



Autoxidation of 2,6-di-*tert*-butylphenol with cobalt Schiff base catalysts by oxygen in CO₂-expanded liquids

Ming Wei,^a Ghezai T. Musie,^b Daryle H. Busch^{*bc} and Bala Subramaniam^{ac}

^a Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, KS 66045-2223, USA

^b Department of Chemistry, The University of Kansas, Lawrence, KS 66045-2223, USA

^c Center for Environmentally Beneficial Catalysis, The University of Kansas, Lawrence, KS, USA

Received 1st September 2003, Accepted 19th January 2004

First published as an Advance Article on the web 4th February 2004

CO₂-expanded acetonitrile and methylene chloride have been used in this first detailed study of catalytic O₂ oxidations in these remarkably effective reaction media. The autoxidation of 2,6-di-*tert*-butylphenol (DTBP) with the cobalt Schiff-base (Co(salen*)) in these so-called CO₂-expanded liquids (CXLs) has been extensively studied using precisely controlled and monitored batch reactions. The dependence of conversion, selectivity and turn-over-frequency on various reaction parameters, including temperature, [O₂], [catalyst], and solvent composition has been evaluated. The rates of O₂-oxidation in CXLs are typically 1–2 orders of magnitude greater than those obtained with either the neat organic solvent or supercritical CO₂ as reaction media. In keeping with the proposed mechanism, the dependence of both the selectivity and conversion on O₂ concentration and catalyst concentration indicates that the O₂ adduct, and not free O₂, serves as oxidant in two critical steps in these systems. The increase in conversion with increasing temperature supports formation of the phenoxy radical as the rate determining step. In contrast, the temperature independence of selectivity is as expected for two competing radical coupling reactions. The balance between O₂ solubility and mixed-solvent dielectric constant determines some of the benefits of the CXLs. Because of the greatly increased solubility of O₂ in CXLs, the conversion in those media is substantially greater than that in either *sc*CO₂ or the neat organic solvent. However, conversion eventually decreases with increasing CO₂ content of the solvent because of the decreasing dielectric constant of the medium. The solubilities of O₂ and Co(salen*) have been determined in CXLs based on methylene chloride.

Introduction

This work exploits the beneficial chemical and physical properties of mixed solvents containing liquid CO₂ (abbreviated CXLs) to perform homogeneous catalytic oxidations. CXLs are produced by condensing relatively large amounts of sub-critical CO₂ into fixed amounts of an organic solvent. Each CO₂-expanded solvent may, in principle, generate a continuum of media ranging from the neat organic solvent to neat CO₂. Thus, the solvent properties may be varied to accommodate contrasting solubilities simultaneously, like those of permanent gases (O₂, H₂ and CO) and homogeneous catalysts based on metallic elements. A large amount of CO₂ favors oxygen solubility and polar organic solvents favor metal catalyst solubility. CXLs have been exploited for performing homogeneous catalysis, including hydrogenations,^{1a–c} oxidations,^{1d–f} and hydroformylations.^{1g} In the referenced applications, dense phase CO₂ is partnered with a variety of solvents such as methanol,^{1a} acetonitrile,^{1d,e} and ionic liquids.^{1c,f,g}

Reactions in CXLs benefit both in terms of improved behavior of the fundamental chemical processes and potential benefits to the environment as shown elsewhere.^{1d,e}

Reaction advantages of CXLs:

- higher oxygen miscibility (as much as two orders of magnitude) compared to organic solvents
- adequate solubility of transition metal catalysts without such ligand modifications as the use of environmentally deleterious fluorination
- enhanced turnover frequencies
- comparable or better product selectivities than in neat organic solvent or *sc*CO₂
- facile catalyst separation following the reaction cycle, by adding more CO₂ and adjusting the temperature

Environmental and economic advantages:

- substantial (up to ~80 vol%) replacement of organic solvents with dense-phase CO₂

- milder process pressure (tens of bars) compared to *sc*CO₂ (hundreds of bars)

• operation with CO₂-based media in the near-critical region (where the specific heat increases with isothermal pressure increases) lessens the risk of reaction runaway and explosions²

- enhanced reaction rates and low process pressures yield process economics that are favorable over those for *sc*CO₂

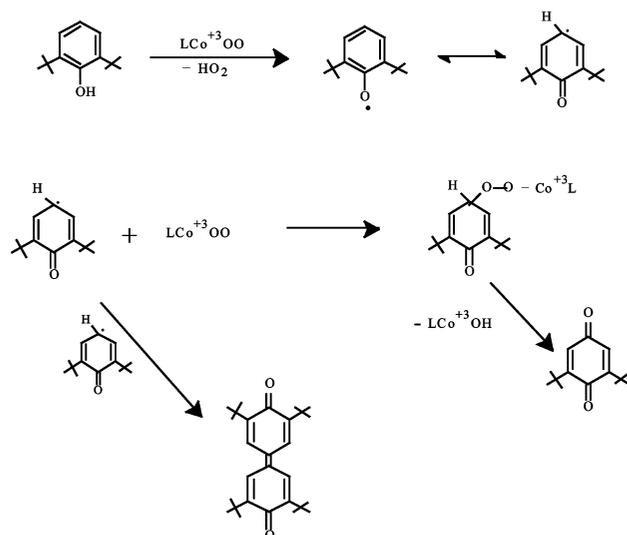
As reviewed elsewhere,^{1d,3} homogeneous “green” oxidation in *sc*CO₂ as the solvent, has been the focus of many investigations. Carbon dioxide is non-toxic, not subject to oxidation, non-flammable, inexpensive, recyclable and has a relatively low critical temperature (31.1 °C) and moderate critical pressure (73.8 bar). The application of CO₂ in catalytic chemistry and reaction engineering satisfies several of the green chemistry and engineering principles.⁴ For instance, dense phases of CO₂ are considered benign alternatives to traditional organic solvents. Further, since traditional organic solvents will always emit their vapors, replacement with CO₂ represents pollution prevention. Further, the toxicity of CO₂ is lower than those of many organic solvents and CO₂ is abundantly available.

During the last decade, many of the advantages of *sc*CO₂ have been demonstrated for chemical reactions on a laboratory scale. While it is recognized that performing catalytic reactions in *sc*CO₂ offers maximum environmental benefit, there exist major barriers impeding the application of CO₂ in industrial chemical processes. In many cases, *sc*CO₂-based homogeneous catalytic reactions are limited by inadequate solubilities of preferred homogeneous catalysts. In addition, CO₂ is non-polar with a non-tunable dielectric constant, which usually results in lower reaction rates compared to those attained with conventional organic solvents. Furthermore, high process pressures (hundreds of bars) are required in most reported applications. This combination of high pressures and low reaction rates clearly does not favor process economics.

We report here a systematic study of homogeneous catalytic oxidation of 2,6-di-*tert*-butylphenol (DTBP) by molecular oxygen

in CO₂-expanded solvent media, CXLs, using cobalt(II) Schiff base complexes as catalysts. This reaction has been studied well in both heterogeneous⁵ and homogeneous⁶ systems, as well as in *sc*CO₂.⁷ DTBP is converted to a mixture of 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'-diphenylquinone (TTDBQ).

Scheme 1 shows the mechanism proposed for this reaction in most media. The first step is rate determining and involves



Scheme 1 The broadly accepted mechanism for the oxidation of 2,6-di-*tert*-butyl phenol by Schiff base cobalt catalysts: Co(salen*) and Co(salen).

conversion of phenol to the phenoxy radical by the oxygen adduct of the catalyst [Co(salen*)O₂]. Subsequently, two parallel reactions compete: capture of the phenoxy radical by a second mole of the oxygen adduct leads to DTBQ, the desired product; the coupling of two phenoxy radicals ultimately yields TTDBQ. In the work that follows, we specifically address the following questions:

1. How do the efficacies of the reactions in CXLs compare with those in *sc*CO₂ or neat organic solvent?
2. How do the operating variables (pressure, temperature, and extent of solvent replacement by CO₂) affect the turnover frequency and product selectivity?
3. How does the mechanism of the O₂ oxidation reaction change in going from *sc*CO₂ or neat organic solvent to CXLs?
4. How does the replacement of an organic solvent by CXLs affect catalyst and oxygen solubilities?

Methylene chloride and acetonitrile are employed as solvents that are expanded by carbon dioxide to provide the new reaction media, CXLs. Our previous studies of this reaction system in CO₂-expanded acetonitrile^{1e} and in *sc*CO₂⁷ provide the bases for comparison.

Experimental section

Apparatus

The experimental units and procedures for measuring the solubilities of oxygen and of the catalyst complexes in CO₂-expanded solvents, including safety features and analytical methods for measuring O₂ concentrations, are described in detail elsewhere.^{1d,e,7} The catalytic oxidation studies, including conversion and selectivity measurements, were performed in specially constructed batch view cells as described elsewhere.⁷

Materials

HPLC grade CH₃CN and CH₂Cl₂, and the catalysts, [(*N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)1,2-cyclohexanediaminato-

(2-)-cobalt(II)], (*i.e.*, Co(salen*)), and, [(*N,N'*-Bis(salicylidene)1,2-cyclohexanediaminato(2-)-cobalt(II)], (*i.e.*, Co(salen)), were purchased from Aldrich Chemical Co., Inc., and used without further treatment. The substrate 2,6-di-*tert*-butylphenol (DTBP) was purchased from Aldrich Chemical Co., Inc., and recrystallized from hexane. Methylimidazole and toluene were purchased from Fisher Scientific and used as received. Coolant grade liquid CO₂, in cylinders with dip tubes, and cylinders of ultra high purity oxygen were purchased from Air Products and Chemicals, Inc.

Results and discussion

Oxidation of substituted phenols by transition metal complexes

Previous studies in these laboratories provided strong support for the mechanism given in Scheme 1 for the O₂ oxidation of DTBP in *sc*CO₂ as the solvent and using Co(salen*) for the catalyst.⁷ The same reaction has now been studied in two families of CXLs using precisely controlled and monitored batch reactions. The influences of reaction parameters (oxygen concentration, catalyst concentration, reaction temperature, and expansion ratio) on DTBP conversion and DTBQ selectivity during the oxidation reaction were determined. The fixed values of the operating parameters are as follows: catalyst concentration, 0.416 mM; reaction temperature, 60 °C; reaction time, 2 h; catalyst : substrate : O₂ mole ratio, 1 : 80 : 800; expansion fold (V/V₀), 2; mole ratio of methyl imidazole to catalyst 1.28; solvent, CH₃CN; effective reaction volume, 10 mL. In a given set of experiments, any of these parameters may be chosen as a reaction variable.

Fig. 1 shows that the DTBP conversion and DTBQ selectivity remain virtually constant when the [O₂] increases from 33.3 mM to

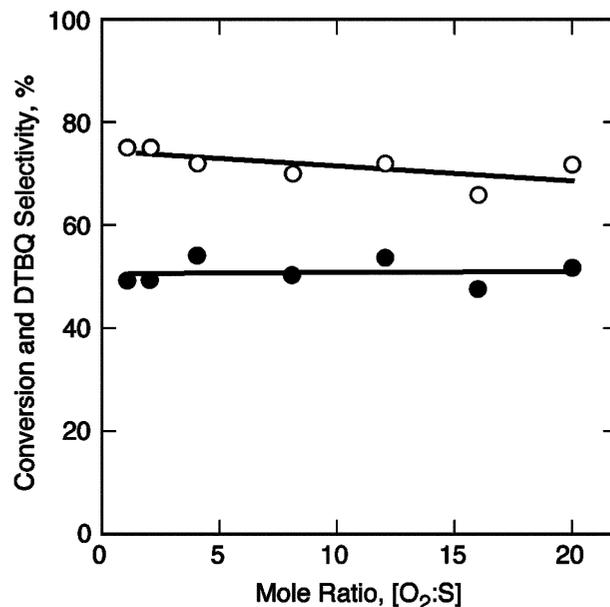


Fig. 1 Effect of O₂ concentration on DTBP (●) conversion and DTBQ selectivity (○) in CO₂-expanded CH₃CN. Reaction conditions: catalyst [Co(salen*)] concentration = 0.416 mM; reaction time = 2 h; reaction temperature = 60 °C; DTBP: catalyst mole ratio = 1:80; expansion ratio (V/V₀) = 2; volume of methyl imidazole = 2 μL.

667 mM. A different behavior is observed in *sc*CO₂⁷ where the DTBP conversion and DTBQ selectivity increase linearly with the oxygen concentration for [O₂]/[DTBP] ratios less than 100, and only reach saturation for greater values of this ratio. The obvious conclusion in both cases is that free oxygen does not contribute to the reactions that determine the conversion and selectivity of these systems. It follows that the cobalt oxygen complex, [Co(salen*)O₂], and not O₂, is the reagent responsible for the initial oxidation, producing the phenoxy radical, and that the only pathway leading to DTBQ formation is the radical coupling

between the phenoxy radical and $[\text{Co}(\text{salen}^*)\text{O}_2]$.⁷ Because O_2 is totally miscible in $sc\text{CO}_2$, the observed saturation behavior in CXLs at much lower $[\text{O}_2]/[\text{DTBP}]$ ratios cannot be attributed to O_2 solubility considerations. However, it seems plausible that the higher dielectric constant in this CXL (due to the presence of acetonitrile) may stabilize $[\text{Co}(\text{salen}^*)\text{O}_2]$ at lower O_2 concentrations compared to $sc\text{CO}_2$, which has a very low dielectric constant. The binding of O_2 to cobalt(II) formally constitutes a redox process producing cobalt(III) and the bound superoxide ion, a highly polar grouping.⁸ Because it is the oxygen adduct, $[\text{Co}(\text{salen}^*)\text{O}_2]$, that oxidizes DTBP to the phenoxy radical and, subsequently, oxidizes that radical to DTBQ, its abundance determines two of the three important reaction rates. (The third reaction is radical-radical coupling between phenoxy radicals.) Therefore, the presence of excess free O_2 is not expected to significantly influence conversion rates and product distribution.

In Fig. 2, the DTBP conversion and DTBQ selectivity are shown as functions of reaction temperature in fixed-time, batch studies.

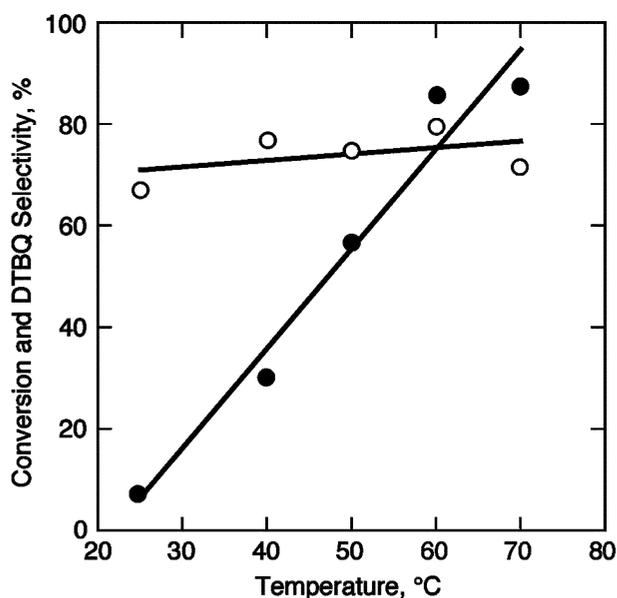


Fig. 2 Effect of temperature on DTBP conversion (●) and DTBQ selectivity (○) in CO_2 -expanded CH_3CN . Reaction conditions: catalyst $[\text{Co}(\text{salen}^*)]$ concentration = 0.25 mg mL^{-1} ; reaction time = 2 h; catalyst : substrate : O_2 mole ratio = 1 : 80 : 800; expansion fold (V/V_0) = 2; volume of methyl imidazole = $2 \mu\text{L}$.

The DTBP conversion increased monotonically from 10% to approximately 90% when the temperature was increased from 25 °C to 70 °C, while the DTBQ selectivity remained virtually constant at ~75%. The constant DTBQ selectivity with increasing temperature is similar to that reported previously for this reaction system in $sc\text{CO}_2$ medium. The mechanism commonly attributed to this reaction in other media⁶ (Scheme 1) is entirely consistent with the behavior just described for the reaction conducted in a CXL. The pathways to both products begin with the formation of a common radical, the phenoxy radical, which appears to be the rate determining event. Selectivity is determined by competition between oxygenation of the first-formed radical and its dimerization. Because the activation energy is very low for radical reactions, one would not expect the product distribution to change with temperature. Thus, the mechanism given in Scheme 1 is appropriate for this reaction in both $sc\text{CO}_2$ and CXLs.

The influence of catalyst concentration on the DTBP conversion and DTBQ selectivity is shown in Fig. 3. As expected, the DTBP conversion increases with increasing catalyst concentration and reaches its highest value of 85% at a catalyst concentration of 1.3 mM, above which the catalyst precipitates and the reaction no longer occurs in a homogeneous phase. Similarly, the DTBQ selectivity increases with increasing catalyst concentration. In both

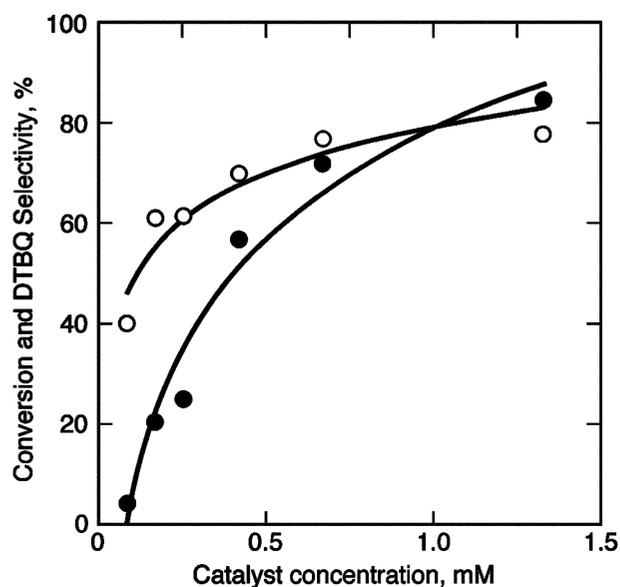


Fig. 3 Effect of catalyst $[\text{Co}(\text{salen}^*)]$ concentration on DTBP conversion (●) and DTBQ selectivity (○) in CO_2 -expanded CH_3CN . Reaction conditions: reaction time = 2 h; reaction temperature = 60 °C; substrate : O_2 mole ratio = 1 : 10; expansion ratio (V/V_0) = 2; volume of methyl imidazole = $2 \mu\text{L}$.

cases, the concentration dependence resembles that commonly observed for saturation processes. This behavior is different than the reported observation for the same reaction system in $sc\text{CO}_2$, where the selectivity was independent of catalyst concentration. This may be attributed to the lower concentration of O_2 in CXLs, compared to $sc\text{CO}_2$, in which the oxygen is completely miscible with the solvent. Under the conditions of the previously reported experiments in $sc\text{CO}_2$, the catalyst is converted entirely to the oxygen adduct at all catalyst concentrations studied; *i.e.*, the adduct formation equilibrium is always saturated. In contrast, because of the lower O_2 concentration in CXLs, the concentration of the oxygen complex, $[\text{Co}(\text{salen}^*)\text{O}_2]$, increases with catalyst concentration. Because the product distribution is determined by competition between the oxidation of the phenoxy radical and its dimerization, higher concentrations of $[\text{Co}(\text{salen}^*)\text{O}_2]$ favor the formation of DTBQ.

The O_2 concentration, the transport properties (diffusivity and viscosity) and the dielectric constant may be tuned in CXLs by simply manipulating the CO_2 fraction. With increasing CO_2 content, the O_2 solubility increases.^{1e} We speculate that the mobility of the radicals increases with CO_2 content in CXLs while the dielectric constant decreases, all relative to the neat organic solvent. Decreased dielectric constant may decrease the stability of the O_2 adduct, $[\text{Co}(\text{salen}^*)\text{O}_2]$, and increased mobility (and collisions) may cause more rapid coupling between pairs of phenoxy radicals. Thus several complicating factors add complexity to conversion and product selectivity. Fig. 4 depicts the DTBP conversion and DTBQ selectivity in CXLs at various levels of expansion. The DTBP conversion decreases with increasing levels of expansion. The reduced dielectric constant at greater levels of expansion with CO_2 hinders DTBP conversion because of the highly polar transition state for the rate determining step. The opposite trend in the case of DTBQ selectivity, which increases moderately with increasing levels of expansion, can be attributed to two factors. The increased CO_2 content increases the oxygen concentration in the liquid phase, thereby converting more of the catalyst into the O_2 adduct, and as discussed above, that favors DTBQ formation. Further, the retarded rate of conversion is, in fact, a decrease in the rate of production of phenoxy radicals, and that works against the undesirable phenoxy radical coupling reaction. The expected enhancement of transport rates with increased CO_2 content does not enter into these explanations. Fundamental studies of the variations of dielectric constant and transport properties of

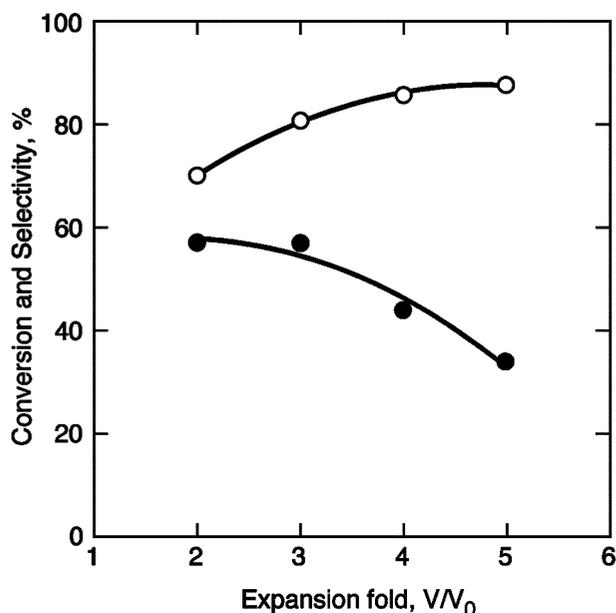


Fig. 4 Effect of solvent expansion by CO_2 on DTBP conversion (●) and DTBQ selectivity (○) in CO_2 -expanded CH_3CN . Reaction conditions: catalyst $[\text{Co}(\text{salen}^*)]$ concentration = 0.25 mg mL^{-1} ; reaction time = 2 h; reaction temperature = 60°C ; catalyst : substrate : O_2 mole ratio = 1 : 80 : 800; volume of methyl imidazole = $2 \mu\text{L}$.

CXLs, and their effects on the concentrations of various species are needed to develop a better understanding of the observed effects.

Comparison of turnover frequencies in different reaction media

The physicochemical properties of CXLs may be tuned, not only by varying the proportion of the CO_2 relative to the chosen organic solvent (as explained above), but also by varying the organic solvent itself. To better understand solvent effects, we compared the DTBP oxidation in different reaction media as follows: neat CH_3CN , scCO_2 , CO_2 -expanded CH_3CN , and CO_2 -expanded CH_2Cl_2 . The reaction conditions are as follows: catalyst concentration, 0.415 mM ; reaction time, 2 h; catalyst : substrate : O_2 mole ratio, 1 : 80 : 800; expansion (V/V_0), 2; mole ratio of methyl imidazole to catalyst, 1.28; effective reaction volume, 10 mL.

Fig. 5 compares the turnover frequency (TOF) (defined as the moles of DTBP converted per mole of catalyst per hour) as a function of reaction temperature in the different reaction media. The TOFs in CO_2 -expanded solvent media ($V/V_0 = 2$; $p = 60\text{--}90$ bars) are between one and two orders of magnitude greater than in scCO_2 ($p = 207$ bar) or neat CH_3CN . Among the CXLs, higher TOF numbers are obtained for the DTBP oxidation in CO_2 -expanded CH_3CN than for those in CH_2Cl_2 . As shown in Fig. 6, although the TOFs in CXLs are one to two orders of magnitude higher than that in scCO_2 , the DTBQ selectivity is more or less similar for all dense CO_2 phases, increasing moderately with reaction temperature. In comparison to DTBQ selectivity obtained in various organic solvents,^{1d} higher DTBQ selectivity is observed in scCO_2 and CXLs. It is not uncommon to observe "ignition" or step-type temperature dependence during oxidation reactions as we do in the case of the CO_2 -expanded CH_2Cl_2 . The reasons for the differing temperature dependence in the various CXLs are not fully understood as yet. Ongoing mechanistic investigations should provide a better understanding in this regard.

The common inexpensive $\text{Co}(\text{salen})$ catalyst is insoluble in scCO_2 and shows no detectable activity as a DTBP oxidation catalyst in that medium. In sharp contrast, $\text{Co}(\text{salen})$ shows remarkable activity in CO_2 -expanded CH_3CN . As shown in Fig. 7, the DTBP conversion increased from less than 5% to around 40% as the temperature increased from 25°C to 70°C , while the DTBQ selectivity increased from 60% to 70% over the same temperature range. This example demonstrates an important advantage of

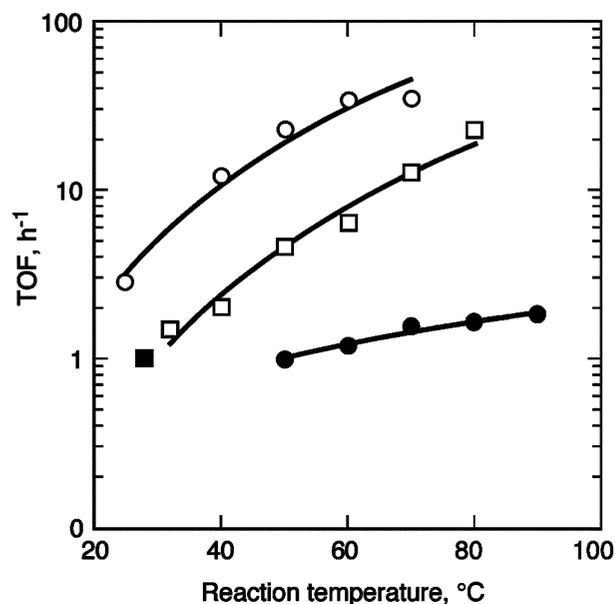


Fig. 5 Effect of temperature on turnover frequencies (TOFs) for 2,6-di-*tert*-butyl phenol oxidation with $\text{Co}(\text{Salen}^*)$ catalysts in supercritical CO_2 (●), neat CH_3CN (■), CO_2 -expanded CH_3CN (○), and CO_2 -expanded CH_2Cl_2 (□). Reaction conditions: total pressure = 1 bar (in neat solvent); 207 bar (in scCO_2) and 50–90 bar (in CO_2 -expanded solvent depending on reaction temperature); Catalyst concentration = 0.25 mg mL^{-1} ; catalyst : substrate : O_2 mole ratio = 1 : 80 : 800; volume of methyl imidazole = $2 \mu\text{L}$; $V/V_0 = 2$ (in the case of CO_2 -expanded solvent media); reaction volume = 10 mL.

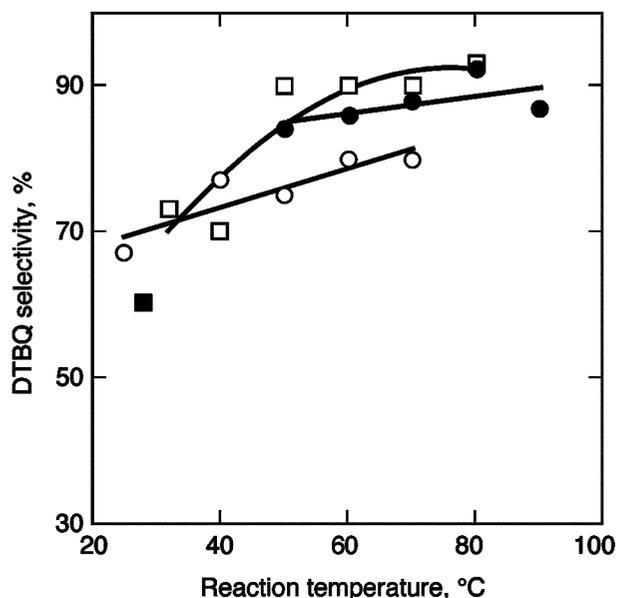


Fig. 6 Influence of reaction temperature on DTBQ selectivity during 2,6-di-*tert*-butyl phenol oxidation with $\text{Co}(\text{salen}^*)$ catalyst in supercritical CO_2 (●), neat CH_3CN (■), CO_2 -expanded CH_3CN (○), and CO_2 -expanded CH_2Cl_2 (□). Reaction conditions: total pressure = 1 bar (in neat solvent); 207 bar (in scCO_2) and 50–90 bar (in CO_2 -expanded solvent depending on reaction temperature); Catalyst concentration = 0.25 mg mL^{-1} ; catalyst : substrate : O_2 mole ratio = 1 : 80 : 800; volume of methyl imidazole = $2 \mu\text{L}$; $V/V_0 = 2$ (in the case of CO_2 -expanded solvent media); reaction volume = 10 mL.

CXLs. Because most conventional solvents are expanded by CO_2 , it is possible to dissolve most homogeneous transition metal catalysts in CXLs containing an appropriate solvent. In contrast, most unmodified transition metal complexes have inadequate solubilities in scCO_2 . These results clearly show that CO_2 -expanded solvents complement scCO_2 as reaction media by broadening the range of conventional catalyst + solvent combinations with which homogeneous O_2 -based oxidations can be performed.

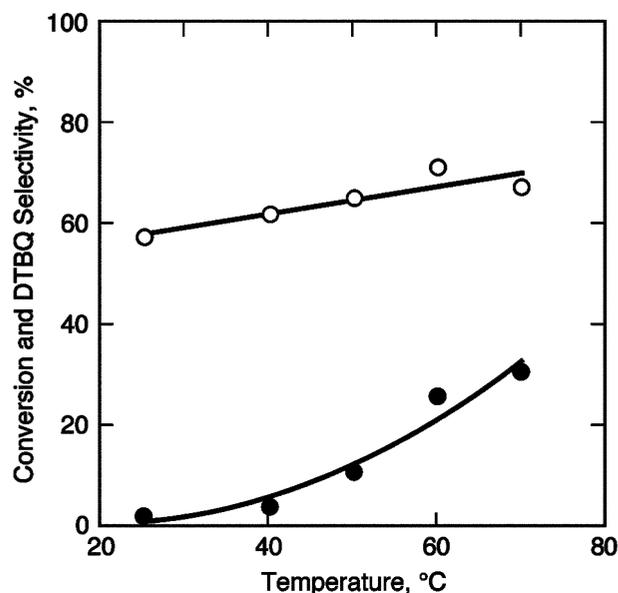


Fig. 7 Effect of reaction temperature on DTBP conversion (●) and DTBQ selectivity (○) during DTBP oxidation by O₂ in CO₂-expanded CH₃CN. Reaction conditions: catalyst [Co(salen*)] concentration = 0.25 mg mL⁻¹; reaction time = 2 h; catalyst : substrate : O₂ mole ratio = 1 : 80 : 800; expansion fold (V/V₀) = 2; volume of methyl imidazole = 2 μL.

Influence of CO₂-addition on solubility of Co(salen*) in CXLs

Adding CO₂ to CO₂-miscible solvents “expands” the solvent volume as the CO₂ pressure is increased. However, the solubilities of polar solutes in CXLs decrease upon CO₂ addition. We investigated the effect of isothermal CO₂ addition on solutions of catalyst in organic solvents. Fig. 8 shows isothermal volumetric

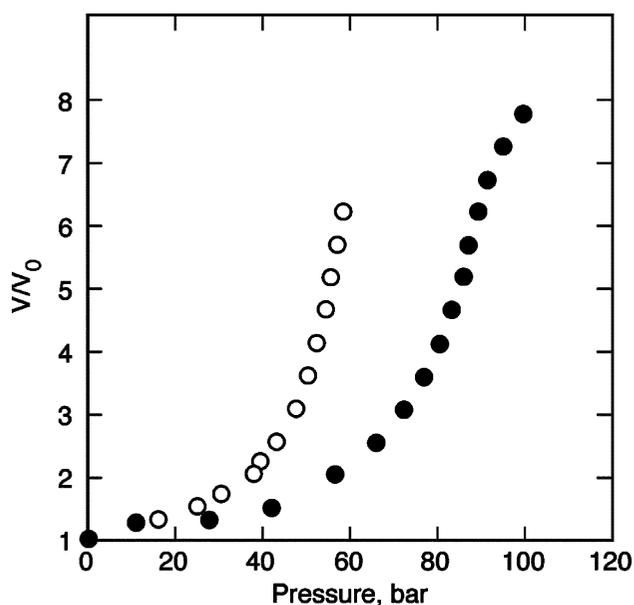


Fig. 8 Volumetric expansion of Co(Salen*) + CH₂Cl₂ solution (0.419 mM) by CO₂ at 25 °C (○) and 50 °C (●).

expansion profiles at 25 °C and 50 °C for the catalyst [N,N'-Bis(3,5-di-*tert*-butylsalicylidene)1,2-cyclohexanediaminato(2-)]cobalt(II) (abbreviated Co(salen*)) in CH₂Cl₂ (0.415 mM). As expected, higher pressures are required at higher temperatures to reach the same expansion level. At both temperatures the catalyst solubility in the expanded solvent decreases with CO₂ addition and catalyst precipitation eventually occurs at a certain expansion level, termed the “maximum homogeneous expansion limit”, MHEL. Fig. 9 shows isothermal MHEL curves for the Co(salen*)/CH₂Cl₂ system. The region below the curves represents the homogenous expanded

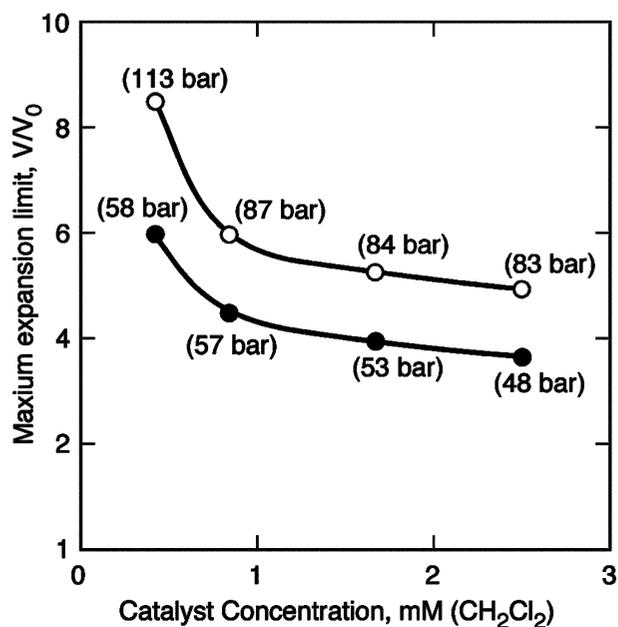


Fig. 9 Maximum limits for homogeneous expansion (MHEL) of CH₂Cl₂ + catalyst solutions by CO₂ at 25 °C (●) and 50 °C (○).

phase available for performing reactions while the region above the curves is suitable for catalyst separation, post reaction. For a given catalyst/solvent combination, the MHEL increases with temperature but decreases with increasing initial catalyst concentration. As shown in Fig. 9, the MHEL at 25 °C is roughly 5 for the 0.4 mM CH₂Cl₂ solution of the Co(Salen*) catalyst and 2.5 for the corresponding 2.5 mM solution. At 50 °C, the MHEL is roughly 4 for the 2.5 mM solution, implying that up to 80 vol.% of the organic solvent may be replaced by CO₂ in the CXL while retaining catalyst solubility. It is noteworthy that the total pressures at the MHEL are tens of bars, as compared to hundreds of bars for scCO₂. MHEL data are clearly essential to define operating conditions both for homogeneous oxidations and for catalyst separation, post reaction.

Enhancement of oxygen solubilities in CXLs

It has been a matter of contention whether O₂ is much more soluble in CXLs than in organic solvents. This issue is important because the concentration, and, therefore, the reactivity of O₂ may be critical to the rates and selectivities of catalytic reactions. We previously reported a method for measuring equilibrium O₂ concentrations in CXLs.^{1b} This method is based on directly sampling the expanded phase and the vapor phase, and employing GC/TCD analysis for measuring the O₂ concentrations in the two phases. We employed the same technique to measure O₂ concentration in liquid CO₂. As shown in Fig. 10, the measured oxygen concentrations in liquid CO₂ are in excellent agreement with the data from literature,⁹ thus confirming the reliability of our method for measuring O₂ concentration in CXLs.

As shown in Fig. 11, the measured O₂ mole fraction in the CO₂-expanded CH₂Cl₂ liquid phase (at V/V₀ = 2) increases approximately linearly with the total oxygen content of the system, the values being on the order of hundredths of a mole fraction. These values are about an order of magnitude greater than the O₂ solubility in neat CH₂Cl₂ (mole fraction = 1 × 10⁻³ at 25 °C and 1 bar¹⁰) and are of the same order of magnitude observed for liquid CO₂.⁹ In contrast, the O₂ solubility in CO₂-expanded CH₃CN is about two orders of magnitude greater than that in neat CH₃CN.^{1c} As shown in Fig. 12, the O₂ concentrations also increase linearly upon CO₂ addition, reaching ~7–8 mol % at expansion levels (V/V₀) of 7 to 8. However, such high expansions are not suitable for homogeneous reactions since the catalyst would precipitate from solution. These new results confirm the significant enhancement of

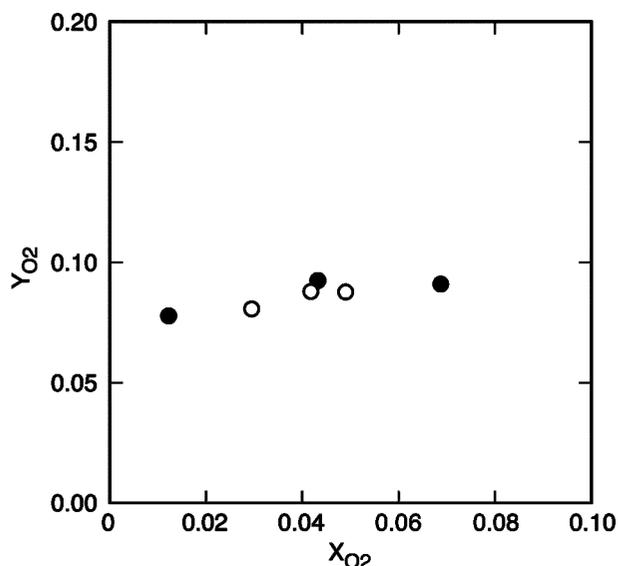


Fig. 10 Comparison of measured solubilities of oxygen in dense CO₂ at 25 °C; This study (●); Data from Battino *et al.*⁹(○).

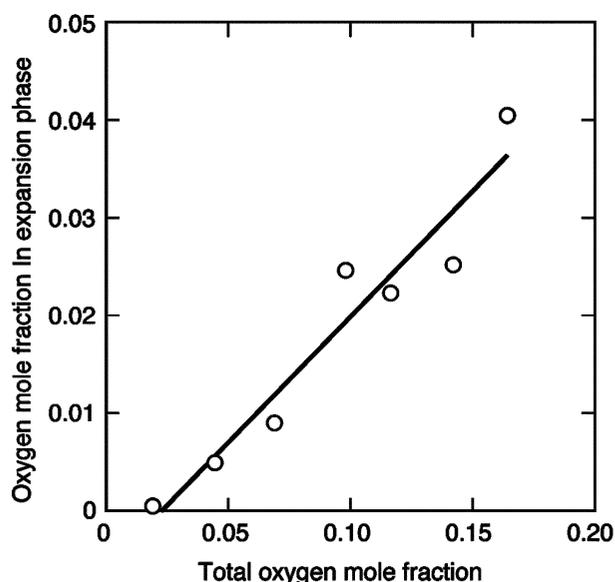


Fig. 11 Variation of O₂ mole fraction in CO₂-expanded CH₂Cl₂ ($V/V_0 = 2$) as a function of total O₂ content in the system ($T = 30$ °C).

O₂ solubilities in CXLs compared to the corresponding neat solvents, albeit the enhancement varies depending on the solvent.

Conclusion

This report demonstrates that continua of CO₂-expanded solvents (CXLs), formed by combining organic solvents and *sc*CO₂, are excellent media for catalytic oxidation reactions. The O₂ oxidation of DTBP to DTBQ with Co(salen*) as the catalyst has been investigated in CO₂-expanded solvent media based on CH₃CN and CH₂Cl₂ and the results have been compared with those obtained in *sc*CO₂, and in the neat organic solvents. Reaction rates, as estimated from turnover-frequencies, are increased by as much as two orders of magnitude over that of the reaction in *sc*CO₂ or neat organic solvents, and with comparable selectivity toward the desired oxidation product DTBQ. Thorough evaluation has been made of the effects on reaction rates and product distribution of reaction parameters (oxygen concentration, catalyst concentration, reaction temperature, extent of expansion, choice of solvent). Dependence on these parameters confirms the same general mechanism for the reactions in CXLs as has been described for other media, including *sc*CO₂.

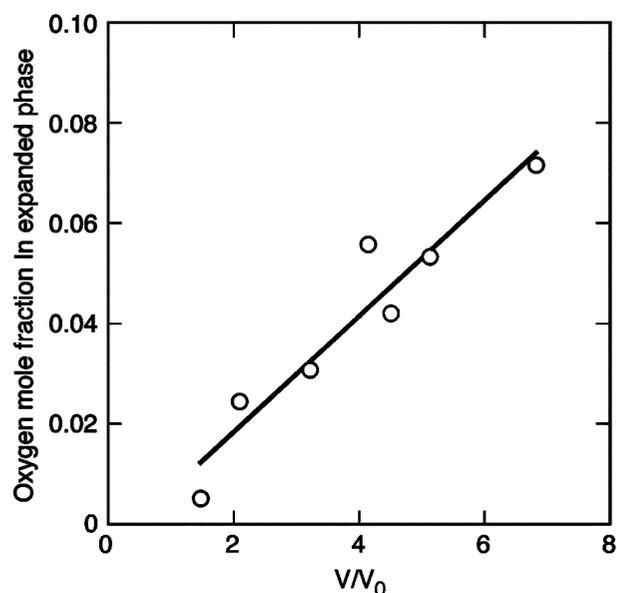


Fig. 12 Variation of O₂ concentration in CO₂-expanded CH₂Cl₂ phase with expansion ratio ($T = 30$ °C; total oxygen mole fraction in the system = 0.11).

The investigation showed that the combination of CO₂ and organic solvents facilitates control of the solubilities of two reaction partners, namely the transition metal catalyst and the preferred terminal oxidant, oxygen. The solubility of the catalyst decreases with further addition of CO₂. The catalyst can be made to precipitate by adding CO₂ in excess of the maximum homogeneous expansion limit, MHEL, which varies with the specific catalyst/solvent system, the catalyst concentration and the temperature. The oxygen solubility was measured for CH₂Cl₂-based CXLs and found to increase with CO₂ expansion. In general (2 examples now), the solubility of oxygen in CXLs exceeds that in the corresponding neat organic solvent, by 1 or 2 orders of magnitude, approximating that in liquid CO₂.

Acknowledgement

This research was supported by research grant CHE-9815321 from the National Science Foundation.

References

- (a) G. B. Combes, F. Deghani, F. P. Lucien, A. K. Dillow and N. R. Foster, in *Reaction Engineering for Pollution Prevention*, ed. M. A. Abraham and R. P. Hesketh, Elsevier, Amsterdam, 2000, 173–181; (b) C. A. Thomas, R. J. Bonilla, Y. Huang and P. G. Jessop, *Can. J. Chem.*, 2001, **79**, 719–724; (c) P. G. Jessop, R. R. Stanley, R. A. Brown, C. A. Eckert, C. L. Liotta, T. T. Ngo and P. Pollet, *Green Chem.*, 2003, **5**, 123–128; (d) G. Musie, M. Wei, B. Subramaniam and D. H. Busch, *Coord. Chem. Rev.*, 2001, **219–221**, 789–820; (e) M. Wei, G. T. Musie, D. H. Busch and B. Subramaniam, *J. Am. Chem. Soc.*, 2002, **124**(11), 2513–2517; (f) Z. Hou, B. Han, L. Gao, T. Jiang, Z. Liu, Y. Chang, X. Zhang and J. He, *New J. Chem.*, 2002, **9**, 1246–1248; (g) M. F. Sellin, P. B. Webb and T. J. Cole-Hamilton, *Chem. Commun.*, 2001, 781–782.
- H. Jin and B. Subramaniam, *Chem. Eng. Sci.*, 2003, **58**, 1897–1901.
- (a) K. W. Hutchenson, in *Supercritical Fluid Technology in Materials Science and Engineering*, ed. Y-P Sun, Marcel Dekker, New York, 2002; (b) P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1999, **99**, 475–494; *Chemical Synthesis Using Supercritical Fluids*, ed. P. G. Jessop and W. Leitner, VCH-Wiley, Weinheim, 1999; (c) E. R. Birnbaum, R. M. Le Lacheur, M. Richard, A. C. Horton and W. Tumas, *J. Mol. Catal. A*, 1999, **139**, 11–24; (d) D. R. Pesiri, D. K. Morita, W. Glaze and W. Tumas, *Chem. Commun.*, 1998, **9**, 1015–1016; (e) G. R. Haas and J. W. Kolis, *Organometallics*, 1998, **17**, 4454–4460; (f) X.-W.

- Wu, Y. Oshima and S. Koda, *Chem. Lett.*, 1997, 1045–1046; (g) E. Sahle-Demessie, M. A. Gonzalez, J. Enriquez and Q. Zhao, *Ind. Eng. Chem. Res.*, 2000, **39**, 4858–4864.
- 4 (a) P. T. Anastas and T. C. Williamson, in *Green Chemistry: Designing Chemistry for the Environment*, ACS Symposium Series, No: 626, ed. P. T. Anastas and T. C. Williamson, Am. Chem. Soc., Washington, D.C., 1996, 1–17; (b) P. T. Anastas and M. M. Kirchhoff, *Acc. Chem. Res.*, 2002, **35**, 686–694; (c) P. T. Anastas and J. B. Zimmerman, *Env. Sci. Technol.*, 2003, **37**, 94A–101A.
- 5 I. Kohara, H. Fujiyama, K. Iwai, S. Nishiyama and S. Tsuruya, *J. Mol. Catal. A: Chem.*, 2000, **153**(1–2), 93–101; I. G. Kolesnik, E. G. Zhizhina and K. I. Matveev, *J. Mol. Catal. A: Chem.*, 2000, **153**, 147–154; R. Pathak and G. N. Rao, *J. Mol. Catal. A: Chem.*, 1998, **130**(3), 215–220.
- 6 (a) Y. Deng and D. H. Busch, *Inorg. Chem.*, 1995, **34**, 6380–6386; (b) M. Yamada, K. Araki and S. Shiraishi, *J. Chem. Soc., Perkin Trans.*, 1990, 2687–2701; (c) B. B. Corden, R. S. Drago and R. P. Perito, *J. Am. Chem. Soc.*, 1985, **107**, 2903–2907; (d) R. S. Drago, J. Gaul, A. Zombeck and D. Straub, *J. Am. Chem. Soc.*, 1980, **102**, 1033–1038; (e) X.-Y. Wang, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, 1984, **22**, 271–275.
- 7 G. Musie, M. Wei, B. Subramaniam and D. H. Busch, *Inorg. Chem.*, 2001, **40**, 3336–3341.
- 8 T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, 1981, **39**, 295–283; R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139–179; G. McLendon and E. A. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1–39.
- 9 *Solubility Data Series: Volume 7, Oxygen and Ozone*, ed. R. Battino, Pergamon Press, Oxford, New York, 1981.
- 10 J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, *Regular and Related Solutions: The Solubility of Gases, Liquids, and Solids*, John Wiley, New York, 1970.