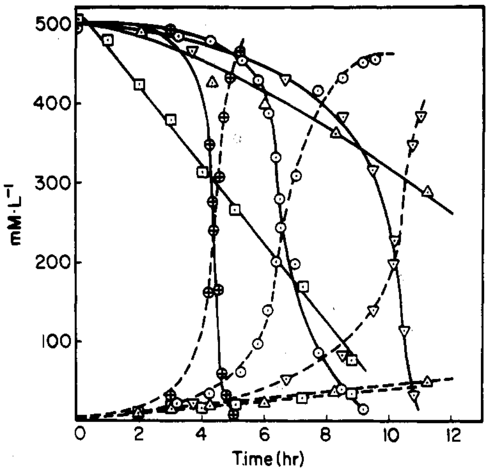


Figure 4. Concentration curves for the oxidation of 2,6-di-*tert*-butylphenol catalyzed by CoTPP at various temperatures (initial [phenol] = 500 mM DMF; [CoTPP]/[phenol] = 0.010): ○, 25 °C; ⊕, 40 °C; ▽, 55 °C; △, 70 °C; □, 85 °C (—, DTBP; ---, BQ).

DPQ is the main product of the oxidation with Fe(TPP)Cl, Mn(TPP)Cl, or VO(TPP). When CoTPP was used as the catalyst for the oxidation of 2,6-di-*tert*-butylphenol, sigmoid-shaped curves were obtained for the extent of phenol reaction, quinone formation, and O_2 uptake with a pronounced induction period that indicates the reaction to be autocatalytic. The reactions catalyzed by other metalloporphyrins have nearly linear kinetic curves, indicating a reaction mechanism or mechanisms that are considerably different from oxidation and oxygenation with CoTPP as catalyst.

Effect of Temperature on the Oxidation Reaction. The kinetic data described above indicate CoTPP to be the best catalyst in both activity and selectivity; it was therefore further investigated at various reaction temperatures. The results are shown in Figures 3–5. At lower temperatures (below 60 °C) the reactions have typical sigmoidal-shaped kinetic curves. However, at higher temperatures the kinetic curves become linear (at 85 °C) or nearly linear, and the selectivity for BQ formation decreases rapidly when the reaction temperature is increased above 55 °C, as shown in Figure 5. Large amounts of DPQ were formed when the reaction was performed at higher temperatures. A plot of $t_{1/2}$ (time required for oxidation of 50% of the phenol) vs. reaction temperature is illustrated in Figure 6 and shows that the reaction has a nonlinear inverse temperature dependence.

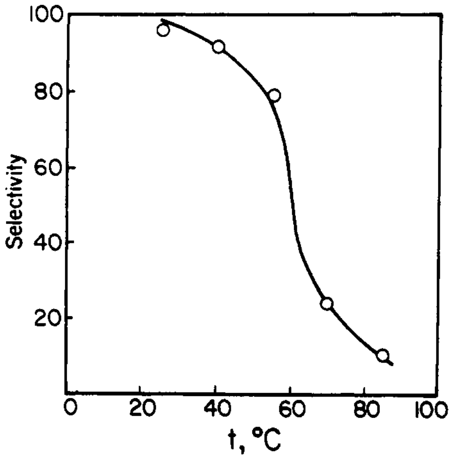


Figure 5. Plot of selectivity vs. temperature for the oxidation of 2,6-di-*tert*-butylphenol catalyzed by CoTPP (initial [phenol] = 500 mM DMF; [CoTPP]/[phenol] = 0.010). Selectivity = 100[BQ formed]/[phenol converted].

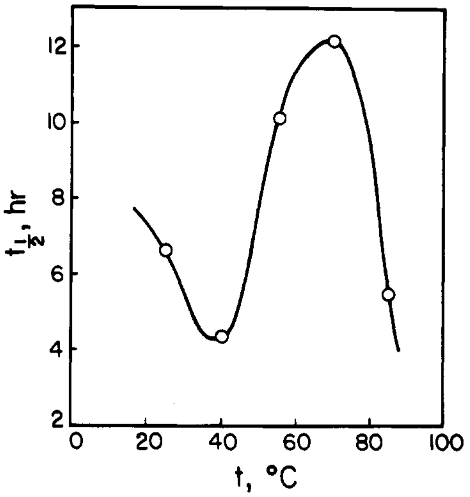


Figure 6. Plot of $t_{1/2}$ vs. temperature for the oxidation of 2,6-di-*tert*-butylphenol with CoTPP as catalyst (initial [phenol] = 500 mM DMF; [CoTPP]/[phenol] = 0.010).

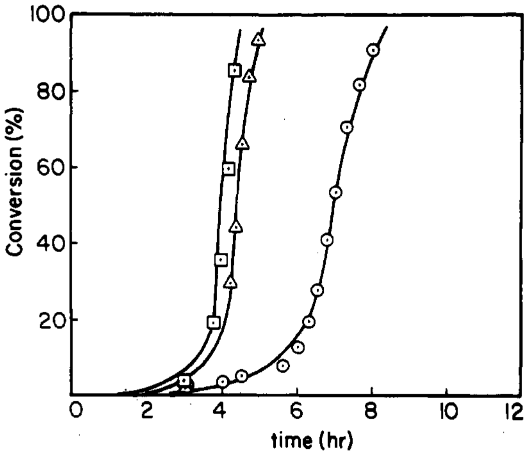


Figure 7. Conversion curves for the oxidation of 2,6-di-*tert*-butylphenol at different concentrations of CoTPP catalyst (t = 40 °C; initial [phenol] = 500 mM DMF): ○, 2.32 mM (0.46%), △, 5.06 mM (1.01%); □, 20.31 mM (4.07%).

Effect of Catalyst Concentration. The reaction was carried out at different concentrations of CoTPP with other conditions held constant (reaction temperature 40 °C; initial [phenol] = 500 mM), and the results are presented in Figures 7 and 8. Although the reaction rate was found to increase with the concentration of catalyst, there is no simple relationship between reaction rate and catalyst concentration. The reaction

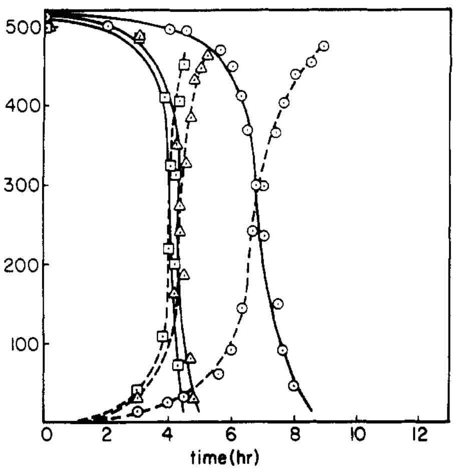


Figure 8. Concentrations of products of oxidation of 2,6-di-*tert*-butylphenol at different concentrations of CoTPP catalyst (t = 40 °,C; initial [phenol] = 500 mM DMF): ○, 2.32 mM (0.46%); △, 5.06 mM (1.01%); □, 20.31 mM (4.07%) (—, phenol; ---, BQ).

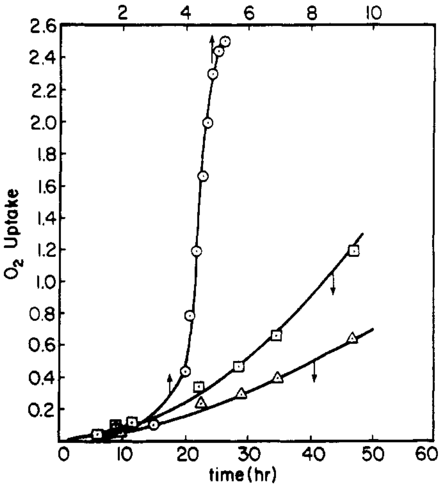
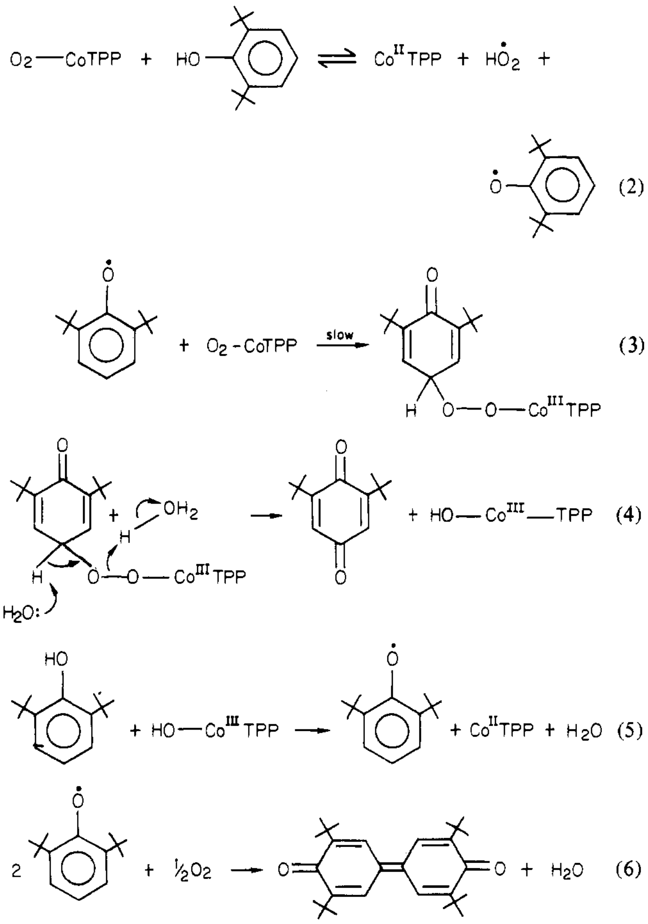


Figure 9. Oxygen uptake and the effect of solvent on the oxidation of 2,6-di-*tert*-butylphenol (t = 40 °C; initial [phenol] = 500 mM; [CoTPP]/[phenol] = 0.010). Solvents employed: ○, DMF; □, toluene–pyridine; △, toluene.

rate was found to increase only marginally when the concentration of the catalyst was increased from about 5 mM/L (corresponding to [CoTPP]/[phenol] = 0.010) to about 20 mM, and there was no appreciable change in the selectivity to BQ when the CoTPP concentration was increased about tenfold from 0.0041 to 0.041 M.

Effect of Solvent. CoTPP-catalyzed oxidation of 2,6-di-*tert*-butylphenol was studied in three solvents (DMF, toluene, and toluene–pyridine (CoTPP:pyridine = 1:1)) under the same reaction conditions (reaction temperature 40 °C; initial [phenol] = 500 mM; [CoTPP]/[phenol] = 0.010). The oxygen uptake curves given in Figure 9 indicate that the rate of the oxidation reaction carried out in DMF is much faster than that carried out in toluene. With 2 mL of pyridine (CoTPP:pyridine = 1:1) added to the toluene reaction medium, an increase in reaction rate occurs, probably because pyridine forms a 1:1 axial complex with CoTPP[18] facilitating the electron transfer from the Co(II) ion to the coordinated dioxygen, thus increasing the strength of metal–dioxygen binding. The coordination of pyridine to CoTPP enhances the reactivity of the dioxygen molecule (probably by enhancing dioxygen complex formation) and thus increases the rate of the oxidation reaction. However, the oxidation rate in this system is still much lower than that in the DMF medium. Pyridine as an axial ligand has been reported to be more effective than DMF in the CoTPP-catalyzed oxidation of acetaldehyde.[18] On the other hand, DMF has also been shown to have a strong stabilizing effect on cobalt–dioxygen complexes with substituted porphyrin ligands.[19] Much more data are needed before the relative effects of solvents and axial ligands on catalytic activity can be understood. ESR data have been employed to demonstrate reversible absorption of molecular oxygen by CoTPP and that the axial ligand at the fifth coordination site influences the dioxygen at the sixth coordination site of the metal. Several investigations have confirmed that an oxygen molecule activated as the superoxide moiety in a CoTPP complex abstracts the hydrogen of acetaldehyde[18] or hydrocarbons[20] to initiate the autoxidation. Therefore, for the oxidation of phenol, it is reasonable to believe that, in a like manner, CoTPP takes up an oxygen molecule to form a dioxygen intermediate that abstracts the hydrogen atom of the OH group of phenol, forming the phenoxide radical and initiating the reaction. The mechanism of oxidation of hindered phenols catalyzed by CoTPP is probably similar to that catalyzed by salcomine or CoSMDPT,[8] as shown in (1)–(6).

$$\mathrm{Co^{II}TPP} \underset{}{\overset{O_2}{\rightleftharpoons}} \mathrm{O_2{-}CoTPP} \qquad (1)$$



According to this mechanism, the cobalt TPP complex plays two important roles: (1) coordination activates the oxygen molecule and enhances its ability to abstract the hydrogen atom of phenol (reaction 2), and (2) coordination enhances the activity of oxygen molecule in the reaction with the phe-

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noxide radical, forming BQ (reactions 3 and 4).

The "non-Arrhenius" temperature dependence for the oxidation of 2,6-di-*tert*-butylphenol catalyzed by CoTPP indicates the complicated nature of the reaction mechanism. High equilibrium concentrations of the dioxygen CoTPP complex are expected at the lower temperature according to reaction 1. Higher temperatures favor increases in the rates of all subsequent reaction steps but also decrease significantly the equilibrium concentration of the dioxygen complex, which is required for the insertion reaction step 3. The sharp drop in the relative rates of formation of BQ illustrated in Figure 5 indicates that there is an optimal temperature for oxygen insertion in an intermediate temperature range. This temperature seems to be about 40 °C. With increase in temperature, the rate of the coupling reaction increases steadily. While the intrinsic insertion reaction rate also increases, the rate of formation of the insertion product BQ decreases with temperature because of the sharp drop in the solubility of dioxygen with increase in temperature.

It is interesting to note that the type of catalysis observed with Co(II)-TPP differs markedly from that observed with the other transition-metal–TPP complexes investigated (Figures 1 and 2), and it is suggested here that this difference is due to the involvement of dioxygen complexes as intermediates in oxygen insertion. The observed rates of oxidation are much higher with the cobalt catalyst. Also, the latter is the only one that produces a significant amount of quinone. According to reaction 3, a dioxygen complex would appear to be necessary for the oxygen insertion step. While the coupling reaction may be promoted by dioxygen complexes, there is no requirement that anything but an effective oxidant is needed, so that the coupling reaction may also be catalyzed by one or more of the Co(III) species present in the reaction mixture. Thus, it is seen that higher temperatures promote the coupling reaction but inhibit oxygen insertion relative to coupling (Figure 5) in accordance with the decreased solubility of dioxygen (and consequent decrease in dioxygen complex formation) at higher temperatures. From the well-known relative tendencies of transition-metal complexes toward dioxygen complex formation,[21] it is apparent that the equilibrium concentrations of dioxygen complexes are orders of magnitude greater for Co(II)–TPP than for the other transition-metal–TPP complexes, thus accounting for the observed differences in the rates of dioxygen insertion to form the benzoquinone derivative. This requirement of dioxygen complexes as intermediates in dioxygen-insertion reactions has also been observed in catalysis of DBP oxygenation with cobalt(II)–polyamine complexes.[22,23]

Acknowledgment. This research was supported by a research grant (A-259) from the Robert A. Welch Foundation.

Registry No. O_2CoTPP, 37249-49-3; CoTPP, 14172-90-8; Fe(TPP)Cl, 16456-81-8; Mn(TPP)Cl, 32195-55-4; VO(TPP), 14705-63-6; CuTPP, 14172-91-9; 2,6-di-*tert*-butyl-*p*-benzoquinone, 719-22-2; 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone, 2455-14-3.

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Contribution from the Chemistry Department, Texas A&M University, College Station, Texas 77843,
and Battelle Pacific Northwest Laboratories, Richland, Washington 99352

Formation and Stabilities of Cobalt(II) Chelates of *N*-Benzyl Triamine Schiff Bases and Their Dioxygen Complexes

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Received May 11, 1983

Equilibrium constants are reported for the formation of six new Co(II) complexes of tridentate and pentadentate *N*-benzyl triamine ligands and for their reactions with dioxygen in a 70% dioxane–30% water solvent. Procedures for synthesis of the new ligands described involve the formation of Schiff bases of 4-benzyldiethylenetriamine and 5-benzyldipropylenetriamine with salicylaldehyde and pyridine-2-carboxaldehyde and the reduction products of these Schiff bases. Complete equilibrium analysis of these ligand systems requires equilibrium studies of Schiff base components and their interactions with cobalt(II). The relationships between ligand structure and dioxygen affinities of the cobalt complexes are discussed. Stability constants and autoxidation tendencies of the dioxygen complexes indicate that the most satisfactory ligand for oxygen binding and recycling is the 4-benzyldiethylenetriamine–salicylaldehyde Schiff base.

Introduction

This research report describes the synthesis and study of a number of polyamine–Co(II) dioxygen complexes as models for the design of high polymer oxygen-carrying systems. In order to attach an oxygen carrier to a polystyrene matrix, parasubstituted methylene groups of the phenyl moieties were utilized for the attachment of the coordinating ligands of the appropriate cobalt(II) complexes. For the development of reasonable estimates of the dioxygen affinities of the monomer units of the polymers, it was decided to synthesize and investigate a series of model mononuclear complexes of the type that could be incorporated readily into the polymer. Since it is advantageous to use readily prepared chloromethylated polystyrene, the model ligands should contain a benzyl group to simulate the steric effects of the point of attachment to the polymer backbone.

Co(saldpt) had been previously attached to polystyrene supports (saldpt = bis(salicylidene)dipropylenetriamine), where it was found to be an active catalyst for the oxidation of alkylphenols.[1] The polymer attachment was through the central secondary nitrogen of dipropylenetriamine (dpt). Further, the polymer-bound Co(saldpt) was shown to reversibly coordinate dioxygen.[2] It has been suggested that large bulky groups (phenyl and benzyl) attached to the secondary nitrogen of dpt offer considerable steric blockage to the position of attack by dioxygen on Co(saldpt) type complexes.[3] Indeed,

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* To whom correspondence should be addressed at Texas A&M University.

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