H₂O₂ in CO₂/H₂O Biphasic Systems: Green Synthesis and Epoxidation Reactions

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Hydrogen peroxide is a "green" oxidant whose relatively high cost has prevented it from being generally applied to commodity chemical processing. In large part, the attributes of the current H_2O_2 process (the anthraquinone, or AQ, route) that contribute to its high cost also contribute to its nonsustainable features: byproduct streams, high energy input and solvent usage, and multiple required unit operations. We have explored the generation of hydrogen peroxide directly from hydrogen and oxygen using liquid CO_2 as the solvent. Producing H_2O_2 directly from H_2 and O_2 in the presence of a CO_2-soluble Pd catalyst could potentially eliminate entire unit operations and reduce raw material costs significantly. Further, homogeneous reaction in liquid CO_2 allows for contact between significant concentrations of O_2 and H_2, high rates of reaction, and ready recovery of the product via stripping into water. Both Pd(+2) and Pd(0) catalysts were explored for the reaction; our results suggest that future work should focus on the optimization of a CO_2-soluble or -dispersible Pd(0) catalyst. Finally, we have found that CO_2/H_2O_2/H_2O mixtures are, themselves, useful reagent systems. A biphasic aqueous H_2O_2/CO_2 mixture is an efficient epoxidizing system, where HCO_4^- is formed through various reactions of water, CO_2, and H_2O_2 and transfers of oxygen to alkenes. From our results, it appears that H_2O_2 can react directly with CO_2, producing more percarbonate ion than in situations that employ only bicarbonate as the precursor.

Introduction

Hydrogen peroxide is widely accepted as a green oxidant, as it is easy to handle and relatively nontoxic and it breaks down readily in the environment to benign byproducts.[1] However, the process by which most of the world's H_2O_2 is produced (the anthraquinone, or AQ, process) employs multiple unit operations, generates considerable waste, and requires significant energy input, lowering the sustainability of the process and raising the production costs. Hydrogen peroxide is a green alternative to conventional oxidants, but its cost limits its application to higher-value operations or areas where replacement of chlorinated oxidants produces a powerful market pull, as in paper bleaching.

The sequential hydrogenation and oxidation of an alkyl species is currently used to produce over 95% of the world's hydrogen peroxide. A 2-alkyl anthraquinone is dissolved in a mixture of an aromatic plus a long-chain alcohol (the "working solution") and then hydrogenated over a palladium catalyst in a three-phase reactor (see Figure 1). The resulting anthrahydroquinone is oxidized by air in a subsequent reactor (two-phase, no catalyst), producing hydrogen peroxide and regenerating the anthraquinone. The H_2O_2 is stripped from the working solution into water in a countercurrent column, producing (typically) 30 wt % H_2O_2, which is then distilled to remove impurities introduced during the production process and also to raise the concentra-
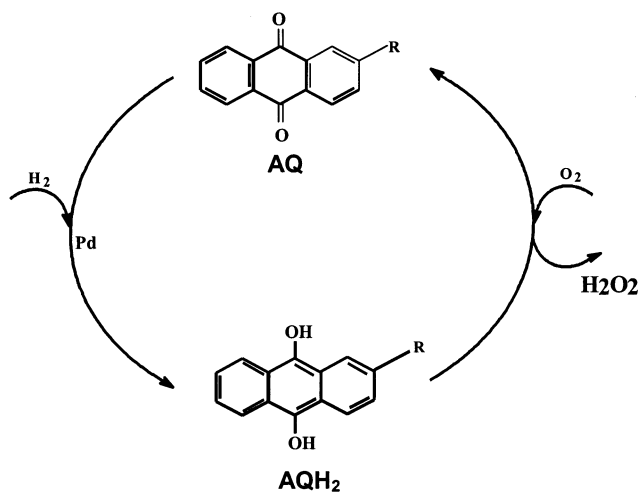

Figure 1. Chemical schematic for the production of hydrogen peroxide using the sequential hydrogenation and oxidation of an alkyl anthraquinone.

tion to as high as 70%. The AQ process has supplanted all of its competitors (electrochemical, secondary alcohol oxidation) because it generates H_2O_2 continuously at mild temperatures (40−60 °C) while preventing contact between H_2 and O_2 during production. The AQ process, however, suffers from innate inefficiencies owing to transport limitations in both reactors and organic contamination of the product during recovery by liquid−liquid extraction. Diffusional limitations on the reaction mandate the use of larger equipment and higher temperatures than desired. Control of the hydrogen/AQ stoichiometry and the anthraquinone residence time during hydrogenation is difficult, promoting byproduct formation. Overhydrogenation of the AQ and the solvent

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during the process cycle requires constant disposal of nonreactive byproducts and AQ makeup. Contact between the water and working solution in the stripping column crosscontaminates the phases; this, plus a nonoptimal partition coefficient (of H_2O_2 between the organic and aqueous phases), mandates the use of distillation to both concentrate and purify the H_2O_2, a major energy sink in the process.[2]

Gelbein[3] has estimated that, of the \$17\$/lb-mol cost of hydrogen peroxide, only \$2/lb-mol derives from the cost of the O_2 and H_2, whereas \$5.40/lb-mol is needed for the solvent and anthraquinone makeup and \$1.50/lb-mol for energy. Because H_2O_2 plants incorporate numerous unit operations, they have relatively large capital costs (and hence fixed costs of over \$7.00/lb-mol of H_2O_2, according to Gelbein[3]). Hence, an intensified process (fewer operations) that uses less energy and wastes fewer raw materials would both be greener and produce H_2O_2 less expensively. Production of H_2O_2 is thus an interesting target for green chemistry/design, in that the features that render the current process "less-than-green" also contribute to added costs, both capital and operating. For H_2O_2 to successfully break into new markets, such as commodity chemical production, the process must become cheaper and, hence, greener. Physically smaller plants would also facilitate applications such as on-site generation for microelectronics processing and would eliminate the need for transportation of aqueous H_2O_2.

Direct Generation of H_2O_2 from H_2 and O_2

Elimination of the anthraquinone from the H_2O_2 process could lead to significant savings in the cost of production. As shown previously by Gelbein,[3] approximately one-half of H_2O_2's cost is due to anthraquinone makeup/regeneration and the many unit operations needed to support the AQ route. Direct production of H_2O_2 from O_2 and H_2 is therefore being investigated by researchers at many companies, as shown by the large number of patents issued since 1980.[4] Clearly, direct contact between H_2 and O_2 presents a significant safety hazard, and yet a potential process *must* employ these two reactants above certain concentrations, and generate H_2O_2 at a certain rate, for the process to be of economical size and productivity. Hence, many of the patents generated since 1980 present innovations designed to balance H_2O_2 productivity with plant safety. The lack of commercial processes employing the direct route suggests that an adequate balance between these requirements has yet to be achieved.

Early work on the direct route involved the reaction of H_2 and O_2 in the gas phase, where the H_2O_2 was then quickly stripped into water. Because the explosive regime for O_2/H_2 coincides with the stoichiometry providing the best selectivity to H_2O_2 (between 5:1 and 20:1), large quantities of nitrogen were added for safety, but quite naturally, this greatly reduced the productivity.[5] Recent work has emphasized the dispersal of the gases in water to maximize the safety of the process, yet because the solubilities of H_2 and O_2 in water are both very low, productivity is still below the point desired. The generation of "microbubbles" of H_2 and O_2, for example, has been proposed to address the inherent transport limitations of the process.[6] The Pd catalysts employed for the direct route also catalyze the decomposition of H_2O_2 in water, and hence, a number of patents disclose means of stabilizing the aqueous H_2O_2,

although there is little discussion of the ultimate fate of these stabilizers.[7] New catalysts and catalyst supports are often described,[8] and recently, catalytic membranes have also been introduced.[9]

Researchers at EniChem recently published a variation of the direct route to H_2O_2, where oxygen, CO, and water are reacted over a palladium catalyst (plus various promoters) to produce H_2O_2 plus CO_2.[10] Although nominally different from the previously mentioned work, research by Sen's group[11] and others would suggest that the first step in such a process is the reaction of CO and water to generate H_2 and CO_2, followed by the combination of hydrogen and oxygen to form H_2O_2. Because hydrogen and oxygen are not premixed, this route is perhaps safer, yet to generate the CO needed for the reaction, one would have to generate syngas and then separate the CO from the hydrogen, rendering the process less "green" and more expensive than would be desired. Patents on this route have been issued to Enichem and Halcon.[12]

To gain the advantages of the direct route to H_2O_2 (no impurities, low cost for raw materials), maintain safe operation, and achieve high productivity, we have investigated the homogeneous production of H_2O_2 from H_2 and O_2 in carbon dioxide. For our system, a palladium catalyst was developed whose ligands allow miscibility with CO_2 at moderate pressures. Above 31 °C, H_2 and O_2 are miscible with CO_2 in all proportions (even under subcritical conditions, the solubilities of H_2 and O_2 are much higher in CO_2 than in organic solvents or water). Further, the heat capacity of CO_2 under our conditions is liquidlike, and hence, the safe-operating regime of a H_2/O_2 mixture is broader in pressurized CO_2 than in a gas. CO_2 is immune to further oxidation, overcoming a significant drawback of using organic solvents in contact with O_2. Operating the reaction homogeneously (i.e., via a CO_2-soluble catalyst) eliminates the transport limitations to reaction inherent in all of the water-based processes described in the patent literature while maintaining safe operation through the use of inert, nonflammable CO_2 as the solvent.

Hydrogen peroxide is soluble in conventional working solutions at levels of 4% and greater. Given CO_2's relatively feeble solvent power, it is likely that the solubility of H_2O_2 in CO_2 will be substantially less than that in organic solvents. Hence, we assume that H_2O_2 will rapidly partition to the aqueous phase, minimizing the chances for product degradation through prolonged contact with the CO_2-soluble catalyst. CO_2 readily dissolves in water, lowering the pH to 2.85, within the range of pH (2−4) typically used to stabilize aqueous hydrogen peroxide. "Contamination" of the aqueous phase by the organic (CO_2) in our case clearly does not require remediation through distillation. Finally, the product (H_2O_2) in our system is recovered from CO_2 without resorting to a large pressure drop. In summary, we believe that identification of an active, CO_2-soluble catalyst for this system will allow for the construction of H_2O_2 plants that incorporate significantly fewer unit operations (and, hence, are more compact), use much less energy, and produce a cleaner product with less waste. The patent literature is divided as to the most appropriate catalyst to use for the direct conversion of hydrogen and oxygen to H_2O_2; both Pd(0) and Pd(+2) catalysts are recommended.[13] We consequently explored the use of each type.

Experimental Section

Synthesis. 1,4-Dibromobenzene (98%, Aldrich), 1-bromo-4-iodobenzene (98%, Aldrich), magnesium (turnings, 99.98%, Aldrich), perfluorohexyl iodide (99%, Aldrich), 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (96%, Aldrich), copper (I) chloride (99.995%, Aldrich), phosphorus trichloride (99.9%, Aldrich), *tert*-butyllithium (1.7 M solution in pentane, Aldrich), trichlorosilane (99%, Aldrich), triethylamine (99.5%, Fluka), bis(acetonitrile)dichloropalladium (II) (99.99%, Aldrich), dichlorobis(triphenylphosphine)palladium(II) (99.99%, Aldrich), cyclohexene (Aldrich), tris(dibenzylideneacetone)-dipalladium(0) (Strem) and Pd/C (1% Pd, Aldrich) were used as received. Cyclohexene (97.5%, Fisher), sodium hydroxide (99.2%, Baker), hydrogen peroxide (30%, Baker), ethanol (99.5%, Aldrich) were also used as received. The TS-1 catalyst (0.97% Ti) was a gift from Lyondell Chemical Company, synthesized according to published procedures.[14] Reactions involving air- or moisture-sensitive materials were performed under argon using Schlenk techniques. All NMR spectra were recorded on a Bruker DMX300 instrument at the base frequencies of 121.49 MHz for ^{31}P and 300.13 MHz for ^{1}H. The samples were prepared in 8-mm NMR tubes placed coaxially in standard thin-walled 10-mm tubes containing CDCl$_3$ as the chemical shift standard. Chemical shifts were reported in parts per million relative to TMS for ^{1}H NMR spectra and to 85% H$_3$PO$_4$ for ^{31}P NMR spectra.

1-Bromo-4-(tridecafluorohexyl)benzene (2a).[15] In a typical experiment, a solution of F(CF$_2$)$_6$I (8.92 g, 0.02 mol) in hexafluorobenzene (20 mL) was added dropwise to a mixture of 4-bromoiodobenzene (**1a**) (5.77 g, 0.02 mol), 2,2′-pypyridine (0.24 g, 1.5 mmol), Cu powder (3.23 g, 0.05 mol), DMSO (20 mL), and hexafluorobenzene (30 mL) at 70 °C under Ar atmosphere. The reaction mixture was stirred for 72 h at 70 °C. After filtration of the catalyst and hydrolysis with 100 mL of water, the product was extracted with dichloromethane (100 cm^3), and the organic layer was subsequently washed with water and dried over MgSO$_4$. Then, the product was extracted with perfluoro-1,3-dimethylcyclohexane (3 × 20 cm^3), and the solvent was removed under vacuum. Distillation gave the product as a colorless liquid (bp 45−47 °C at 5 × 10^{-3} mmHg) (72%). ^{1}H NMR (δ, CDCl$_3$, 300 MHz) 7.72 (2H, d, 2,6-ArH), 7.48 (2H, d, 3,5-ArH).

1-Bromo-4-(1H,1H,2H,2H-perfluorooctyl)benzene (2b).[16] A 100-mL three-neck flask equipped with a dropping funnel and thermometer, previously evacuated and then filled with Ar, was charged with Mg turnings (2.07 g, 0.0862 mol) and Et$_2$O (ca. 5 mL) such that the solvent fully covered the magnesium particles. A solution of *p*-dibromobenzene (18.06 g, 0.075 mol) in Et$_2$O (ca. 35 mL) was added dropwise to the reaction mixture slowly enough to maintain gentle boiling of the solvent. The mixture was subsequently stirred at room temperature overnight. After filtration, the resulting yellowish solution was added dropwise to 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (31.9 g, 0.0675 mol) and CuCl (0.2 g) in dry tetrahydrofuran (ca. 45 mL) over 1 h at −20 °C. The slightly yellow reaction mixture was allowed to warm slowly to room temperature over a 4-h period. The mixture was hydrolyzed with 10% aqueous NH$_4$Cl (50 cm^3), and the organic layer was collected, washed with water (2 × 30 cm^3), and dried over MgSO$_4$. The solvent was then removed under vacuum to afford 19 g of a brownish yellow oil. Distillation gave the product as a colorless liquid [9.5 g (28%), bp 95−100 °C

at 10^{-2} mmHg]. ^{1}H NMR (δ, CDCl$_3$, 300 MHz) 7.42 (2H, d, 2,6-ArH), 7.06 (2H, d, 3,5-ArH), 2.84 (2H, m, H$_2$C$^\alpha$), 2.30 (2H, m, H$_2$C$^\beta$).

Tris(4-tridecafluorohexylphenyl)phosphine (3a).[17] A three-neck flask equipped with a dropping funnel and thermometer was charged with **2a** (4 g, 8.4 mmol) in anhydrous diethyl ether (50 cm^3), cooled in a liquid nitrogen/acetone bath at −78 °C, evacuated for 10 min, and then filled with dry Ar. A 1.7 M pentane solution of *t*-butyllithium (9.9 cm^3, 0.017 mol) was added dropwise under stirring over 1 h at −78 °C, and the resulting slightly yellow mixture was stirred at this temperature for 30 min. Subsequently, phosphorus trichloride (0.424 g, 3.1 mmol) in diethyl ether (5 cm^3) was added dropwise over 1 h at −78 °C, and the reaction mixture was kept at this temperature (−78 °C) for an additional hour and then allowed to warm to room temperature over a 12-h period. After hydrolysis with 10% aqueous NH$_4$Cl (50 cm^3), the organic layer was washed with water and dried over MgSO$_4$. The water phase was washed with diethyl ether (3 × 20 cm^3). The combined organic layers were concentrated to 5 cm^3 and then passed through a silica gel column, using a 95% hexane/5% ethyl acetate mixture as the eluent. Evaporation of the solvent yielded **3a** as a white solid [2.1 g (53%), mp 63 °C]. ^{1}H NMR (δ, CDCl$_3$, 300 MHz) 7.6 (6H, d, 2,6-ArH), 7.4 (6H, t, 3,5-ArH). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 121.49 MHz) −5.6.

Tris(4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octylphenyl))phosphine (3b). This compound was prepared by the same method as used for **3a** by using **2b** (4.23 g, 8.4 mmol) to afford **3b** as a white solid [1.8 g (45%), mp 58 °C]. ^{1}H NMR (δ, CDCl$_3$, 300 MHz) 7.3 (6H, d, 2,6-ArH), 7.1 (6H, t, 3,5-ArH), 2.84 (6H, m, H$_2$C$^\alpha$), 2.30 (6H, m, H$_2$C$^\beta$). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 121.49 MHz) −7.1.

Tris(4-trifluoromethylphenyl)phosphine (3c). This compound was prepared by the same method as the one used for **3a** by using 4-trifluoromethylbromobenzene, **2c** (1.89 g, 8 mmol), to afford **3c** as a white solid [0.79 g (55%), mp 70 °C]. ^{1}H NMR (δ, CDCl$_3$, 300 MHz) 7.6 (6H, d, 2,6-ArH), 7.4 (6H, t, 3,5-ArH). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 121.49 MHz) −5.3.

Dichlorobis(tri-(4-tridecafluorohexylphenyl)phosphine)-palladium(II) (4a). A solution of **3a** (1.3 g, 1 mmol) in chloroform (15 cm^3) was mixed with [Pd(MeCN)$_2$]Cl$_2$ (0.13 g, 0.5 mmol) for 15 min. The resulting yellow-orange solution was concentrated and passed through a silica gel column using a hexane/ethyl acetate mixture of increasing polarity as the eluent. Evaporation of the solvent from the fractions obtained with 10% ethyl acetate/90% hexane mixture gave the product, **4a**, as a yellow solid (0.79 g, 55%). ^{1}H NMR (δ, CDCl$_3$, 300 MHz) 7.6 (12H, d, 2,6-ArH), 7.4 (12H, t, 3,5-ArH). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 121.49 MHz) 23.8.

Dichlorobis(tri-(4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octyl)phenyl)phosphine)palladium(II) (4b). This compound was prepared by the same method as described for **4a** by using **3b** (1.37 g, 1 mmol) to afford **4b** as a yellow solid (0.91 g, 62%). ^{1}H NMR (δ, CDCl$_3$, 300 MHz) 7.6 (12H, d, 2,6-ArH), 7.3 (12H, t, 3,5-ArH),), 2.9 (6H, m, H$_2$C$^\alpha$), 2.3 (6H, m, H$_2$C$^\beta$). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 121.49 MHz) 22.5.

Dichlorobis(tri-(4-trifluoromethylphenyl)phosphine)-palladium(II) (4c). This compound was prepared by the same method as described for **4a** by using **3c** (0.5 g, 1 mmol) to afford **4c** as a yellow solid (0.36 g, 62%). ^{1}H

NMR (δ, CDCl$_3$, 300 MHz) 7.61 (12H, d, 2,6-ArH), 7.4 (12H, t, 3,5-ArH). ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 121.49 MHz) 23.9.

Solubility of Catalysts in Carbon Dioxide. The phase behavior measurements of the "CO$_2$-philic" Pd catalysts in liquid CO$_2$ were conducted as described elsewhere.[21,22]

Reaction of H$_2$ and O$_2$ in Carbon Dioxide. Direct reaction of H$_2$ and O$_2$ in liquid CO$_2$ was conducted in a high-pressure batch reactor at room temperature and 170 bar. The experimental setup consists of (1) a 35-cm^3 high-pressure batch reactor (University of Pittsburgh) whose walls were previously passivated with 35% HNO$_3$ at 65 °C for 2 h to avoid decomposition of H$_2$O$_2$ on the stainless steel, (2) two manual syringe pumps (HIP, Erie, PA) in which H$_2$/CO$_2$ and air/CO$_2$ mixtures were prepared, and (3) two high-pressure HPLC injection valves (Rheodyne) for precise measurement of the amounts of air and H$_2$ added to the system.

In a typical experiment, the reactor was charged with deionized water (3.5 cm^3), H$_2$SO$_4$ (96%, 0.04 g, 0.3 mmol), Pd catalyst (PdCl$_2$[P(C$_6$H$_5$)$_3$]$_2$, 0.0188 g, 0.017 mmol), and NH$_4$Cl (0.0077 g, 0.1 mmol). After 15 min of evacuation, air (31 cm^3 of air at 10.9 bar) was injected into the reactor, and one of the syringe pumps (SP1) was charged with hydrogen (2 cm^3, 6.2 bar). The system (SP1 and the reactor) was then pressurized with CO$_2$ (172 bar), and injection of the CO$_2$/H$_2$ mixture into the reactor started the reaction. After 3 h of reaction (25 °C, 172 bar) the system was slowly depressurized, and the Pd catalyst extracted with CDCl$_3$. The aqueous phase (3 cm^3) was diluted with deionized water to 15 cm^3 and titrated with 0.05 M KMnO$_4$ in the presence of 96% H$_2$SO$_4$ to determine the concentration of hydrogen peroxide.

Epoxidation of Cyclohexene in CO$_2$ Using Pd/TS-1 Catalysts. Epoxidation of cyclohexene by H$_2$ and O$_2$ was conducted using a Pd-based catalyst in conjunction with the titania silicate catalyst TS-1. Reactions were run in liquid CO$_2$ in a high-pressure batch reactor at room temperature and 131 bar. In a typical experiment, the reactor was charged with deionized water (5.0 cm^3), TS-1 (0.15 g), a Pd-based catalyst (1% Pd with respect to the TS-1), and cyclohexene (0.8 g, 9.75 mmol). After 15 min of evacuation, air (80 cm^3 air at 10.9 bar) was injected into the reactor, and one of the syringe pumps (SP1) was charged with hydrogen (20 cm^3, 6.2 bar). The system (SP1 and the reactor) was then pressurized with CO$_2$, and the reaction was started by injecting the CO$_2$/H$_2$ mixture into the reactor. After 3 h of reaction (25 °C, 131 bar), the system was slowly depressurized, and the organic phase was extracted with CHCl$_3$ and then analyzed by GC for cyclohexene oxide. No cyclohexene oxide was produced in the absence of palladium.

Epoxidation of Cyclohexene via Percarbonate Route. Epoxidation experiments in CO$_2$ were performed in a high-pressure batch reactor at room temperature and a pressure of 241 bar for 3 h. Typically, the reactor was charged with known amounts of ethanol (14 g), hydrogen peroxide (11.0 g, 30 wt %, 0.1 mol), buffer (NaOH, 5.5 mmol), and unsaturated compound (cyclohexene, 0.035 mol) and then pressurized with supercritical CO$_2$ (11 g) at the operating pressure (241 bar, 24 °C). The kinetics was followed by sampling both the CO$_2$ phase and the organic phase under pressure via multiport HPLC injection valves. The resulting liquid

PdL2Cl2

1. m = 0; n = 6
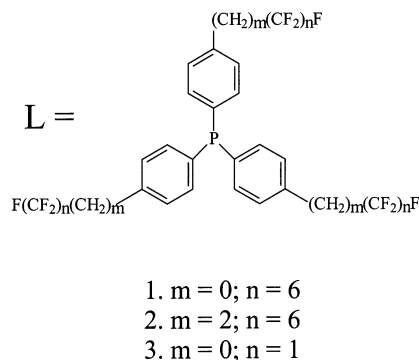2. m = 2; n = 6
3. m = 0; n = 1

Figure 2. Pd(+2) catalysts employed for this study; synthetic details are provided in ref 11.

samples (!1 mL each) were diluted in chloroform (2 mL) and then analyzed on a HP 5890 gas chromatograph featuring a cross-linked methyl silicone gum column.

Control epoxidation experiments were conducted under ambient conditions for 24 h. In a typical experiment, a three-neck flask equipped with a water-cooled condenser was charged with acetonitrile (7 g), ethanol (7 g), hydrogen peroxide (5.5 g, 30 wt %, 48 mmol), buffer (NaHCO$_3$ or NaOH, 2.75 mmol), and the unsaturated substrate (cyclohexene, 17 mmol). The composition of the reaction mixture was analyzed by GC using the method described for the experiments in CO$_2$.

Results and Discussion

Pd(+2) Catalysts for H$_2$ + O$_2$ → H$_2$O$_2$. A large body of previous work [18] has shown that the use of fluorinated ligands creates organometallic catalysts with significantly higher solubilities in carbon dioxide than their hydrocarbon analogues. Increasing the fluorine content of the ligand tends to lower the miscibility pressure of the catalyst (by rendering the molecule, on balance, more CO$_2$-philic), yet it can also greatly increase the cost. The use of fluorinated ligands can also change the electronic character of the active center of the catalyst; this effect increases as the extent of fluorination increases. We generated a series of fluorinated Pd(+2) catalysts to examine the role of fluorine content, plus the presence or absence of a spacer between the metal and the fluorinated "tails", on the CO$_2$ solubility, activity in the reaction between H$_2$ and O$_2$ in CO$_2$, and cost (as evidenced by ease of synthesis). The catalysts are shown in Figure 2; the phase behavior in CO$_2$ is shown in Figure 3.

As shown previously, increasing the length of a fluorinated "ponytail" tends to decrease the pressure required for miscibility, as the enthalpy of mixing (between solute and CO$_2$) becomes more favorable. Eventually, however, a point of diminishing returns will be reached, such that further increases in the length of the fluorinated tail will increase miscibility pressures (owing to unfavorable entropic effects). Further, it should be noted that the trifluoromethyl variant, although not as CO$_2$-philic as the version with the longer tail, was assembled using commercially available materials, whereas the other required a multistep synthesis to construct. Hence, we are confronted with an optimization problem, where increasing the length of
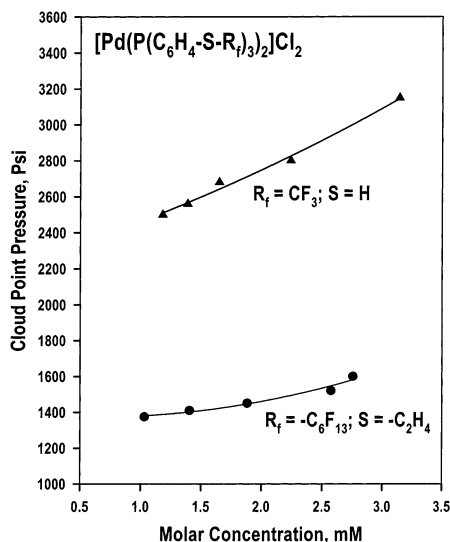
Figure 3. Phase behavior of two of the catalysts from Figure 2 in CO_2 at 22 °C.
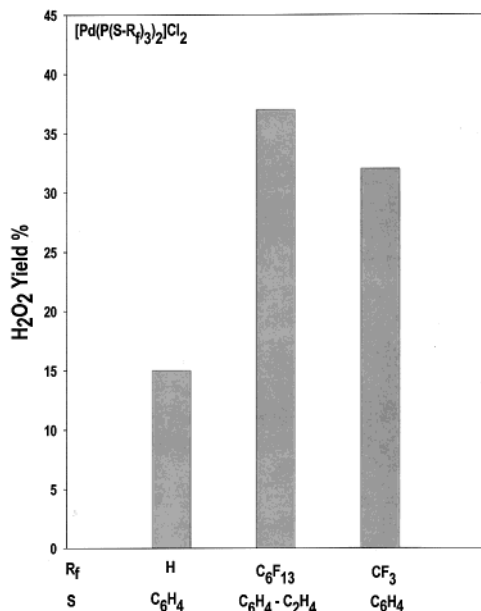

Figure 4. H_2O_2 yield after 3 h over three catalysts in CO_2 at 22 °C and 170 bar. The catalysts were typically used at 0.02 mM concentration; the aqueous phase (10 vol %) also contained H_2SO_4 and NH_4Cl to stabilize H_2O_2.

Figure 5. Yield of epoxidation of cyclohexene by H_2 and O_2 in CO_2 (22 °C, 160 bar) after 3 h. The reactor was charged with deionized water (5.0 cm³), TS-1 (0.15 g), a Pd-based catalyst (1% Pd with respect to the TS-1) and cyclohexene (0.8 g, 9.75 mmol); 80 cm³ of air at 10.9 bar and 20 cm³ of hydrogen at 6.2 bar were injected. The organic phase was extracted with $CHCl_3$ and then analyzed by GC for cyclohexene oxide. No cyclohexene oxide was produced in the absence of palladium.

the fluorinated tail raises the cost of the ligand but lowers the required miscibility pressure and, hence, the capital cost of a process. It should be noted that previous patents on the direct route employed total pressures (usually $N_2/O_2/H_2$ mixtures) in the 50−200 bar range.[19]

Reactions were conducted in a biphasic system (water/ CO_2) where H_2, O_2, and the catalyst reside in the CO_2 phase (nitrogen was also present, as air was employed as the reactant). We used an O_2/H_2 ratio of 7:1, as suggested by the previous patent literature as a means to suppress the formation of water from H_2 and O_2. Stabilizers were added to the water to inhibit the degradation of H_2O_2 via contact with the steel walls of the reactor vessel. Samples of the aqueous phase were removed after 3 h (at room temperature) and titrated against potassium permanganate to determine the H_2O_2 concentration. In general (Figure 4), we found that all of the Pd(+2) catalysts were active in the generation of H_2O_2 and that neither the length of the fluorinated tail
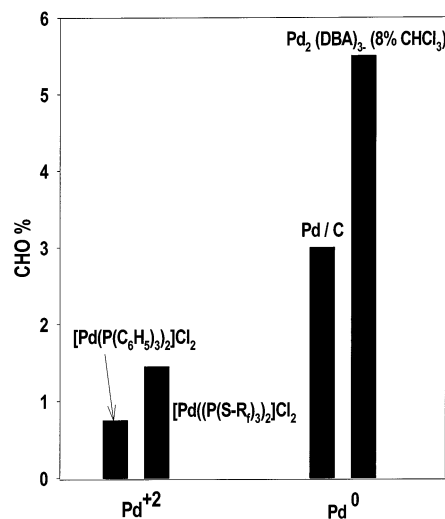
nor the presence of a spacer between the fluorinated tail and metal significantly affected the yield of H_2O_2 after 3 h. Further, as noted in Figure 4, simple hydrocarbon versions of the catalysts also produced H_2O_2, although only half as much as their fluorinated cousins. The hydrogenated catalysts do exhibit some solubility in CO_2, but unlike their fluorinated cousins, only part of the initial catalyst charge is actually dissolved in the carbon dioxide.

The turnover frequencies for the reactions described in Figure 4 are not high, only approximately 10 h^{-1}, but they do demonstrate that H_2O_2 can be generated using this type of system despite operating at 22 °C. Because we could not sample the system on-line, we do not as yet know the selectivity of the reaction to H_2O_2 (vs water).

Pd(0) Catalysts for $H_2 + O_2 \rightarrow H_2O_2$. Although we found that we could produce H_2O_2 in CO_2, the methodology in the previous section was less than ideal because we could not sample for the product on-line, and hence, it is likely, despite our best efforts, that some of the product decomposed through interactions with the steel reactor and tubing or was lost during depressurization. Hence, we examined an indirect method for measuring the H_2O_2 production. Here we took advantage of the known rapid reaction of H_2O_2 with cyclohexene over a titanium silicalite catalyst (TS-1) to produce cyclohexene oxide. The rapid reaction of H_2O_2 with cyclohexene thus provides less opportunity for H_2O_2 degradation. We compared the performance of two Pd(+2) catalysts (both fluorinated triphenyl phosphine and the unfluorinated analog) to that of two Pd(0) catalysts [heterogeneous palladium on carbon and a dibenzylidene acetone (DBA)− Pd complex]. Rather than synthesizing a fluorinated version of the DBA−Pd catalyst, we added a cosolvent (8% chloroform) to allow the catalyst to dissolve in CO_2 at the operating temperature and pressure.

The results (Figure 5) after 3 h suggest that Pd(0) catalysts are superior in the generation of H_2O_2 (and hence cyclohexene oxide) to the Pd(+2) catalysts employed previously. Interestingly, simple Pd/C produced
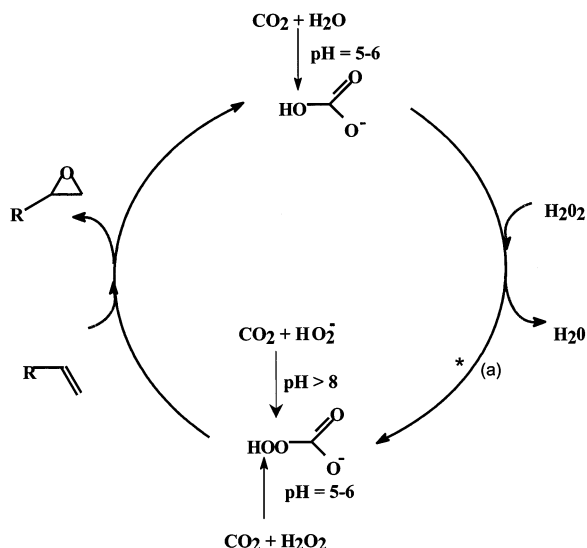
Figure 6. Possible pathways for the generation of HCO_4^- in a $CO_2/H_2O/H_2O_2$ biphasic mixture.

significant amounts of product, likely owing to the solubilization of H_2 and O_2 in water under the high pressures employed and the rapid reaction of any H_2O_2 formed with cyclohexene. Nevertheless, these results suggest that a Pd(0) catalyst that can be dissolved or dispersed in CO_2 might ultimately prove to be the most useful for this system.

$H_2O_2/H_2O/CO_2$ as an Epoxidation Reagent. Our initial aim was to create a means for the green production of H_2O_2 using CO_2 as the primary "organic" solvent. However, we also found that a biphasic mixture of aqueous H_2O_2 and CO_2 is an interesting system for the production of epoxides from alkenes. The epoxidation of alkenes has been widely explored, as it has significant commercial importance. Because it is an environmentally benign reagent, hydrogen peroxide has been extensively investigated as an epoxidation reagent, typically in the presence of a heterogeneous catalyst.[20] Recent work by Richardson's group[21] has shown that H_2O_2 will react with aqueous bicarbonate to form percarbonate (HCO_4^-) and that this species will perform epoxidations of hydrophilic alkenes and oxidations of sulfides in the absence of any catalyst. Consequently, we decided to explore the potential for using CO_2 as the bicarbonate source,[22] given that liquid CO_2 (at room temperature and pressures higher than its vapor pressure) will dissolve in water at molar concentrations. Further, we noted that, when CO_2 is used as the reactant/solvent, three pathways for the production of percarbonate are possible (depending on pH), as shown in Figure 6.

We began by comparing the rate of epoxidation of cyclohexene in a biphasic CO_2/aqueous H_2O_2 mixture with that in acetonitrile/water. Our initial results suggested that multiple pathways are indeed operative in forming percarbonate. As shown in Figure 7, the rate of epoxidation in the CO_2 biphasic system is significantly higher than that in MeCN. Despite the relatively high solubility of CO_2 in water, preliminary estimates suggest that the percarbonate concentration should be higher in the acetonitrile system, yet the rate of production of cyclohexene oxide in CO_2 is higher. These data suggests that percarbonate is being produced via more than one of the mechanisms shown in Figure 6.
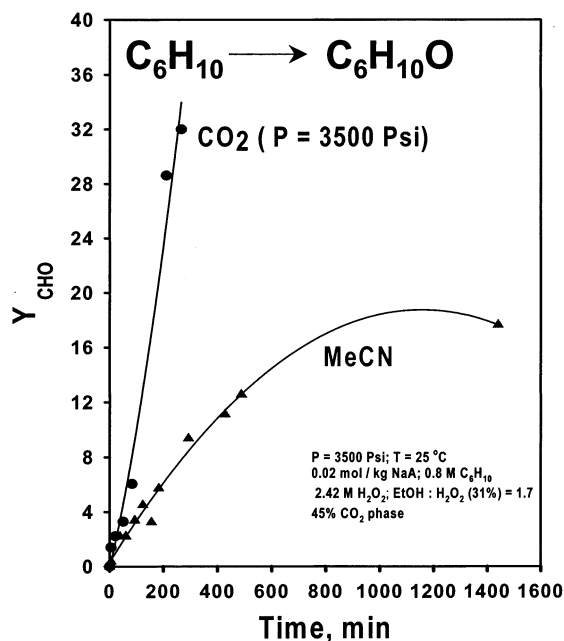

Figure 7. Effect of solvent type on yield of cyclohexene oxide from cyclohexene versus time. Conditions: 241 bar (CO_2 occupies 45% of the reactor volume), 25 °C, 0.02 mol/kg NaOH, 0.8 M cyclohexene at $t = 0$, 2.42 M H_2O_2 (added as 31% aqueous solution), EtOH/H_2O_2 = 1.7
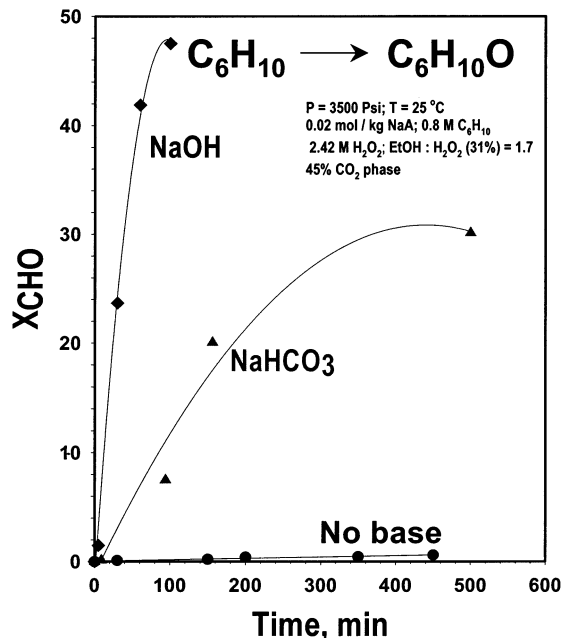

Figure 8. Effect of type of base on yield of cyclohexene oxide from cyclohexene versus time; same experimental conditions as in Figure 7.

Richardson's group[21] has noted that the system pH has a strong effect on the rate of epoxidation using percarbonate, where pH's above 7 are recommended. We noted that both the nature and concentration of the base affect the epoxidation rate. Figure 8 shows that almost no reaction occurs in the absence of base (pH $\approx$ 2.85 for a CO_2/water mixture), whereas addition of NaOH provides the best results. We assume that these results are tied to the fact that the addition of NaOH increases the pH in the CO_2/water system more efficiently than the addition of sodium bicarbonate does. At pH's higher than 8, HCO_4^- could also be formed from the reaction of HO_2^- and CO_2. As the nucleophilic species in this case
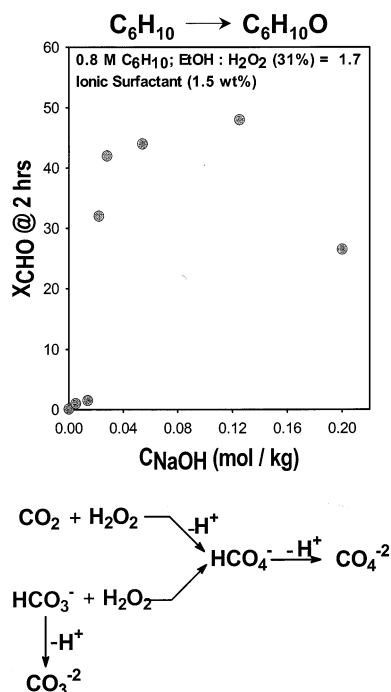
Figure 9. Effect of NaOH concentration on yield of cyclohexene oxide from cyclohexene after 2 h; other conditions are the same as in Figure 7.

is an anion, it is conceivable that this process is faster than the other two pathways shown in Figure 6 (reaction of CO_2 and H_2O_2 and reaction of H_2O_2 and HCO_3^-). However, in Figure 9, it can be seen that an optimal base concentration exists, where further increases in the concentration of NaOH lead to a dramatic drop in the yield of epoxide after 2 h. This result can be explained by the effect of higher pH on the deprotonation of HCO_3^- and HCO_4^-, lowering the concentration of the epoxidation agent. This reaction is consequently more important than the proposed formation of percarbonate via the nucleophilic attack of HO_2^- on CO_2 at higher pH's.

Unlike in Richardson's work,[21] our system employs a hydrophobic organic solvent (CO_2) and a hydrophobic alkene (cyclohexene) and, hence, might be transport-limited (by the rate at which the alkene diffuses into the aqueous phase). If transport across the interface is indeed limiting, then either an increase in interfacial surface area or use of a phase transfer catalyst (PTC) should improve the observed rate. In addition, one could add a surfactant to reduce the hindrance to transport across the hydrophile/hydrophobe interface. Whereas traditional alkyl-functional surfactants exhibit very poor solubilities in carbon dioxide, it has been shown that the fluorinated analogues are effective at producing emulsions in CO_2/water mixtures. As such, we evaluated the efficacy of a fluoroether-functional sulfate surfactant on the rate of epoxidation of cyclohexene in a CO_2/water/H_2O_2 mixture. We have observed that addition of a CO_2-soluble anionic surfactant[23] (Figure 10) produces a significant rate increase, supporting the view that the reaction is indeed transport-limited. Tumas and co-workers have also shown that the use of a surfactant can greatly enhance the rate of an interfacial reaction in a CO_2/water biphasic system.[24] Furthermore, we also explored the use of a phase transfer catalyst to enhance the reaction in the absence of surfactant. Because the active species is assumed to be a percarbonate ion, we surmised that a PTC might enhance its transport across
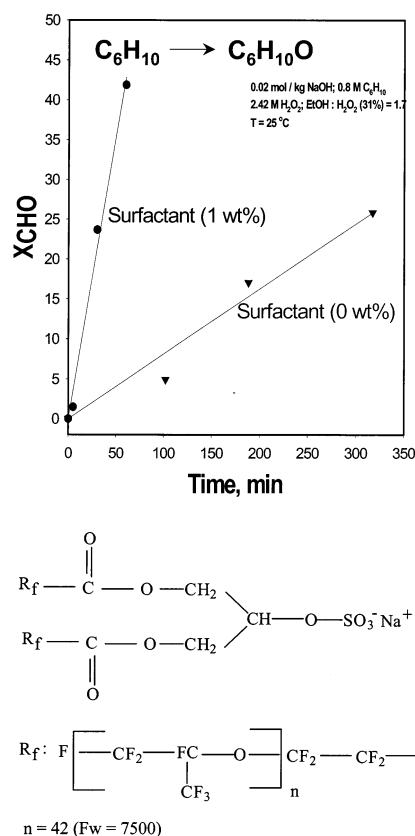

Figure 10. Effect of a fluoroether-functional, CO_2-soluble surfactant on the yield of cyclohexene oxide from cyclohexene versus time; other conditions are the same as in Figure 7.

the interface. We found that the use of tetraheptylammonium bromide at 1 mol % loading (relative to the cyclohexene) doubled the yield, whereas the use of 0.5 mol % produced little yield enhancement at 40 °C.

Another means by which the accessibility of the percarbonate to the alkene substrate can be enhanced is via gross changes in the phase behavior of the system. In Figure 11, we show the effect of adding ethanol to the system on the yield of epoxide after 3 h. Ethanol is miscible with both water and organics, and we expect that its addition allows for greater solubility of both the alkene and CO_2 in the aqueous phase. On the other hand, high concentrations of ethanol will eventually reduce the solubilities of the bicarbonate and percarbonate ions. Consistent with this hypothesis, we note a steady increase, followed by a dramatic drop-off, in the epoxide yield as the water/ethanol ratio increases.

Nolen and colleagues[25] recently published results of a study similar to that described above—a biphasic mixture of aqueous hydrogen peroxide and CO_2 was employed to epoxidize cyclohexene. Many of the trends found by Nolen are similar to those reported above: yields generally increased in the presence of base ($NaHCO_3$), and higher base concentrations produced higher yields of cyclohexene oxide. Transport also governed the system studied by Nolen, in that increases to the stirring rate increased the yield of epoxide. The addition of cosolvent (of various types) always improved the epoxide yield. However, the yields reported by Nolen are an order of magnitude lower than those reported above, likely because Nolen had not optimized the cosolvent loading. As shown in Figure 11, the use of an insufficient volume of the proper cosolvent leads to very low yields, similar to what Nolen obtained. In addition,
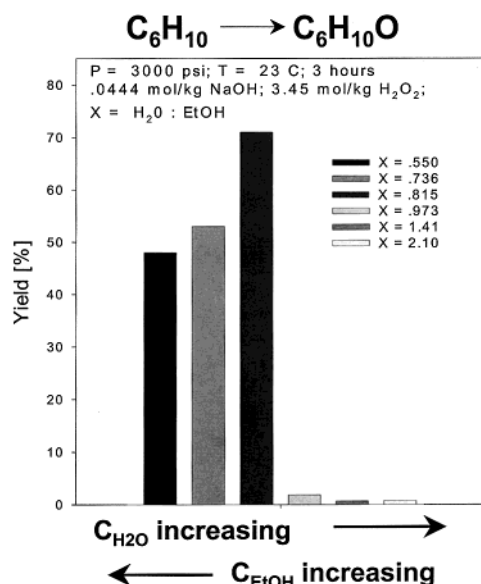
Figure 11. Effect of the yield of cyclohexene oxide from cyclohexene after 3 h as a function of water-to-ethanol ratio (X in the figure) in the reactor. Conditions: 23 °C, 207 bar, 0.044 mol/kg NaOH, 3.45 mol/kg H_2O_2.

Table 1. Yield of Alkylene Oxides Produced from Various Substrates[a]

substrate	yield (%)
1-hexene	12
cyclohexene	50
1-pentene	4
styrene	25
2-methyl-2-pentene	1

[a] Conditions: 241 bar, 23 °C, 3 h, 0.045 mol/kg NaOH, 11 mol/kg EtOH, 15 mol/kg H_2O, 3.5 mol/kg H_2O_2.

Nolen employed $NaHCO_3$ as the base, whereas Figure 8 shows that NaOH provides superior epoxide yields.

Finally, we also examined the ability of the percarbonate system to epoxidize alkenes other than cyclohexene (see Table 1). Epoxide was produced in all cases, although clearly the linear *n*-alkenes were less reactive than either cyclohexene or styrene, and the sterically hindered alkene produced the least product. No diols were produced, at least insofar as could be detected by GC.

Summary

The production of hydrogen peroxide directly from O_2 and H_2 using CO_2 as the solvent could provide a route to H_2O_2 that is both less expensive than the current process and significantly greener. Our results show that one can produce H_2O_2 in CO_2 via the direct reaction of H_2 and O_2 using either CO_2-soluble Pd(+2) or Pd(0) catalyst. Conducting the reaction homogeneously in CO_2 addresses the key issue involved in the direct route to H_2O_2: how to balance productivity with safety appropriately. Further, the reaction of H_2 and O_2 to form H_2O_2 takes full advantage of the properties of carbon dioxide as a solvent. First, the reaction employs gaseous reactants (completely miscible with CO_2), including oxygen (CO_2 is a nonoxidizable and nonflammable organic solvent), and we can eliminate all transport limitations by employing a homogeneous catalyst. The product, H_2O_2, can be recovered from CO_2 without resorting to large (and expensive) pressure drops.

Contact between water and CO_2, unlike that between water and organic solvents, presents no remediation problems. Finally, the pH of a CO_2/water biphasic system is 2.85, within the 2−4 range of pH used in H_2O_2 stabilization.

Not only is CO_2 a useful reaction medium for H_2O_2 production, but biphasic mixtures of CO_2 with aqueous H_2O_2 can also be used in green epoxidations of alkenes. In this chemistry, both the type and concentration of added base are important in generating high rates of reaction. Furthermore, because the reaction occurs through transport of the substrate or the percarbonate across an interface, the use of a surfactant (to increase interfacial area) or a phase transfer catalyst is advised.

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