Autoxidation of Substituted Phenols Catalyzed by Cobalt Schiff Base Complexes in Supercritical Carbon Dioxide

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This first study of O_2 oxidation (autoxidation) of substituted phenols catalyzed by a dioxygen carrier in supercritical carbon dioxide ($sc CO_2$) provides additional insights into the established mechanism of reactions that have been much studied in conventional solvents. As has been long believed, the cobalt(II) dioxygen carriers of the class represented by [{*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato(2−)}cobalt(II)], Co(salen*), show both oxidase and oxygenase activities during oxygenation of substituted phenols in $sc CO_2$. The catalytic autoxidation of 2,6-di-*tert*-butylphenol (DTBP) and 3,5-di-*tert*-butylphenol (35-DTBP) in $sc CO_2$ was studied by analysis of products in batch reactions with carefully controlled variables, in the presence of a large excess of O_2, at 207 bar of total pressure and a reaction temperature of 70 °C. The oxidation of 35-DTBP yielded only traces of products under the same experimental conditions that converted DTBP totally to a mixture of the oxygenation product 2,6-di-*tert*-butyl-1,4-benzoquinone (DTBQ) and the related product of radical coupling 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (TTDBQ). The effects on conversion of DTBP to products and on selectivity between the two products were studied for variations in temperature and the concentrations of catalyst, oxygen, and methylimidazole. Selectivity in favor of the O-transfer product DTBQ over the self-coupling of the phenoxy radical was observed upon changing the oxygen concentration. In contrast, selectivity remained unaffected over a wide range of temperatures and catalyst concentrations. The oxygen dependence of both the conversion and selectivity showed saturation effects identifying the dioxygen complex as the effective oxidant in both the initial radical formation step and the oxygenation of that radical. No direct reaction is observed between the electrophilic phenoxy radical and O_2.

Introduction

Supercritical carbon dioxide ($sc CO_2$) as a solvent medium for homogeneous catalytic oxidations is a dynamic and highly promising growth area;[1] recent reviews may be found elsewhere.[2] Touted advantages include the complete miscibility of oxygen in $sc CO_2$, the environmental benefit of replacing organic solvents by benign $sc CO_2$, and the inertness of CO_2 toward oxidation. A primary advantage of supercritical fluids is the pressure-tunability of density and transport properties from gaslike to liquidlike values with relatively small changes in pressure in the vicinity of the critical point. When using $sc CO_2$, pressure-tuning effects on conversion and selectivity may be investigated with minimal change in solvent dielectric constant, since the dielectric constant remains relatively unaffected during pressure tuning.[2a] When one factors in the residues associated with the manufacture of other attractive terminal oxidants, only elemental oxygen remains as the unique genuinely green oxidant. This underscores the importance of discovery and understanding of catalytic oxidations making use of O_2 . The oxidation of phenols by the oxygen complexes of cobalt(II) is among the few well-studied examples of such autoxidation reactions and is deserving of investigation in this exciting new medium. In fact, certain dialkylquinones are important to the pharmaceutical industry (vide infra).

The majority of the reported oxidation studies in $sc CO_2$ deal with the oxidation of either olefins or alkanes. Among these, only a few use dioxygen and all others organic peroxides as terminal oxidants. Although we find no reports on metal complex catalyzed phenol oxidations in $sc CO_2$, Hammond and co-workers have investigated the enzymatic oxidation of *p*-cresol and *p*-chlorophenol to their corresponding benzoquinones in this medium.[3]

The activation of O_2 by reversible coordination to cobalt complexes and its subsequent oxygenation of organic substrates are of considerable importance in applications of organic synthesis and in furthering our understanding of oxidations in biological systems.[4] The oxidation of substituted phenols to their

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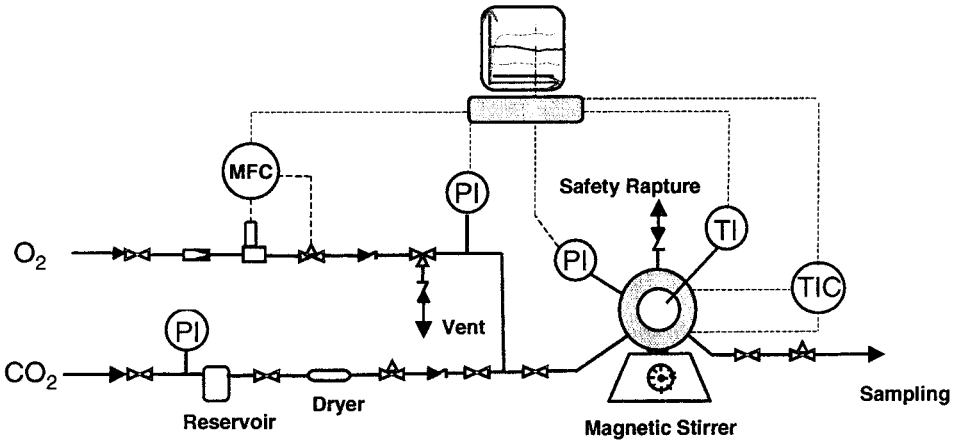

Figure 1. Schematics of the experimental setup for performing catalytic oxidations in supercritical carbon dioxide. MFC = mass flow controller, PI = pressure indicator, TI = temperature indicator, and TIC = temperature indicator control.

corresponding quinones is of interest to the pharmaceutical and perfume industries. Some alkyl-substituted quinones are intermediates along the way to certain medicinal and fragrant chemicals.[5] It has also been reported that the hydroquinone derived from 2,6-di-*tert*-butyl-1,4-benzoquinone (DTBQ) is a highly active antioxidant with possible anti-aging properties.[6] As specific examples, the family of cobalt(II) Schiff base complexes has been found to afford effective catalysts for the oxidation of phenols in a variety of organic solvents. To elucidate the reaction mechanism, several research groups have investigated the effects of varying the reaction conditions and the specific complex on the distribution of oxidation products and on the reaction kinetics.[7,8] The low solubility of oxygen in organic solvents may limit the efficiency of the catalytic reaction for some of the metal complexes. In contrast, the complete miscibility of O_2 in *sc*CO_2 provides an opportunity to investigate the intrinsic efficacy of these metal complexes without the limitation of poor oxygen miscibility, for those cases in which the catalyst and substrate are sufficiently soluble in *sc*CO_2. In this paper, we report the results of our comprehensive investigations of the activity of the well-designed and well-known cobalt Schiff complex in the oxidation of 2,6-di-*tert*-butylphenol (DTBP) in *sc*CO_2. The effects of catalyst concentration, oxygen/substrate ratio, temperature, and methylimidazole concentration on substrate conversion and product selectivity are reported, and mechanistic implications are discussed.

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Experimental Section

Solvents and Materials. HPLC grade CH_2Cl_2, for use in solvent dilution experiments and in GC and GC/MS measurements, and the catalyst [{*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato(2−)}cobalt(II)], abbreviated as Co(salen*), were purchased from Aldrich Chemical Co., Inc., and used without further treatment. The substrates 3,5-di-*tert*-butylphenol and 2,6-di-*tert*-butylphenol were purchased from Aldrich and recrystallized from either hexane or ethanol. Methylimidazole and toluene were purchased from Fisher Scientific and used as received. Coolant grade liquid CO_2, filled in cylinders with dip tubes, and cylinders of ultrahigh purity oxygen were purchased from Air Products and Chemicals, Inc.

Physical Measurements. The maximum adiabatic temperature rise for total combustion of the substrate used was estimated to be 212 K on the basis of the heat capacities of the reaction mixture, 2.5 mg of catalyst, 80 mg of DTBP, and 6.6 g of CO_2. In the practical sense the estimated pressure rise due to the temperature jump is around 47 bar. The initial temperature and pressure of the system were kept identical to experimental conditions at 70 °C and 205 bar, respectively.

A Hewlett-Packard model 5890 gas chromatograph with a model 5970 series mass-selective detector was used to obtain GC/MS data. The mass-selective detector was calibrated on the basis of the 28 and 32 amu signals for N_2 and O_2, respectively. The instrument was equipped with a 30 m Alltech RSL-160 column (5 μm thick poly(dimethylsiloxane) film, 0.32 mm i.d.). A Hewlett-Packard 5890 gas chromatograph with FID detector, equipped with the same column, was used for routine quantitative analysis of reaction products.

Apparatus. A schematic drawing of the experimental apparatus is shown in Figure 1. The apparatus is capable of operating at pressures up to 400 bar and temperatures from ambient to 300 ^{o}C. We used two reactors with different capacities (10 and 17 mL effective reactor volume). The reactors are 316 stainless steel hallow cylinders (Thar Designs) with sapphire windows at each end, sealed by O-rings and screw caps. Each reactor has five ports located on the outer body for connections to a gas inlet system, a sampling system, and a pressure transducer (Validyne DP15), and to accommodate a thermocouple and a liquid injection/safety rupture disk (HIP, 336 bar). All connections use Swagelok tube fittings.

Oxidation Reaction Experiments. For reaction studies, known amounts of a substrate and catalyst were initially charged into the reactor, in which a Teflon-coated magnetic stirring bar was placed. The reactor was closed, and methylimidazole was metered through the sampling port with a syringe. The reactor was heated with a heating tape bound around the reactor. Liquid CO_2 (Air Products, coolant grade) was pumped from the cylinder into the reactor, raising the pressure to an approximate predetermined value that was less than the ultimate operating pressure. The CO_2 was passed through a bed of Drierite to remove moisture traces. The contents of the reactor were then stirred while the system was warmed to the desired reaction temperature. With

the help of the mass flow controller (Brooks, 5850E), a predetermined amount of ultra-high-purity oxygen (Air Products, 99.99%) was charged into the reactor. Finally, more CO_2 was introduced, as necessary, to reach the desired pressure. This procedure is typically completed in 10 min. The beginning of the reaction time was defined as the moment when the reaction pressure was reached. A computer-controlled data acquisition system (Camile TG) was utilized for continuous control and/or monitoring of reactor temperature, reactor pressure, and O_2 flow rate. All experiments were run in batch mode as explained in the following section.

Sample Treatment. After a predetermined reaction time, the reactor pressure was gradually released (over 2 h) by transferring the reactor contents into a cold trap containing an organic solvent, typically methylene chloride. Following depressurization, the reactor was thoroughly washed with several injections of ethylene chloride. The trapped and washed reactor contents were mixed, and an external standard, such as toluene, was added. The mixture was further diluted with ethylene chloride to a precise 100 mL volume. Aliquots of the diluted samples were then transferred into vials and analyzed by GC/FID and/or GC/MS. A total carbon balance determination indicated less than 5% material loss during the process.

Results and Discussion

Oxidation of Substituted Phenols. Guided by the substantial literature on the subject (vide supra), DTBP and 3,5-di-*tert*-butylphenol (35-DTBP) were selected for catalytic oxidation in *sc*CO_2. In the presence of large excesses of O_2, at 207 bar of total pressure, at 70 °C reaction temperature, and with a reaction time of 21 h, the oxidation of 35-DTBP yielded only trace amounts of products. In contrast, under similar conditions, DTBP was totally converted to a mixture of DTBQ and the related product of radical coupling 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (TTDBQ). The first may be considered an oxygenation product, whereas the latter is the product of an oxidase-like reaction.

Catalyst Selection. The catalytic oxidation of substituted phenols by the oxygen complexes of cobalt has been widely studied in conventional solvents.[8] The first study that used the prototypic Schiff base formed between ethylenediamine and salicylaldehyde (salen) was reported in 1967.[9] Although that particular complex, Co(salen), was found to be insoluble in *sc*CO_2, the complex of a well-known modified salen, *N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato(2−) (salen*),[10] showed sufficient solubility to warrant detailed study in *sc*CO_2.

Effect of Temperature. The effect of temperature on the conversion of substituted phenol into products and on the selectivity of the reaction was studied from 50 to 90 °C using fixed-time batch reactions. For this study, selectivity is taken to be the percentage of corresponding substituted quinone in the product mixture. Single homogeneous phases were attained only at temperatures greater than 50 °C, and the results obtained at and above that temperature are presented in Figure 2. The conditions are a total pressure of 207 bar, O_2:DTBP:catalyst = 1500:20:1 with a methylimidazole:catalyst ratio of 1.28, and a reaction time of 21 h. The conversion of DTBP to products increased continuously from 50% to around 100% as the temperature increased from 50 to 90 °C. Unlike conversion, and of mechanistic significance, the selectivity remains almost constant at 85% over the entire temperature range.

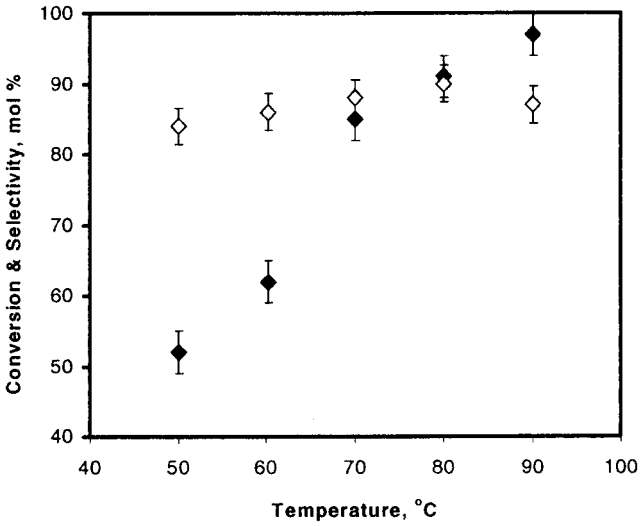
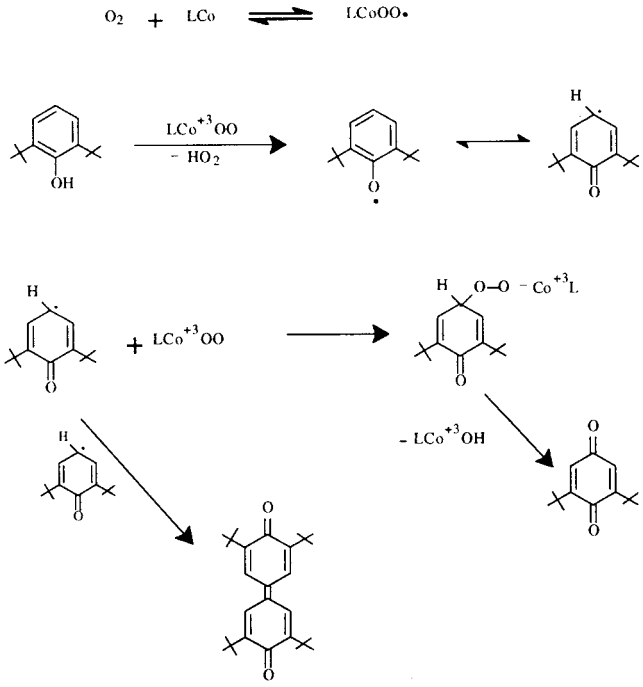


Figure 2. Conversion (◆) and selectivity (◇) for the oxygenation of DTBP by Co(salen*) at various temperatures (initial [DTBP] = 9.2 mM; [Co(salen*)] = 0.46 mM; [O_2] = 690 mM; [Me-Im] = 0.59 mM; p_{total} = 207 bar; reaction time = 21 h). Selectivity = ([DTBQ] × 100)/{[TTBDQ] + [DTBQ]}.

Scheme 1. Broadly Accepted Reaction Mechanism



The constant selectivity at various temperatures is mechanistically revealing because it indicates similar activation energies for the two parallel reaction pathways. Scheme 1 represents the mechanism as described in the literature. Accumulated understanding requires that the pathways to both products begin with the formation of a common radical, the phenoxy radical, and this appears to be the rate-determining event. Selectivity is determined by competition between oxygenation of the first-formed radical and its dimerization. If the activation energies of the parallel reactions were different and of significant magnitude, one would expect the selectivity to change with temperature. The obvious conclusion is that the competing processes have very similar activation energies, and this is consistent with the usual proposal that both involve radical reactions, having very small activation enthalpies. Alternative mechanistic models would require coincidentally similar activa-

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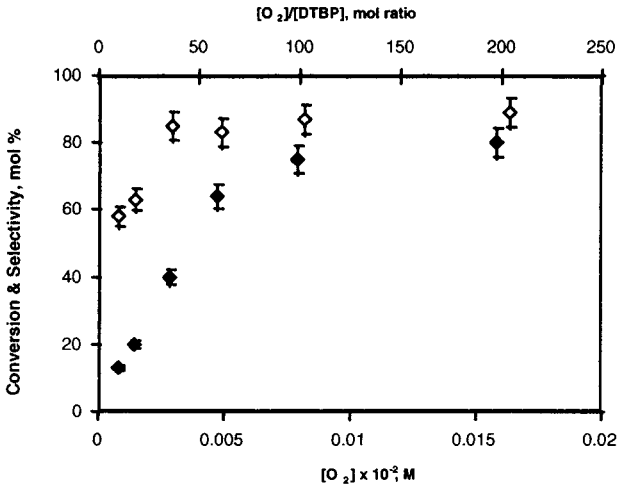

Figure 3. Conversion (◆) and selectivity (◇) for the oxygenation of DTBP by Co(salen*) at various oxygen concentrations (initial [DTBP] = 9.2 mM; [Co(salen*)] = 0.46 mM; [Me-Im] = 0.59 mM; p_{total} = 207 bar; T = 70 °C; reaction time = 21 h). Selectivity = ([DTBQ] × 100)/{[TTBDQ] + [DTBQ]}.

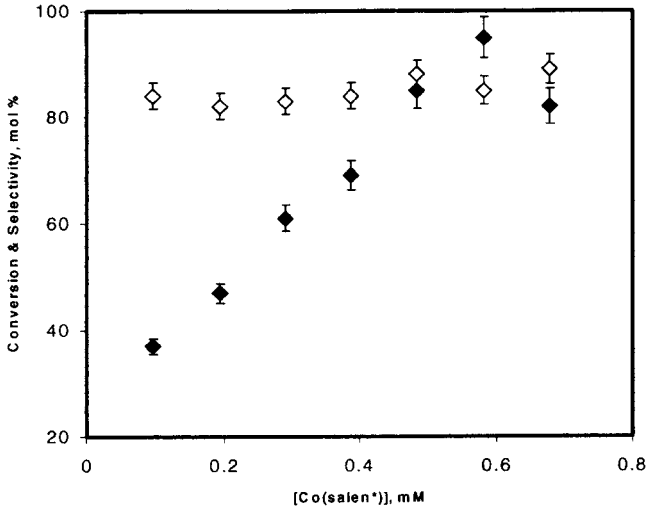

Figure 4. Conversion (◆) and selectivity (◇) for the oxygenation of DTBP by Co(salen*) at various catalyst concentrations (initial [DTBP] = 9.2 mM; [O_2] = 690 mM; p_{total} = 207 bar; T = 70 °C; reaction time = 21 h). Selectivity = ([DTBQ] × 100)/{[TTBDQ] + [DTBQ]}.

tion enthalpies and imply that the radical coupling is not rate-determining for formation of the coupling product, an unlikely scenario. The constant selectivity is also an indication that the mobility of the radicals and/or the transport properties (diffusivity and viscosity) of the medium do not change significantly within this temperature range. Thus, the temperature independence of the selectivity in these simple batch reactions is revealing with respect to both mechanistic and transport properties.

Effect of Oxygen Concentration. Whereas oxygen solubility in all conventional organic solvents is limited, O_2 is completely miscible with *sc*CO_2. In this study, the molar ratio of oxygen to substrate was varied while the other reaction parameters were held constant. In Figure 3, the conversion and selectivity are plotted against [O_2]/[DTBP] molar ratios, with those values varying from 0 to 200. The conversion increases linearly with the oxygen concentration for [O_2]/[DTBP] less than 100, and reaches saturation for greater values of this ratio. The curve is typical of the oxygen dependence associated with the formation of an oxygen complex by a metal ion derivative.[11] From this, it is clear that the oxygen complex, and not free oxygen, is responsible for the conversion of the phenol into products.

As shown in Scheme 1, in the accepted mechanism for phenol oxidation by these cobalt complexes, the oxygen adduct plays two major roles: (1) in the rate-determining step, it abstracts a hydrogen atom from the phenol, forming a phenoxy radical, and (2) a second molecule of the same adduct links its bound O_2 moiety to a phenoxy radical in the initial step of the oxygenation process. Focusing on the first role, the cobalt complex both activates the dioxygen by coordinating to it and facilitates the acceptance of an electron to generate the phenoxy radical. Increasing the oxygen concentration in solution increases the abundance of the $LCo^{III}OO\cdot$ species, and since $LCo^{III}OO\cdot$ is responsible for the formation of the phenoxy radical, its abundance determines the reaction rate. Given that the formation of the phenoxy radical is rate-limiting and that it is produced by reaction of the phenol with $LCo^{III}OO\cdot$, the presence of oxygen in excess of that necessary to convert all of the cobalt into its oxygen adduct has no effect on conversion of reactants to products.

As shown in Figure 3, an increase in oxygen concentration increases the selectivity of DTBQ, but similar to the conversion behavior, the selectivity reaches saturation as [O_2]/[DTBP] continues to increase. To form DTBQ, it is necessary that a phenoxy radical capture an oxygen atom from some source. Clearly the reaction is not affected by oxygen in excess of the concentration necessary to convert all of the cobalt into the oxygen complex. The revealing conclusion is that this saturation dependence identifies the cobalt oxygen complex $LCo^{III}OO\cdot$, and not O_2, as the reagent responsible for the initial oxygenation of the phenoxy radical. The slight increase in the DTBQ selectivity at lower [O_2]/[DTBP] values is attributed to the increase in relative abundance of $LCo^{III}OO\cdot$ in this range. The fact that the selectivity remains constant thereafter suggests that the electrophilic phenoxy radical does not react with molecular oxygen. In summary, the only pathway leading to DTBQ formation is the radical coupling between the phenoxy radical and $LCo^{III}OO\cdot$.

Effect of Catalyst Concentration. The effects of catalyst concentration on the conversion and selectivity of DTBP oxidation are summarized in Figure 4. At 70 °C, the selectivity favoring DTBQ formation remains constant at 85% as the concentration of the catalyst increases. In contrast, the conversion to products is not monotonic in its catalyst dependence. As expected for a homogeneous catalytic process, the conversion increases linearly with catalyst concentration over most of the available range of the variable, but eventually it decreases. This decline in activity at higher catalyst concentrations is claimed on the basis of a single concentration point. In defense of this conclusion, these data are the results of multiple determinations and the error bars are appropriate. Koda and co-workers reported similar observations in the aerobic oxidation of cyclohexane catalyzed by {5,10,15,20-tetrabis(pentafluorophenyl)porphyrinato}iron(III) chloride (PFTPPFeCl).[1d] The decrease in conversion at high catalyst concentrations could arise from competitive formation of catalytically inactive dimeric μ-oxo- and/or μ-peroxo-bridged dicobalt species. Such dimeric cobalt species are not active in catalyzing this reaction. The accompanying loss in catalyst concentration would affect the parallel reactions that produce DTBQ and TTDBQ equally, and this is consistent with the insensitivity of selectivity to catalyst concentration.

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Effect of Methylimidazole Concentration. The beneficial effects of methylimidazole are 2-fold. Methylimidazole enhances catalyst activity when it binds to the cobalt center by favoring formation of the oxygen adduct,[12] and it increases the solubility of the catalyst in the *sc*CO_2 medium. The improved catalyst solubility is attributed to both a cosolvent effect and also methylimidazole, when bound to the cobalt, amplifying the nonpolar character of the catalyst molecule. The total conversion of DTBP increases with increasing methylimidazole concentration, but only to the point where the amount added is the molar equivalent of the catalyst concentration. Since the binding affinity between the first equivalent of *N*-methylimidazole and cobalt(II) is great, at equimolar concentrations, all the cobalt centers are expected to bind to this ligand and form five-coordinate species that are excellent O_2 binding sites. The addition of this base in amounts greater than the first molar equivalent has deleterious effects, because binding of a second mole of methylimidazole results in the formation of the coordinately saturated, six-coordinated cobalt complex, which no longer has a site available for binding to dioxygen. This accounts for the decline in total conversion as the concentration of the base increases beyond the first mole. The decline proceeds at a modest rate because the affinity of the cobalt(II) for the second mole of methylimidazole is not great.

It is highly meaningful and critical to the understanding of this very interesting process that selectivity behaves in an entirely parallel fashion. As the molar ratio of methylimidazole increases from 0 to 1, the conversion of reactant to products increases by only 8% while the selectivity jumps by 37%. The 37% jump in selectivity shows that the oxygenation of the phenoxy radical is favored in the presence of methylimidazole. In turn that is consistent with the higher O_2 affinity of the cobalt complex having methylimidazole as its axial ligand. We suggest that there is also a second advantage. Not only does the oxygen complex equilibrium saturate at lower oxygen concentration, but the metal center is relatively electron rich and more effective at reacting with electrophilic radicals.

Reaction Mechanism. The mechanism described earlier for the cobalt(II)-catalyzed oxygenation of phenols has been extensively studied by a number of research groups, including ours,[7,8,13] and this is summarized in Scheme 1. As first suggested by Nishinnaga[4c] and later confirmed by Drago and co-workers, using EPR studies,[14] the $LCo^{III}OO\cdot$ species abstracts a hydrogen atom from DTBP, producing the phenoxy radical. Competing parallel pathways then lead either to oxygenation by coupling between the phenoxy radical and a second mole of $LCo^{III}OO\cdot$ or to TTDBQ by the coupling of 2 mol of the phenoxy radical. Our results are fully consistent with that model, dramatizing some of the relationships. The dioxygen and *N*-methylimidazole dependences strongly support preequilibrium formation of the primary oxidant, the dioxygen complex. The importance of the oxygen complex as the sole oxidant is established by the fact that both conversion and selectivity show the same dioxygen and *N*-methylimidazole dependences. The temperature dependence of the selectivity is easily explainable only on the basis that the two parallel reactions that determine the selectivity are both radical reactions with small activation enthalpies.

Some questions remain even for these much studied systems. As shown in Scheme 1, the first step of the mechanism produces the phenoxy radical along with the peroxide complex of cobalt(III), $LCo^{III}OOH$. Further, the step in which the phenoxy radical is oxygenated produces an equivalent of $LCo^{III}OH$. This introduces intrinsic complications in the system that have not been resolved: (1) How does the catalyst recycle from these two products? (2) What is the fate of the hydrogen peroxide? Our results agree with those in other media; the reaction is truly catalytic so that catalyst turnover is a facile, if partially understood, process.

Also, what determines the selectivity of this chemical reaction system? The frequency of the oxygenation process relative to that of the radical dimerization process, called the *oxygenation frequency*, reveals how selective the process is under a given set of conditions. On the basis of the accepted general mechanism and the corresponding stoichiometry, the commonly observed selectivity of 85% represents an oxygenation frequency of approximately 6. As discussed above changes in reaction temperature and in the concentrations of solution components (O_2, catalyst, and methylimidazole) all affect the total conversion of DTBP to its oxidation products, but the selectivity is affected only by changes in the concentrations of O_2 and methylimidazole. Since increasing these concentrations promotes saturation of the preequilibrium formation of the oxygen complex, it may be concluded that the formation of $LCo^{III}OO$ is the key to selectivity. The critical intermediate in the oxygenation process, $LCo^{III}OO-C_6H_3R_2O$, is an example of a family of organic peroxo complexes of cobalt(III) that have become well-known in the past several years.[15] In this medium, as in others, $LCo^{III}OO-C_6H_3R_2O$ undergoes distinctly clean reactions, cleaving the O−O bond heterolytically, and forming only DTBQ and TTDBQ. Finally, the results of this study have shown that *sc*CO_2 is a suitable solvent for the cobalt Schiff base catalyzed oxidation of DTBP, and that the system can be tuned for product-selective oxidation.

Comparison with Oxidations in Organic Solvents. Over the years a number of cobalt(II) complexes have been used as catalysts for phenol oxidations.[19] The results of some of these studies are summarized in Table 1. All except $Co_{0.5}H_6PMo_8V_4O_{40}^{4-}$ are homogeneous systems, and all use O_2 as the terminal oxidant. In all systems, oxidations were performed with an excess of O_2. Systems 1 and 2 oxidize 2,6-dimethylphenol using the cobalt complex based on the pentadentate Schiff base ligand (SMDTP) catalyst in the nonpolar solvents benzene and toluene. The rest of the systems in Table 1 use DTBP as substrate and polar solvents. From Table 1, it is evident that catalytic efficiency and product selectivity are dependent on solvent, temperature, substrate:catalyst mole ratio, and the nature of the catalyst. For example, systems 1 and 2 use similar solvents, but the smaller substrate:catalyst ratio in system 1 resulted in higher selectivity, but with a decreased conversion. However, relationships of this kind are only valid for a given reaction system. A contrast is found in the $Co_{0.5}H_6PMo_8V_4O_{40}^{4-}$

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(19) Abbreviations for the catalysts: SMDTP is bis(3-salicylideneaminopropyl)methylaminato; MeVD is from a family of cyclidene ligands with the chemical name methylene(piperazineEthi)$_2$Me$_2$[16]tetraene-N$_4$; TPP is 5,10,15,20-tetraphenylporphyrinato; $Co_{0.5}H_6PMo_8V_4O_{40}^{4-}$ is Co−Mo−V base heteropolyacid. The chemical structures of the cobalt(II) complex of the ligands are shown in Figure 5.

Table 1. Comparison with Other Oxidation Systems Performed in Organic Solvents

catalyst	solvent	*T* (°C)	time (h)	substrate:catalyst ratio	conversion (%)	selectivity (%)	ref
(1) Co(SMDTP)	benzene	30		20	67	86	16
(2) Co(SMDTP)	toluene	25	24	384	100	43	8g
(3) Co(TPP)	DMF	70	10	100	40	25	17
(4) $Co_{0.5}H_6PMo_8V_4O_{40}^{4-}$	chloroform	60	1	7.5	100	56	18
(5) $[CoMeVD](PF_6)_2$	acetonitrile	25	24	10	37	27	13a
(6) Co(salen*)	acetonitrile	25	16	20	24	69	
(7) Co(salen*)	methylene chloride	25	16	20	20	80	

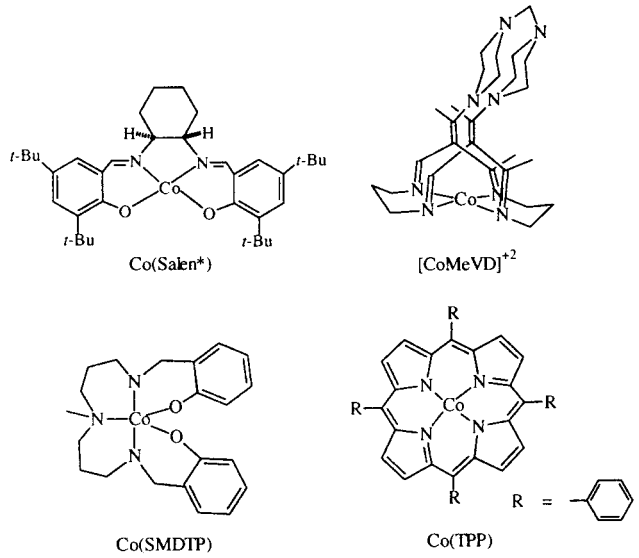

Figure 5. List of chemical structures of catalysts used in the oxidation of substituted phenols.

system, where a low substrate:catalyst ratio of 7.5 produced only 56% selectivity. From systems 6 and 7 (our data), it is also clear that the results are dependent on the nature of the solvent. One may conclude that it is only appropriate to compare efficiency and selectivity from system to system, recognizing that mechanisms and kinetic behavior may be very different.

Given sufficient reaction time, several of the systems presented in Table 1 gave 100% conversion. However, complete selectivity to the quinone is not reported. On the basis of our study, the solvent medium *sc*CO_2 provides some guidance toward resolving that issue. As shown in Figure 3, the selectivity increases to more than 90% at an $[O_2]/[DTBP]$ ratio of 200. Because of the complete miscibility of O_2 in *sc*CO_2, there is relatively little limit on accessible O_2 concentrations so that still greater selectivity is possible. The low solubilities of O_2 in organic solvents place those media at a clear disadvantage because attaining the requisite high O_2 concentrations is impractical for their solutions. It follows that *sc*CO_2 is a preferred reaction medium for complete conversion of reactant phenols and unit selectivity in favor of quinone as the product.

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Supporting Information Available: One figure showing the variation in conversion and selectivity with concentration of the axial ligand *N*-methylimidazole. This material is available free of charge via the Internet at http://pubs.acs.org.

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