

H₂O₂ in CO₂: Sustainable Production and Green Reactions

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ABSTRACT

Hydrogen peroxide is a “green” oxidant whose relatively high cost has prevented it from being applied to commodity chemical processing. Interestingly, those attributes of the current H₂O₂ process that contribute to the high cost also contribute to its nonsustainable features. We have consequently explored the generation of hydrogen peroxide both by the AQ route and directly from hydrogen and oxygen using liquid CO₂ as the solvent, because CO₂ provides some unique advantages to H₂O₂ synthesis.

Introduction

Hydrogen peroxide is widely accepted as a green oxidant, because it is relatively nontoxic and breaks down readily in the environment to benign byproducts.¹ However, the process by which most of the world's H₂O₂ 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 cost. 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 anthraquinone 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

Eric Beckman received his B.S. degree in chemical engineering from MIT in 1980. Following a short industrial career (first at Monsanto's Plastics & Resins Division, then Union Carbide's Silicones and Urethane Intermediates Group), he attended the University of Massachusetts-Amherst, where he received a Ph.D. in polymer science & engineering under the direction of Roger Porter. Following a postdoctoral appointment at Battelle's Pacific Northwest Laboratories, he joined the University of Pittsburgh in 1989, where he is currently Bayer Professor of Chemical Engineering. Dr. Beckman's group has published over 150 papers (and 15 patents) on design of highly CO₂-soluble polymers, use of CO₂ as both solvent and raw material in chemical processing, and design of polymers for use in medical applications. He currently supervises a research group of 10 graduate students and postdoctoral researchers.

Dan Hâncu received his B.S. in chemical engineering from the University of Bucharest in 1994, then M.S. (1997) and Ph.D. (1999) degrees in chemical engineering from the University of Pittsburgh under the direction of Eric Beckman. From 1999 to 2001, Dr. Hâncu worked for Lyondell Chemical Co. (Newtown Square, PA) on development of new propylene oxide processes. Dr. Hâncu recently (2002) moved to GE (Shenectady, NY), where his responsibilities will include investigating combinatorial approaches to catalyst development.

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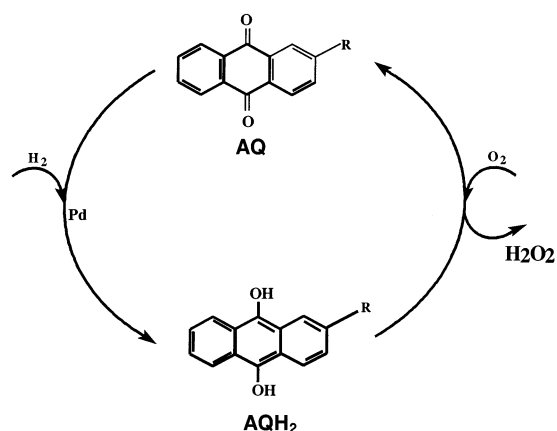


FIGURE 1. Chemical (top) and process (bottom) schematic representations for the production of hydrogen peroxide using the sequential hydrogenation and oxidation of an alkyl anthraquinone.

alcohol (the “working solution”) and then is hydrogenated over a palladium catalyst in a 3-phase reactor (see Figure 1). The resulting anthrahydroquinone is oxidized by air in a subsequent reactor (2-phase, no catalyst), producing hydrogen peroxide and regenerating the anthraquinone. The H₂O₂ is stripped from the working solution into water in a counter-current column, producing (typically) 30 wt % H₂O₂, which is then distilled to remove impurities introduced during the production process and also to raise the concentration. The AQ process has supplanted all of its competitors (electrochemical, secondary alcohol oxidation), because it generates H₂O₂ continuously at mild temperatures (40–60 °C) while preventing contact between H₂ and O₂ 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 to reaction mandate use of larger equipment and higher temperatures than are desired. Control of hydrogen/AQ stoichiometry and anthraquinone residence time during hydrogenation is difficult, promoting byproduct formation. Overhydrogenation of the AQ and the solvent during the process cycle requires constant disposal of nonreactive byproducts and AQ makeup. Contact between the water and working solution in the stripping column cross-contaminates the phases; this, plus a nonoptimal partition coefficient (of H₂O₂ between organic and aqueous phases), mandates use of distillation to both concentrate and purify H₂O₂, a major energy sink in the process.²

Gelbein³ has estimated that of the \$175/lb-mol cost of hydrogen peroxide, perhaps \$2/lb-mol derives from the cost of the O₂ and H₂, but \$5.40/lb-mol is needed for solvent and anthraquinone makeup and \$1.50/lb-mol for energy. Because H₂O₂ plants incorporate numerous unit operations, they have relatively large capital costs (and, hence, fixed costs of over \$7.00/lb-mol of H₂O₂). An

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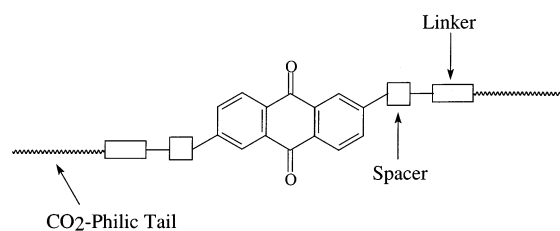
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intensified process (fewer operations) that uses less energy and wastes fewer raw materials would be both greener and less expensive. Production of H₂O₂ is thus an interesting target for green chemistry/design, in that those features that render the current process “less than green” also contribute to added costs, both capital and operating. For H₂O₂ 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 H₂O₂.

Generation of H₂O₂ in CO₂. Synthesis of H₂O₂ in CO₂ creates a fortuitous match between a solvent that can provide significant engineering advantages to the reaction with chemistry that by its nature eliminates some of the common problems encountered in the application of CO₂ to chemical processing. Hydrogen peroxide is produced in organic solvent and is then stripped into water during liquid–liquid extraction, a process that contaminates the aqueous phase with trace amounts of the organic solvent mixture, necessitating energy-intensive distillation. Use of CO₂ as the solvent eliminates the need for remediation, because CO₂ “contamination” of the aqueous phase is both benign and readily reversible. Each of the reactions involved in the AQ route is transport-limited in that the rate of reaction is tied to the rate at which the gaseous reactant (O₂ or H₂) diffuses into the liquid phase. Hydrogen and oxygen are completely miscible with CO₂ above 31°C, and thus, use of CO₂ as the solvent eliminates the gas–liquid interface entirely, removing one of the leading obstacles to higher rates of reaction. Further, unlike organic solvents, CO₂ cannot be further oxidized.

Although CO₂ could provide specific advantages to the H₂O₂/AQ process, the AQ process also exhibits certain characteristics that make it an ideal match for CO₂. When examining the economics of any CO₂-based process, four issues tend to dominate economic calculations: process configuration (batch versus continuous), absolute operating pressure (and its effect on capital costs), concentration (the more dilute the solution, the higher the required CO₂ flow rate, the larger the equipment), and the number and size of pressure drops encountered in the system. Ideally, to minimize costs in a CO₂-based process, one should operate continuously (minimize equipment size), operate at as high a concentration as is practical (minimizes CO₂ flow rate and, hence, equipment size), operate at as low an operating pressure as possible (reduces equipment cost), and recover products from CO₂ solution without resorting to large pressure reductions. The latter point can appear counterintuitive when discussing CO₂-based processing (after all, reduction in pressure to 1 atm results in total precipitation of solutes), but it has a significant effect on utility costs (related to the cost of recompressing CO₂). Indeed, the well-known coffee decaffeination process recovers caffeine from CO₂ not via depressurization, but rather via liquid–liquid extraction into water.

If we were to synthesize H₂O₂ in CO₂, we could clearly run the process continuously and recover the product via



Linker - OC(O) or N(H)-C(O)

Spacer - (CH₂)_m; m = 0,1

Tail Position - (1,2); (1,4); (1,6)

CO₂-Philic Tail - Poly(hexafluoropropylene oxide)

FIGURE 2. General structure of fluoroether-functional anthraquinones (FAQs), showing fluoroether “ponytails”, types of linking groups, and alkyl spacers.

stripping into water without a large pressure drop (in direct analogy to caffeine recovery in the coffee process). However, the solubility of an alkyl anthraquinone in CO₂ is less than 0.1 mM at pressures above 250 bar.⁴ Given that the conventional process operates at concentrations near 0.4 M, CO₂ cannot be employed as a simple drop-in replacement for the currently used organic solvent mixture. Hence, without further modification, we cannot generate H₂O₂ in CO₂ and operate at high concentration at low pressure.

Creating a CO₂-Soluble Anthraquinone. Using a well-known strategy for creating a CO₂-soluble analogue to a conventional compound,^{5,6} we functionalized anthraquinones (at several positions on the aromatic rings) with poly(perfluoroethers) of various chain lengths using ester or amide linking groups (Figure 2). These fluorinated anthraquinones (FAQs) are liquids or amorphous solids at room temperature; phase envelopes in CO₂ are, thus, of the liquid–liquid type (Figure 3), rather than the liquid–solid behavior found for alkyl anthraquinone/CO₂ mixtures. We observed that all FAQs exhibited complete miscibility with CO₂ at pressures accessible to our equipment (500 bar) and room temperature, although we observed significant differences in phase behavior deriving from relatively small changes in FAQ structure.

Hydrogenation and Oxidation of FAQs To Produce H₂O₂ in CO₂.^{7,8} Using high-pressure UV spectroscopy, we examined the rate of hydrogenation (see Figure 4) of various FAQs in CO₂ (over a heterogeneous Pd/Al₂O₃ catalyst) with the goal of finding regimes for which transport limitations could be completely eliminated. In the conventional AQ process for the generation of H₂O₂, the rate at which hydrogenation takes place is governed by a series of resistances to transport of reactants to the active sites on the catalyst, much like a group of resistors in series governs voltage in an electrical circuit. The global rate might be dominated by the rate at which hydrogen moves across the gas–liquid interface, the rate at which it migrates to the surface of the solid catalyst, or the rate at which it diffuses inside the porous catalyst to the active

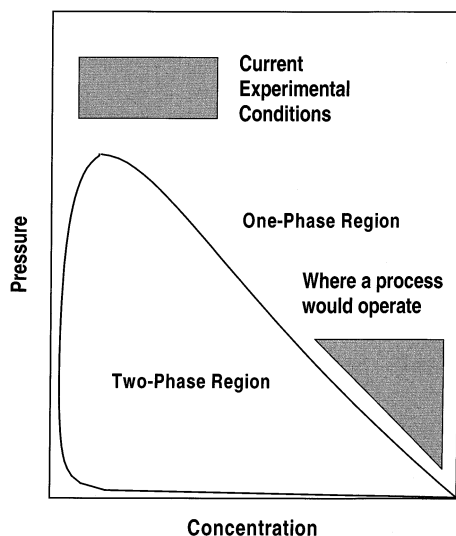


FIGURE 3. Generic phase diagram of the CO₂–FAQ binary mixture, showing liquid–liquid–phase envelope. In this figure, the y-axis represents 100% solvent (here, carbon dioxide). Whereas experiments were conducted in dilute solution (to accommodate analytical requirements) and, hence, at high pressure, an actual process could employ CO₂ as the minor component and, hence, operate at lower pressures.

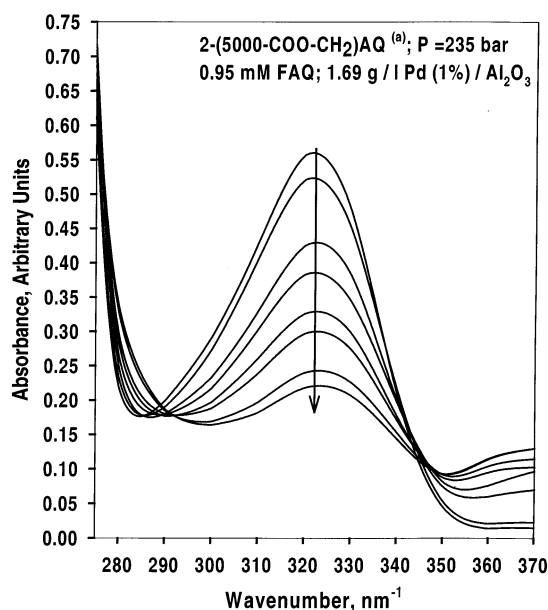


FIGURE 4. UV spectrum of a fluoroether-functional anthraquinone (2 tails, 5000 MW, linked via ester groups, 0.95 mM) in CO₂ at 22 °C and 235 bar in the presence of a 10-fold molar excess of H₂. Catalyst employed is 1% Pd/alumina.

sites. In our CO₂-based system, there is no gas–liquid interface, so one of the major resistances to transport is eliminated, leaving the other two to be dealt with. External transport resistance (liquid-to-solid-surface) is eliminated simply by increasing the stirring rate. Eliminating internal transport resistance requires deeper analysis, as shown in detail in ref 7. We ultimately found that one could achieve kinetic control over the hydrogenation reaction if one employed catalyst particles of sufficiently small size and an FAQ whose tail length was not too large. The catalyst particle size effect is well-known; the underlying

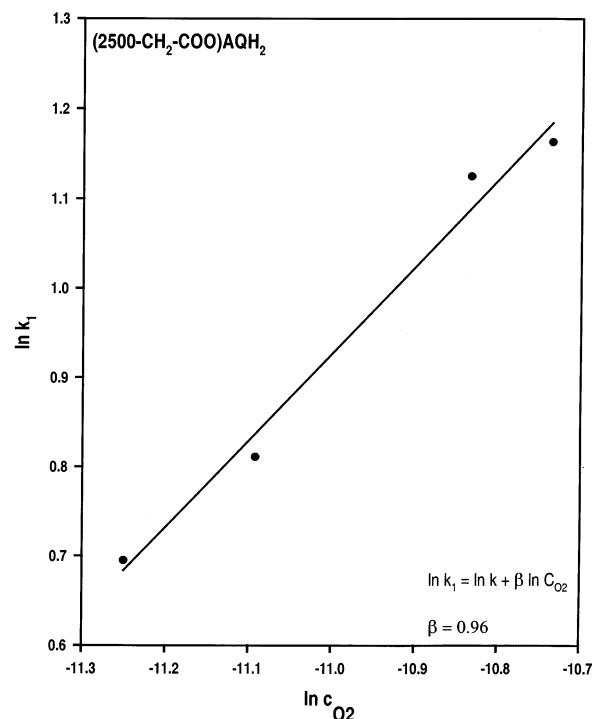


FIGURE 5. Effective rate constant versus oxygen concentration for the oxidation of a fluoroether-functional anthrahydroquinone to the analogous anthraquinone in CO₂ at 22 °C and 235 bar (experimental details shown in ref 8). Regression of the data shows that the reaction is first-order in oxygen, as expected.

rationale for the effect of FAQ tail size is that shorter tail lengths, not surprisingly, permit faster diffusion within the catalyst pores.

In the conventional AQ process, the oxidation reaction is performed without a catalyst, and the rate is entirely limited by the rate of diffusion of oxygen (from air) across the gas–liquid interface. In our CO₂-based analogue the oxidation should follow simple second-order kinetics, given that there is no gas–liquid interface. In an analysis of the kinetics, we found that the rate is indeed first-order in both oxygen and anthrahydroquinone (Figure 5) and that the rate constant is quite similar to that found by Santacesaria and colleagues for the oxidation of an alkylhydroquinone in an organic solvent.⁹ Whereas the rate constant for the two processes (FAQ/CO₂ versus AHQ/organic solvent) are essentially the same, it should be remembered that the actual rate of oxygen consumption in CO₂ is an order of magnitude higher because the CO₂-based system is under kinetic control, but the organic solvent system is transport-limited.

Although we were successful at demonstrating that the conventional AQ process for H₂O₂ production could be translated to a CO₂ basis through derivitization of an anthraquinone with a fluorinated “tail”, the cost of such tails will ultimately prevent commercialization of such a process. Thus, we considered two modifications to our original CO₂-based design: (a) creation of a nonfluorous (and hence, inexpensive) CO₂-phile, or (b) exploration of a route to H₂O₂ that does not require an anthraquinone. We have been successful in the design of nonfluorous

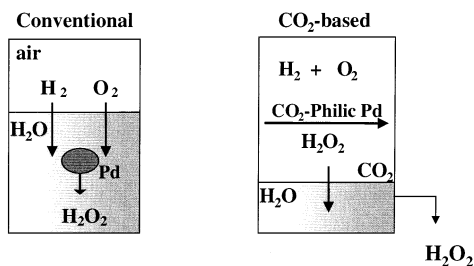


FIGURE 6. Generation of H₂O₂ directly from H₂ and O₂, conducting the reaction in water (left) versus in CO₂ (right).

CO₂-philes,¹⁰ but given space limitations, we will consider only route (b) in this Account.

Direct Generation of H₂O₂ from H₂ and O₂.¹¹ Elimination of the anthraquinone from the H₂O₂ process could lead to significant savings in the cost of production. As shown previously by Gelbein, about one-half of H₂O₂'s cost is due to anthraquinone's makeup/regeneration and the many unit operations needed to support the AQ route. Direct production of H₂O₂ from O₂ and H₂ is, therefore, being investigated by researchers at many companies, as shown by the large number of patents issued since 1980.¹² Clearly, direct contact between H₂ and O₂ presents a significant safety hazard, and yet a potential process *must* employ these two reactants above certain concentrations and generate H₂O₂ at a certain rate in order for the process to be of economical size and productivity. Hence, many of the patents generated since 1980 present innovations designed to balance H₂O₂ 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 H₂ and O₂ in the gas phase, where the H₂O₂ was then quickly stripped into water. Because the explosive regime for O₂/H₂ coincides with the stoichiometry providing the best selectivity to H₂O₂ (5:1 to 20:1), large quantities of nitrogen were added for safety, but quite naturally, this greatly reduced productivity.¹³ Recent work has emphasized the dispersal of the gases in water to maximize the safety of the process, yet because the solubility of both H₂ and O₂ in water is very low, productivity is still below the point desired. Generation of "microbubbles" of H₂ and O₂, for example, has been proposed to deal with the inherent transport limitations of the process.¹⁴ The Pd catalysts employed for the direct route will also catalyze the decomposition of H₂O₂ in water, and hence, a number of patents disclose means of stabilizing the aqueous H₂O₂, although there is little discussion of the ultimate fate of these stabilizers.¹⁵ New catalysts and catalyst supports are often described,¹⁶ and recently, catalytic membranes have also been introduced.¹⁷

To gain the advantages of the direct route to H₂O₂ (no impurities, low cost for raw materials), maintain safe operation, and achieve high productivity, we have investigated the homogeneous production of H₂O₂ from H₂ and O₂ in carbon dioxide (Figure 6). In our system, a palladium catalyst is developed whose ligands allow miscibility with CO₂ at moderate pressures. Above 31 °C, H₂ and O₂ are

miscible with CO₂ in all proportions (even under subcritical conditions, the solubilities of H₂ and O₂ in CO₂ are much higher than in organic solvents or water). Further, the heat capacity of CO₂ under our conditions is liquidlike, and hence, the safe operating regime of a H₂/O₂ mixture is broader in pressurized CO₂ than in a gas. CO₂ is immune to further oxidation, overcoming a significant drawback of using organic solvents in contact with O₂. Operating the reaction homogeneously (i.e., via a CO₂-soluble catalyst) eliminates the transport limitations to reaction inherent to all of the water-based processes described in the patent literature while maintaining safe operation through use of inert, nonflammable CO₂ as the solvent.

Hydrogen peroxide is soluble in conventional "working solutions" at levels of 4% and greater. Given CO₂'s relatively feeble solvent power, it is likely that the solubility of H₂O₂ in CO₂ will be substantially less than that in organic solvents. Hence, we assume that H₂O₂ will rapidly partition to the aqueous phase, minimizing the chances for product degradation through prolonged contact with the CO₂-soluble catalyst. CO₂ readily dissolves in water, lowering the pH to 2.85, within the range (2–4) typically used to stabilize aqueous hydrogen peroxide. "Contamination" of the aqueous phase by the organic (CO₂) in our case clearly does not require remediation through distillation. Finally, the product (H₂O₂) in our system is recovered from CO₂ without resorting to a large pressure drop. In summary, we believe that identification of an active, CO₂-soluble catalyst for this system will allow construction of H₂O₂ plants that incorporate significantly fewer unit operations (and are, hence, more compact), will use much less energy, and will 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 H₂O₂; both Pd(0) and Pd(II) catalysts are recommended.¹⁸ We consequently explored the use of each type.

Pd(II) Catalysts for H₂ + O₂ → H₂O₂. A large body of previous work¹⁹ has shown that use of fluorinated ligands creates organometallic catalysts with significantly higher solubility 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 "CO₂-philic"), yet can also greatly increase the cost. Use of fluorinated ligands may also change the electronic character of the active center of the catalyst. We generated a series of fluorinated Pd(II) catalysts to examine the role of fluorine content, plus the presence or absence of a spacer between the metal and the fluorinated "tails", on CO₂ solubility, activity in the reaction between H₂ and O₂ in CO₂, and cost (as evidenced by ease of synthesis). The catalysts are shown in Figure 7; phase behavior in CO₂ is shown in Figure 8.

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 CO₂) becomes more favorable, but eventually, a point of diminishing returns will be reached such that further

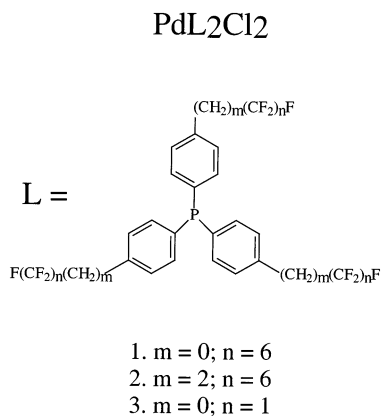


FIGURE 7. Pd(II) catalysts employed for this study; synthetic details are shown in ref 11.

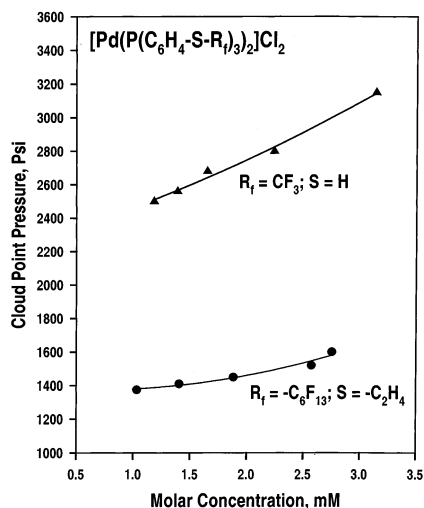


FIGURE 8. Phase behavior of two of the catalysts from Figure 8 in CO₂ at 22 °C.

increases to 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 so “CO₂-philic” as the version with the longer tail, was assembled using commercially available materials, and the other required a multistep synthesis to construct. Hence, we are confronted with an optimization problem in which increasing the length of 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 N₂/O₂/H₂ mixtures) in the 50 to 200 bar range.²⁰

Reactions (see ref 11 for details) were conducted in a biphasic system (water/CO₂) where H₂, O₂, and the catalyst reside in the CO₂ phase (nitrogen was also present; we employed air as our reactant). We employed an O₂/H₂ ratio of 7:1, as suggested by the previous patent literature as a means to suppress formation of water from H₂ and O₂. We found that all of the Pd(II) catalysts were active in the generation of H₂O₂ and that neither the length of the fluorinated tail nor the presence of a spacer between fluorinated tail and metal significantly affected the yield of H₂O₂ after 3 h. Further, simple hydrocarbon versions

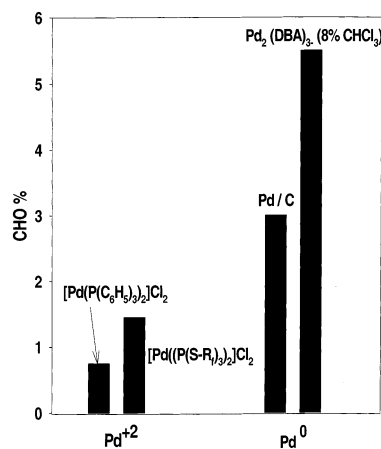


FIGURE 9. Epoxidation of cyclohexene by H₂ and O₂ in CO₂ (22 °C, 160 bar); yield after 3 h. The reactor was charged with deionized water (5.0 cm³), TS-1 (0.15 g), a Pd-based catalyst (1% Pd with respect to the TS-1), and cyclohexene (0.8 g, 9.75 mmol). Air (80 cm³) at P = 10.9 bar and 20 cm³ of hydrogen, P = 90 Psi, were injected. The organic phase was extracted with CHCl₃ and then analyzed by GC for cyclohexene oxide. No cyclohexene oxide was produced in the absence of palladium.

of the catalysts also produced H₂O₂, although only one-half as much (15% yield versus 35–40% after 3 h) as their fluorinated cousins. The hydrogenated catalysts do exhibit some solubility in CO₂, but unlike their fluorinated cousins, only part of the initial catalyst charge is actually dissolved in the carbon dioxide.

The turnover frequencies for these reactions are not high, only ~10 hr⁻¹, but they do demonstrate that H₂O₂ can be generated despite operating at only 22 °C. Because we could not sample the system on-line, we do not as yet know the selectivity of the reaction to H₂O₂ (vs water).

Pd(0) Catalysts for H₂ + O₂ → H₂O₂. Although we found that we could produce H₂O₂ in CO₂, the methodology was less than ideal, because we could not sample for the product online, 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 H₂O₂ production. Here we took advantage of the known rapid reaction of H₂O₂ with cyclohexene over a titanium silicalite catalyst (TS-1) to produce cyclohexene oxide. The rapid reaction of H₂O₂ with cyclohexene thus provides less opportunity for H₂O₂ degradation. We compared the performance of two Pd(II) catalysts (both fluorinated triphenyl phosphine and the unfluorinated analog) to two Pd(0) catalysts (heterogeneous palladium on carbon and a dibenzylidene acetone–Pd complex). Rather than synthesizing a fluorinated version of the DBA–Pd catalyst, we added a cosolvent (here, 8% chloroform) to allow the catalyst to dissolve in CO₂ at the operating temperature and pressure.

Results (Figure 9) after 3 h suggest that Pd(0) catalysts are superior to the Pd(II) catalysts we have employed previously in the generation of H₂O₂ (and, hence, cyclohexene oxide). Interestingly, simple Pd/C produced significant amounts of product, likely owing to the solubi-

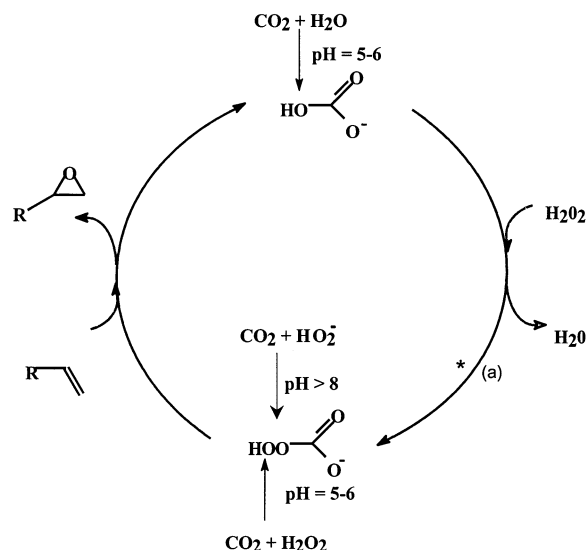


FIGURE 10. Possible pathways for the generation of HCO_4^- in a $\text{CO}_2/\text{H}_2\text{O}/\text{H}_2\text{O}_2$ biphasic mixture.

lization of H₂ and O₂ in water under the high pressures employed and the rapid reaction with cyclohexene of any H₂O₂ formed. Nevertheless, these results suggest that a Pd(0) catalyst that can be dissolved or dispersed in CO₂ will ultimately prove to be the most useful for this system. Most of the research carried out in industry on the direct reaction of hydrogen and oxygen employs heterogeneous Pd(0) catalysts.

H₂O₂/H₂O/CO₂ as an Epoxidation Reagent. Our initial aim was to create a means for the green production of H₂O₂ using CO₂ as the primary “organic” solvent. However, we also found that a biphasic mixture of aqueous H₂O₂ and CO₂ is an interesting system for the “green” production of epoxides from alkenes. Recent work by Richardson’s group²¹ has shown that H₂O₂ will react with aqueous bicarbonate to form percarbonate (HCO_4^-) and that this species will perform epoxidations of hydrophilic alkenes and oxidations of sulfides. Consequently, we decided to explore the potential for using CO₂ as the bicarbonate source,²² given that liquid CO₂ (at room temperature and pressures higher than the vapor pressure) will dissolve in water at molar concentrations. When using CO₂ as reactant/solvent, three pathways for the production of percarbonate are theoretically possible (depending on pH), as shown in Figure 10.

We began by comparing the rate of epoxidation of cyclohexene in a biphasic CO₂/aqueous H₂O₂ mixture with that in acetonitrile/water. Our initial results suggested that multiple pathways are indeed operative in forming percarbonate. As shown in Figure 11, the rate of epoxidation in the CO₂ biphasic system is significantly higher than that in MeCN. These results cannot be explained simply by larger amounts of carbonate in the CO₂-based system, because increasing bicarbonate concentration in the MeCN case does not produce a rate equivalent to the CO₂ case. Our data suggests that percarbonate is being produced via more than one of the mechanisms shown in Figure 10.

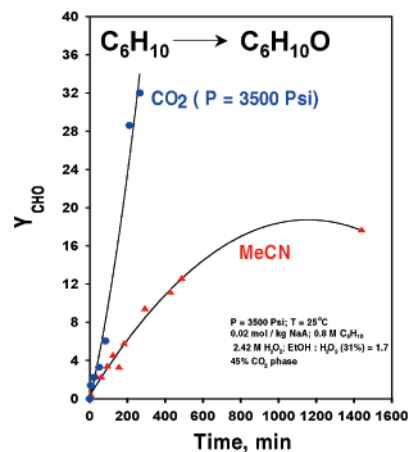


FIGURE 11. Effect of organic solvent type on yield of cyclohexene oxide from cyclohexene versus time. $P = 3500$ psi (CO_2 occupies 45% of the reactor volume), $T = 25$ °C, 0.02 mole/kg NaOH, 0.8 M cyclohexene at $t = 0$, 2.42 M H₂O₂ (added as 31% aqueous solution), and EtOH/H₂O₂ = 1.7.

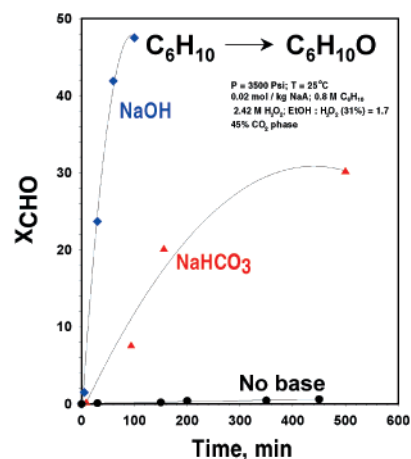


FIGURE 12. Effect of type and concentration of base on yield of cyclohexene oxide from cyclohexene versus time; experimental conditions same as those in Figure 12.

Richardson’s group has noted that system pH has a strong effect on the rate of epoxidations using percarbonate, where pHs above 7 are recommended. We noted that both the nature and concentration of the base affects the epoxidation rate. Figure 12 shows that almost no reaction occurs in the absence of base (pH \sim 2.85 for a CO₂/water mixture), whereas addition of NaOH provides the best results. We assume that these results are tied to the fact that NaOH increases the pH in the CO₂/water system more efficiently than sodium bicarbonate. Further, at pHs higher than 8, HCO_4^- can be also formed from the reaction of HO₂⁻ and CO₂. Because the nucleophilic species in this case is an anion, it is conceivable that this process is faster than the other two pathways shown in Figure 10 (reaction of CO₂ and H₂O₂ and reaction of H₂O₂ and HCO₃⁻).

Unlike in Richardson’s work, our system employs a hydrophobic organic solvent (CO₂) 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

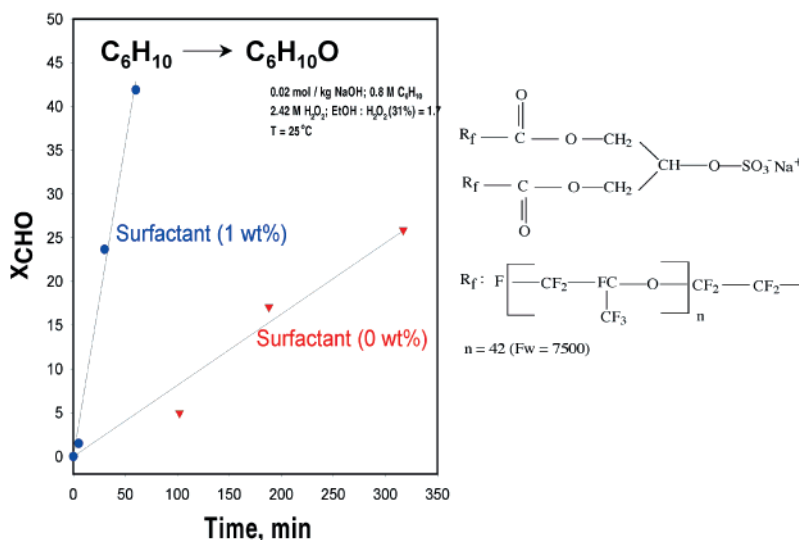


FIGURE 13. Effect of a fluoroether-functional, CO₂-soluble surfactant on the yield of cyclohexene oxide from cyclohexene versus time; other conditions same as in Figure 12.

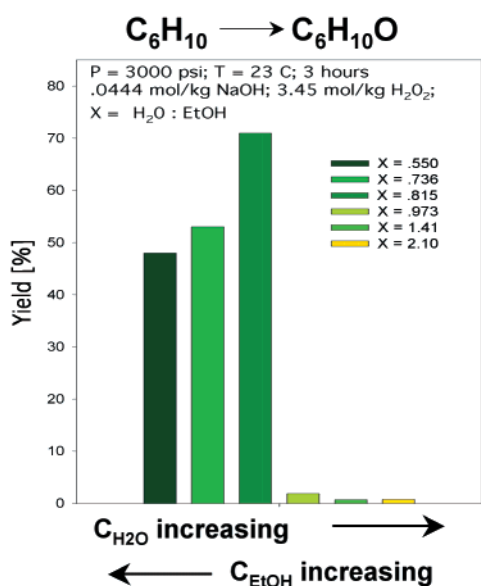


FIGURE 14. Effect of the yield of cyclohexene oxide from cyclohexene at 3 h as a function of water-to-ethanol ratio (X in the figure) in the reactor. $T = 23^\circ C$, $P = 3000$ psi, 0.044 mol/kg NaOH, and 3.45 mol/kg H_2O_2 .

limiting, then either an increase in interfacial surface area or use of a phase transfer catalyst should improve the observed rate. We have observed that this is the case, because addition of a CO₂-soluble anionic surfactant²³ (Figure 13) to the cyclohexene/CO₂/H₂O/H₂O₂ system shows a significant rate increase.

Another means by which to enhance the accessibility of the percarbonate to the alkene substrate is via gross changes to the phase behavior of the system. In Figure 14, 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 CO₂ in the aqueous phase. On the other hand, high concentrations of ethanol will eventually reduce the solubility of the bicarbonate and percarbonate ions. Consistent with this

hypothesis, we note a steady increase then a dramatic drop-off in epoxide yield as the water/ethanol ratio increases.

Recently, Nolen and co-workers²⁴ also examined the use of the biphasic mixture of H₂O₂/NaHCO₃/water/CO₂ to epoxidize cyclohexene. Trends reported by Nolen are similar to those found by us: some base is required for reactivity, the reaction is limited by transport across the interface (Nolen employed increased stirring rates to investigate this), and the cosolvent affects the yield. However, conversions were generally lower than those reported here by a factor of 10. This may be because Nolen employed a different base at a different concentration than in our system or because the amount of cosolvent (see Figure 14) was substantially different from optimal.

Summary

The production of hydrogen peroxide directly from O₂ and H₂ using CO₂ as the solvent could provide a route to H₂O₂ that is both less expensive than the current process and significantly "greener". Our results show that one can produce H₂O₂ in CO₂ using a CO₂-based analogue of the current anthraquinone process, or the direct reaction of H₂ and O₂ using either CO₂-soluble Pd(II) or Pd(0) catalyst. Conducting the reaction homogeneously in CO₂ addresses the key issue involved in the direct route to H₂O₂: how to adequately balance productivity with safety. Further, the reaction of H₂ and O₂ to form H₂O₂ takes full advantage of the properties of carbon dioxide as solvent.

Not only is CO₂ a useful reaction medium for H₂O₂ production, but biphasic mixtures of CO₂ with aqueous H₂O₂ can also be used in green epoxidations of alkenes. In this chemistry, both the type and concentration of added base are important to generating high rates of reaction. Further, because the reaction occurs through transport of the substrate or the percarbonate across an interface, use of a surfactant (to increase interfacial area) or a phase transfer catalyst is advised.

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