

# Metalloporphyrin-catalyzed homogeneous oxidation in supercritical carbon dioxide

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## Abstract

We report results from a study of the reactivity of the halogenated porphyrins tetrakis(pentafluorophenyl)porphyrinato iron(III) chloride [Fe(TFPP)Cl] and  $\beta$ -octabromo-tetrakis(pentafluorophenyl)porphyrinato iron(III) chloride [Fe(TFPPBr<sub>8</sub>)Cl] with dioxygen and cyclohexene in supercritical carbon dioxide. A lower limit for the solubility of the iron porphyrins in sc CO<sub>2</sub> was determined. Both halogenated metalloporphyrins were active catalysts for oxidation of cyclohexene to epoxide and allylic oxidation products in sc CO<sub>2</sub>. In 12 h at 80°C, up to 350 and 580 turnovers were observed for Fe(TFPP)Cl and Fe(TFPPBr<sub>8</sub>)Cl, respectively. We have also explored several organic solvent reactions at high temperature and pressure to benchmark relative activity and selectivity. Activity is higher in organic solvent, but accompanied by substantial oxidation of, or reaction with the solvent. Selectivity for epoxidation with Fe(TFPPBr<sub>8</sub>)Cl is higher in sc CO<sub>2</sub> than in organic solvents, with up to 34% cyclohexene oxide produced. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Oxidation; Supercritical carbon dioxide; Metalloporphyrins

## 1. Introduction

The selective catalytic oxidation of hydrocarbons with molecular oxygen is an important chemical challenge [1]. Dioxygen is an ideal oxidant, as it is inexpensive, readily available, and if reaction selectivity is 100%, has only water as a byproduct. Despite these advantages, the use of dioxygen is limited due to a number

of concerns, including gas transport problems, high potential for side reactions, safety, and the inability of many catalysts to activate O<sub>2</sub>. Supercritical fluids (SCFs) have some potential to mitigate these problems, making them attractive solvents for oxidation chemistry. For example, rates of oxygen activation by homogenous catalytic systems in organic solvents are often limited by low oxygen solubility in organic solvents and oxygen diffusion into the solvent [2]. The use of a SCF as a solvent could eliminate mass-transfer problems, as gases are miscible in this medium. Of the commonly used supercritical fluids, supercritical carbon dioxide (sc CO<sub>2</sub>) is an attractive choice for an inert

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solvent because it is highly resistant towards oxidation. Since  $\text{CO}_2$  is fully oxidized, it also compares favorably with flammable organic solvents that it might replace in the liquid phase. With regard towards selectivity issues, the low temperatures and pressures available within the relatively mild critical regime of supercritical carbon dioxide ( $T_c = 31^\circ\text{C}$ ,  $P_c = 1071$  psi) suggest the potential for controlled, partial oxidation chemistry in this solvent. Finally, flammability and explosive range are much safer in  $\text{CO}_2$  than in the gas phase [3], reducing safety concerns of working with dioxygen. The above properties prompted our group to investigate supercritical carbon dioxide as a medium for homogeneous oxidation chemistry. A key goal of our research is to investigate the activity level of simple oxidation catalysts in sc  $\text{CO}_2$  and compare the selectivity to comparable systems in organic solvents. Herein we report the oxidation of cyclohexene using molecular oxygen catalyzed by halogenated iron porphyrins in supercritical carbon dioxide.

## 2. Background

Supercritical carbon dioxide has recently been shown to be a versatile new medium for a variety of types of catalysis [4–6], including free-radical polymerization [7], hydroformylation [8–10], hydrogenation [5,10–14], and enzymatic processes [15–17]. Supercritical fluids have lower viscosity and density, and higher diffusivity relative to conventional solvents [18], and these properties are sensitive to relatively small changes in temperature and pressure, particularly near the critical point. The ability to tune the solvent properties of a SCF may potentially allow control of both reactivity and selectivity in a number of chemical transformations [19,20]. Indeed, several reactions show higher activity or selectivity relative to comparable reactions in conventional organic solvents. High reaction rates have been observed in the catalytic formation of dimethylformamide [12] and

formic acid [13] in sc  $\text{CO}_2$ . Carbon dioxide serves as both solvent and reactant in these systems, driving the reactions at rates considerably above those in organic solvents. Selectivity enhancements have also been observed. For example, ruthenium and rhodium complexes are found to catalyze the asymmetric hydrogenation of olefins in sc  $\text{CO}_2$  with increased enantioselectivity relative to reactions in conventional solvents [11].

Several oxidation reactions have also been investigated in supercritical carbon dioxide, mostly focused in the area of heterogeneous catalysis. Supported Pt and Co catalysts in sc  $\text{CO}_2$  have been examined for potential use in waste remediation, where supercritical fluid extraction is combined with on-line catalytic destruction of organic pollutants. Complete oxidation of ethanol [21], tetralin [22], and toluene [22,23] to carbon dioxide and water can be achieved, but rather high temperatures are required (420–650 K). Selective, partial oxidation of cyclohexane [24–26] and cumene [27,28] in sc  $\text{CO}_2$  has also been explored. Temperature and pressure were shown to affect the reaction rate and total conversion in the oxidation of cyclohexane, indicating the tunability of reactions in SCFs. The cyclohexanone/cyclohexanol ratio was also influenced, increasing with pressure [24]. Critical mixture oxidations of cumene with dioxygen were observed to be slightly slower than in neat cumene, but short induction periods and low distributions of side products were also observed. These reactions have capitalized on the oxidative stability of carbon dioxide and the miscibility of dioxygen above the critical point to drive free radical chemistry in sc  $\text{CO}_2$ .

Despite these encouraging results, homogeneous oxidation catalysis remains relatively unexplored in sc  $\text{CO}_2$ . We chose to study the reactivity of the halogenated porphyrins tetrakis(pentafluorophenyl)porphyrinato iron(III) chloride [ $\text{Fe}(\text{TFPP})\text{Cl}$ ] and  $\beta$ -octabromo-tetrakis(pentafluorophenyl)porphyrinato iron(III) chloride [ $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$ ] with dioxygen and

cyclohexene in supercritical carbon dioxide (Fig. 1). The fluorinated phenyl rings were anticipated to enhance solubility in sc CO<sub>2</sub>, allowing homogeneous oxidation chemistry to be investigated in a SCF. In addition, these complexes are more resistant than most porphyrins to degradation or  $\mu$ -oxo formation under conditions used for catalysis. Cyclohexene was chosen because it is an excellent substrate to probe selectivity between epoxidation and allylic oxidation.

Fe(TFPP)Cl and Fe(TFPBr<sub>8</sub>)Cl have been shown to be active catalysts for alkene and alkane oxidation using molecular oxygen in organic solvents [29–33]. The halogenated porphyrins are superior to most Fe porphyrin catalysts in their ability to activate O<sub>2</sub> without added coreductant. The mechanism for oxidation of hydrocarbons has been shown to involve in situ formation of alkyl hydroperoxides, followed by porphyrin-catalyzed decomposition of these peroxides to form products [29,32]. The success of free radical initiated oxidation chemistry in sc CO<sub>2</sub> suggested that the catalyzed production of radicals would also be facile in this medium. Here we report the homogeneous oxidation of cyclohexene by halogenated metalloporphyrins in supercritical carbon dioxide. We have found that selectivity for epoxidation of

cyclohexene is considerably higher in sc CO<sub>2</sub> than in organic solvents.

### 3. Results and discussion

#### 3.1. Spectroscopy

High-pressure in-situ UV–Vis spectroscopy has been used to measure solubility and explore solvent effects on the electronic structure of solubilized complexes under unusual conditions [34,35]. The electronic absorption spectra of porphyrins are extremely sensitive, making UV–Vis a powerful tool for elucidating information about their environment. In particular, the Soret band (a high intensity  $\pi \rightarrow \pi^*$  transition around 400–440 nm) will shift dramatically upon binding of substrate or an axial ligand, dimerization, or distortions in the porphyrin structure. Changes relative to solution spectra could indicate local solvation effects or pressure effects on the porphyrins, prompting us to measure their spectra under catalytic conditions. Spectra were obtained in a 316 stainless steel cell with 2 sapphire windows, designed to withstand over 6000 psi of pressure. A small amount of solid porphyrin was sealed inside the cell, which was then placed inside the spectrophotometer, filled with liquid CO<sub>2</sub> and heated. Neither porphyrin was soluble in room temperature, liquid carbon dioxide, but as the critical pressure and temperature were exceeded, the porphyrins began to dissolve. At 5000 psi and 40°C, the mildest experimental conditions for catalysis, both porphyrins were soluble in sc CO<sub>2</sub>.

The spectrum of Fe(TFPP)Cl is relatively unchanged from that in methylene chloride (Fig. 2a). In sc CO<sub>2</sub>, a slight blue shift in all the bands is observed (i.e., 300 cm<sup>-1</sup> shift in the Soret band), consistent with destabilization of the polar excited states in the less-polar solvent. No changes in the spectrum were observed from 2000 to 5000 psi. Solubility near the critical point (1200 psi) was very low, and band shifts

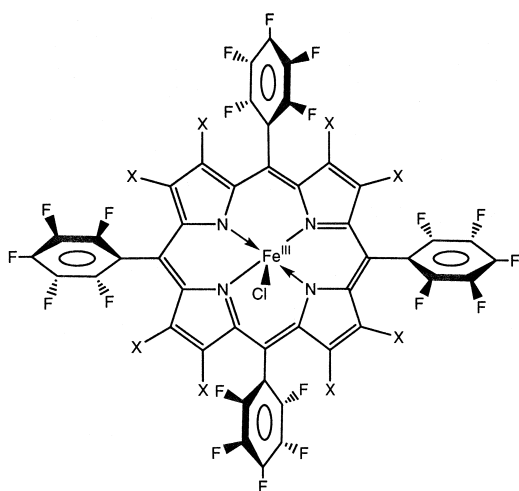


Fig. 1. Iron porphyrin catalysts Fe(TFPP)Cl [X = H] and Fe(TFPBr<sub>8</sub>)Cl [X = Br].

as a function of pressure or density were not fully explored.

The bands of  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$  are slightly more perturbed, with a  $1560\text{ cm}^{-1}$  blue shift in the MLCT from 404 to a shoulder at approximately 380 nm, and a  $1310\text{ cm}^{-1}$  blue shift in the Soret band to 418 nm (Fig. 2b). The MLCT is more affected than the Soret by the solvent change, consistent with a charge transfer transition. The increase in the energy difference between the MLCT and the Soret decreases the mixing of these bands, resulting in a more ‘normal-type’ porphyrin spectrum [36] for  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$ . The larger blue shift for the fully halogenated porphyrin could also be at-

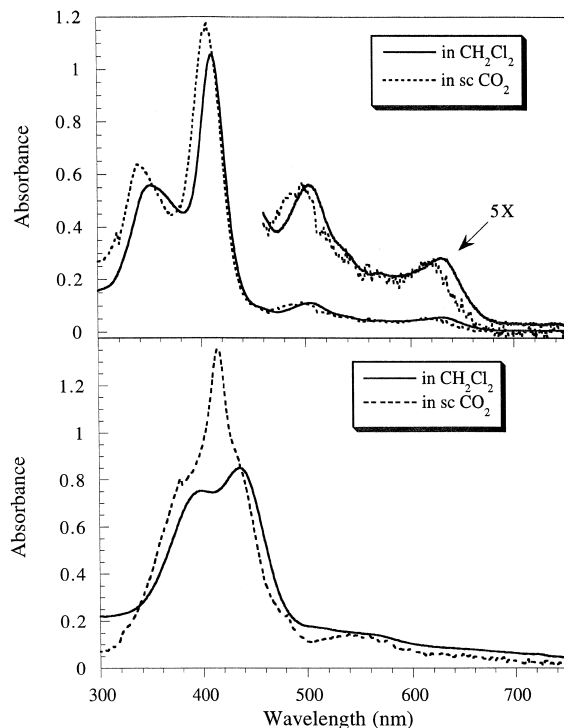
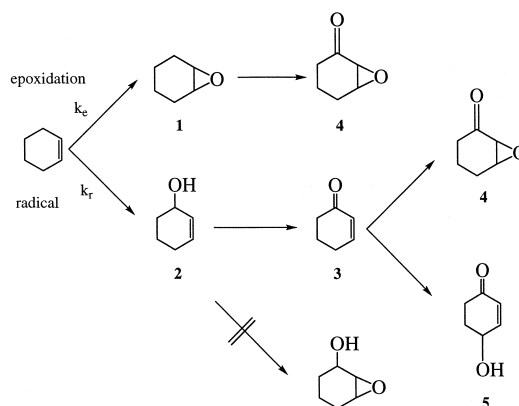


Fig. 2. (a) UV-Vis spectra (upper traces) of  $\text{Fe}(\text{TFPP})\text{Cl}$  in methylene chloride and supercritical carbon dioxide, indicating that the halogenated porphyrin is soluble at conditions used for catalysis experiments. A slight blue shift in both the MLCT (360 nm) and porphyrin  $\pi \rightarrow \pi^*$  transitions (Soret and Q bands) occur in the SCF. (b) UV-Vis spectra (lower traces) of  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$  in methylene chloride and supercritical carbon dioxide, indicating that the perhalogenated porphyrin is soluble at experimental conditions. The Soret band (440 nm) shifts to higher energy and increases in intensity in  $\text{sc CO}_2$ .



Scheme 1.

tributed to some flattening of the distorted porphyrin core at high pressures, but this could not be confirmed. Addition of a small amount of cyclohexene to either porphyrin in  $\text{sc CO}_2$  had little effect on the spectra, suggesting that as in organic solvents, olefin binding does not occur.






The maximum concentration of  $\text{Fe}(\text{TFPP})\text{Cl}$  and  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$  in solution was measured to be 18 and  $10\text{ }\mu\text{M}$ , respectively. Solubility measurements by this method were limited by saturation of the UV-Vis detector at higher porphyrin concentrations, so these numbers are lower limits rather than true solubility values.<sup>3</sup> However, we were able to determine that the porphyrins are at least soluble at the concentrations used in catalytic reactions in conventional organic solvents, allowing analogous homogeneous catalysis to be probed in  $\text{sc CO}_2$ . As both porphyrins are also soluble in the chosen substrate, cyclohexene, solubility in the ternary reaction system may be even higher.

### 3.2. Catalysis

We explored the air-oxidation of cyclohexene in supercritical carbon dioxide catalyzed by halogenated iron porphyrins. Oxidation reac-

<sup>3</sup> The concentration of porphyrin in solution is calculated assuming the extinction coefficients are similar in methylene chloride and in  $\text{sc CO}_2$ .

Table 1  
Cyclohexene oxidation with Fe(TFPP)Cl

Run <sup>a</sup>	Reaction Conditions <sup>b</sup> (hrs/°C/psig air)	% product					Turnovers <sup>c</sup>	Conversion (% substrate)	Conversion (% O <sub>2</sub> )
									
1	3/ CH <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>	13	47	40	—	—	8.7	0.2	2.1
2	12/ CH <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>	9	47	44	—	—	31	0.6	7.5
3	4/ 40/ 150	11	19	44	22	3.9	30	0.9	7.3
4	12/ 40/ 150	9.1	11	45	32	3.1	65	1.7	16
5	4/ 80/ 150	23	10	41	24	2.2	120	3.5	33
6	4/ 80/ 500	19	11	45	24	2.2	190	5.5	16
7	12/ 80/ 500	17	5.5	38	38	1.6	350	9.0	29
8	18/ 80/ 500	15	4.3	41	38	2.0	460	12	39






<sup>a</sup>Data are the average of a minimum of five separate reactions.

<sup>b</sup>Reactions were run in a 316 SS cell at 5000 psi CO<sub>2</sub> with a catalyst/oxidant/substrate ratio of 1/400/2000 (150 psig air) or 1/1500/2000 (500 psig air).

<sup>c</sup>Turnovers counts ketone as 2, and oxabicyclo[4.1.0]heptan-2-one and 4-hydroxy-2-cyclohexen-1-one as 3 each, assuming progressive oxidation.

<sup>d</sup>Methylene chloride data from Ref. [29], using similar concentrations of reactants (1 atm O<sub>2</sub>, 25°C).

Table 2  
Cyclohexene oxidation (12-h reactions) with Fe(TFPPBr<sub>8</sub>)Cl

Run	Reaction Conditions <sup>a</sup> (hrs/°C/psi air)	% product					Turnovers <sup>b</sup>	Conversion (% substrate)	Conversion (% O <sub>2</sub> )
									
9	12/ CH <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>	8.0	52	40	—	—	49	0.5	49
10	12/ 40/ 150	14	10	41	31	4.0	250	3.4	33
11	12/ 80/ 500	34	5.2	35	23	1.9	580	8.9	25
12	18/ 80/ 500	22	3.5	35	37	1.8	1000	15	46
13	24/ 80/ 500	23	3.0	35	37	1.0	1530	22	67

<sup>a</sup>Data are the average of a minimum of five separate reactions.

<sup>b</sup>Reactions were run in a 316 SS cell at 5000 psi CO<sub>2</sub> with a catalyst/oxidant/substrate ratio of 1/700/3000 (150 psig air) or 1/2500/3000 (500 psig air).

<sup>c</sup>Turnovers counts ketone as 2, and oxabicyclo[4.1.0]heptan-2-one and 4-hydroxy-2-cyclohexen-1-one as 3 each, assuming progressive oxidation.

<sup>d</sup>Methylene chloride data from Ref. [29], using similar concentrations of reactants (1 atm O<sub>2</sub>, 25°C).

tions were run in batch mode with analysis of the entire cell contents at a specified time. Reactions were run for periods of 4–48 h in a 316 SS cell with a magnetic stirring bar. The reactor was charged with catalyst, cyclohexene, then air (150 or 500 psig); the system was then brought up to full CO<sub>2</sub> pressure (5000 psi) and temperature for the duration of the reaction.<sup>4</sup>

<sup>4</sup> Air was used rather than pure oxygen to avoid hazards associated with pressurized oxygen. All systems were barricaded behind Lexan shielding, and tubing and valves were secured to the work tables in case of explosion.

As neither porphyrin is soluble in liquid carbon dioxide, reaction before the system equilibrates should be minimal. Products were collected by trapping of the reaction into a let-down solution of cold acetone which was analyzed by GC/MS [4].

Cyclohexene was chosen as a model substrate because both allylic oxidation and epoxidation are possible. A comparison of the ratio of radical-derived products to epoxides formed in organic solvent vs. sc CO<sub>2</sub> is a rough measure of the degree of selectivity in the supercritical medium. We found that cyclohexene is oxidized

to a mixture of cyclohexene oxide (**1**), 2-cyclohexen-1-ol (**2**), 2-cyclohexen-1-one (**3**), 7-oxabicyclo[4.1.0]heptan-2-one (**4**) and 4-hydroxy-2-cyclohexen-1-one (**5**)<sup>5</sup> in supercritical carbon dioxide (Scheme 1; Tables 1 and 2). Product **1** is derived from epoxidation, **2** from allylic oxidation; **3**, **4**, and **5** are higher oxidation products. Partitioning of 2-cyclohexen-1-ol (**2**) to its epoxidation product, 7-oxa-bicyclo[4.1.0]heptan-2-ol (**6**) is not observed. We defined turnover number in terms of oxidations per mole of catalyst:  $\text{TON} = [\mathbf{1} + \mathbf{2} + 2x(\mathbf{3}) + 3x(\mathbf{4}) + 3x(\mathbf{5})]/\text{mol catalyst}$ , as products **3**, **4**, and **5** are the result of multiple oxidations of a single substrate molecule.

Initial experiments in carbon dioxide with both porphyrins were conducted at 40°C using 150 psig of air and a total pressure of 5000 psi. At 4 h, catalysis by Fe(TFPP)Cl and air in supercritical carbon dioxide yields more product (30 TON at 40°C) than that in room temperature methylene chloride (11 TON). Increasing reaction time, temperature, or concentration of oxygen all resulted in greater amounts of product formation, with the highest turnover numbers achieved at higher temperature (80°C) rather than at longer reaction time. A UV–Vis spectrum of the reaction let-down solution after a 12-h reaction indicated significant porphyrin degradation, and the remaining complex had converted to the  $\mu$ -oxo dimer, (FeTFPP)<sub>2</sub>O. The loss of active porphyrin catalyst is consistent with only a 2-fold increase in product from the 4-h reaction. The catalyst is not completely deactivated, however, as product formation continues through 18 h at 80°C, the longest reaction time tested for Fe(TFPP)Cl (Fig. 3). An 18-h reaction at 80°C with 500 psig of air had the highest turnover number for Fe(TFPP)Cl at 460 turnovers. As with the 40°C reactions, this reac-

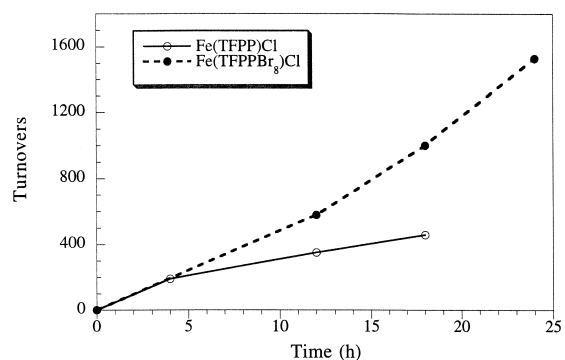


Fig. 3. Turnovers vs. time for cyclohexene oxidation by Fe(TFPP)Cl and Fe(TFPPBr<sub>8</sub>)Cl in sc CO<sub>2</sub>. Reactions were run at 5000 psi with 500 psig air at 80°C. The fall off in catalysis by Fe(TFPP)Cl indicates some porphyrin decomposition at longer time periods.

tion slows down after 4 h, suggesting that the porphyrin catalyst is deactivated under these conditions.

The increase in activity in sc CO<sub>2</sub> relative to room temperature CH<sub>2</sub>Cl<sub>2</sub> is more pronounced with Fe(TFPPBr<sub>8</sub>)Cl (Table 2). A 5-fold increase in turnover number for 12-h reactions is observed, suggesting that sc CO<sub>2</sub> is an excellent solvent for the fully halogenated porphyrin.<sup>6</sup> Again, increasing temperature and dioxygen concentration results in more product formation, although the increase is not as dramatic as with Fe(TFPP)Cl. The fully halogenated porphyrin shows less evidence for decomposition, with fairly linear increases in turnover number with time (Fig. 3) up to the maximum of 1530 turnovers at 24 h (80°C and 500 psig of air). Also, a UV–Vis of the let-down solution shows that the majority of the porphyrin is intact, although some decomposition products and loss in the reactor tubing are observed.

As in organic solvents [29], the more robust and fully halogenated porphyrin, Fe(TFPPBr<sub>8</sub>)Cl, is a more active catalyst than

<sup>5</sup> All products were verified by GC/MS injection of authentic samples except 4-hydroxy-2-cyclohexen-1-one, which is assumed based on retention time, mass spectrum, and as the logical partitioning product from 2-cyclohexen-1-one.

<sup>6</sup> We also attempted the oxidation of 3-methylpentane, in attempts to directly compare our data with the results of Ellis and Lyons (Refs. [30,31,33]). However, we observed no oxidation of the alkane substrate with either porphyrin catalyst, even after 24 h at 80°C.

Fe(TFPP)Cl, with over three times as much activity in 12 h in sc CO<sub>2</sub> (65 vs. 250 TON at 40°C). This is most likely due to a combination of the higher initial activity of Fe(TFPPBr<sub>8</sub>)Cl, and lower decomposition rates, as described above.

The product analysis for air-oxidation of cyclohexene shows a surprising mixture of products for both catalysts in sc CO<sub>2</sub>. While reactions in room temperature methylene chloride are only found to produce cyclohexene oxide (**1**), 2-cyclohexen-1-ol (**2**), and 2-cyclohexen-1-one (**3**), reactions in sc CO<sub>2</sub> also produced the multiply oxidized products **4** and **5** (Tables 1 and 2). Both Fe(TFPP)Cl and Fe(TFPPBr<sub>8</sub>)Cl reactions showed substantially less 2-cyclohexen-1-ol than in methylene chloride. Most notably, cyclohexene oxide production increased for both Fe(TFPP)Cl and Fe(TFPPBr<sub>8</sub>)Cl reactions at higher temperatures and oxidant ratios, comprising a full 34% of the products in the Fe(TFPPBr<sub>8</sub>)Cl-catalyzed reaction at 80°C and 500 psig of air. Both epoxides (**1** and **4**) together comprised 43 to 53% of the products in Fe(TFPP)Cl-catalyzed reactions (Runs 5–8), and 45 to 60% of the products in Fe(TFPPBr<sub>8</sub>)Cl-catalyzed reactions (Runs 11–13) in sc CO<sub>2</sub>. The relative amount of epoxidation is substantial for radical chemistry and not readily explained by a simple solvent effect.

### 3.3. Catalysis in organic solvents






As stated above, reactions with both Fe(TFPP)Cl and Fe(TFPPBr<sub>8</sub>)Cl in sc CO<sub>2</sub> show significant amounts of epoxidation. To ascertain that the selectivity is due to the use of sc CO<sub>2</sub> as a solvent and not a simple temperature or pressure effect, a series of controls were conducted in several organic solvents at identical temperatures and pressures. Because methylene chloride boils at the temperatures used in the sc CO<sub>2</sub> experiments, the solvent reactions were conducted in the same high pressure apparatus, using 5 ml of solvent, and an inert gas (nitrogen) to bring the pressure up to 5000 psig.

Although the conditions are not identical, as the organic solvent reactions will have both gas and liquid phases, this series of reactions attempts to remove as many as possible of the differences in how the solvent and the supercritical fluid experiments were conducted.

High turnover numbers were observed in all organic solvents at 80°C and with 500 psig of air. In 12 h, Fe(TFPP)Cl-catalyzed oxidations of cyclohexene in benzene, methylene chloride, and acetonitrile all had similar activity, with 1230 to 1340 turnovers (Table 3). The comparable sc CO<sub>2</sub> reaction had only one-third the activity, with 350 turnovers. A similar ratio in activity was observed in Fe(TFPPBr<sub>8</sub>)Cl-catalyzed oxidations in benzene and methylene chloride, with the organic reactions at 80°C and 500 psig of air showing approximately three times the activity of the sc CO<sub>2</sub> reaction. Despite the higher activity observed, UV–Vis of the let-down solutions for both porphyrins indicated significantly more porphyrin degradation than in sc CO<sub>2</sub>. In addition, after solvent reactions, the reaction cell had to be completely dismantled and thoroughly scrubbed to remove residues of porphyrin degradation products.

Selectivity differences between these organic solvent reactions and those at room temperature were also noted. Similar to the sc CO<sub>2</sub> reactions, all solvent reactions at 5000 psi and 80°C yield fairly low amounts of 2-cyclohexen-1-ol, suggesting that higher pressure and/or temperature favor the multiply oxidized products. This is further borne out by the appearance of products **4** and **5** in organic solvent reactions with either catalyst, which are not present in the room temperature, 1 atmosphere methylene chloride reactions. Significant concentration of free radicals in the organic solution reactions was also evidenced by the formation of new products that resulted from oxidation of, or reaction with the solvent. Several different chlorinated cyclohexene products were identified by GC/MS in the methylene chloride reactions, and the acetonitrile and benzene reactions also had evidence of solvent-related products. It is

Table 3  
Cyclohexene oxidation in different solvents

Run <sup>a</sup>	Catalyst	Solvent	% product					Turnovers	Conversion (% substrate)	Conversion (% O <sub>2</sub> )
										
7	F <sub>20</sub>	CO <sub>2</sub>	17	5.5	38	38	1.6	350	9.0	29
14		Benzene/N <sub>2</sub>	6.1	5.1	51	27	11	1320	32	105
15		CH <sub>2</sub> Cl <sub>2</sub> /N <sub>2</sub>	21	4.0	40	29	5.7	1340	38	115
16		Acetonitrile/N <sub>2</sub>	15	6.0	42	31	6.0	1230	32	102
11	Br <sub>8</sub>	CO <sub>2</sub>	34	5.2	35	23	1.9	580	8.9	25
17		Benzene/N <sub>2</sub>	8.8	6.8	50	24	10	1520	20	71
18		CH <sub>2</sub> Cl <sub>2</sub> /N <sub>2</sub>	16	9.2	45	25	5.3	2170	29	87
19	none	CO <sub>2</sub>	9.9	19	52	17	1.8	38	1.0	3.0
20		CH <sub>2</sub> Cl <sub>2</sub>	–	75	25	–	–	15	0.4	1.2

<sup>a</sup>Data are the average of a minimum of five separate reactions. All reactions were run for a duration of 12 h at 80°C using 500 psig of air as the oxidant.

CO<sub>2</sub> reactions were pressurized to 5000 psi as described in the text; organic solvent reactions were pressurized to 5000 psi with nitrogen.

apparent that the organic solvents assist the propagation of free radical chemistry under these conditions, but also that solvent-derived by-products are formed, which are not seen in CO<sub>2</sub>.

As shown in Scheme 1, the ratio of **1** to **2** is the initial selectivity of the oxidation reaction. This ratio is complicated by the fact that we observe large amounts of the higher oxidation products **3**, **4**, and **5** even at low conversion. The benzene (Runs 14 and 17) and methylene chloride (Runs 15 and 18) reactions with Fe(TFPP)Cl and Fe(TFPPBr<sub>8</sub>)Cl, respectively, have product distributions that track with solvent rather than with catalyst. The dependence of selectivity on solvent suggests that the solvent plays a large role in determining product ratios. For example, in benzene, the epoxide products (**1** and **4**) comprise 33% of the total, regardless of catalyst. If selectivity for epoxidation is defined as a ratio of epoxide to radical products, these values can be calculated and plotted against various solvent parameters. Ideally, this ratio would be a calculation of the actual rates of epoxidation ( $k_e$ ) and radical oxidation ( $k_r$ ). As we were unable to measure these rates by our batch reaction methods, we define the selectivity as the ratio of products:  $[1 + 4]/[2 + 3 + 5]$ . Attempts to correlate this

selectivity ratio with a solvent parameter such as solvent dielectric were not very successful. Supercritical CO<sub>2</sub> and benzene, which have very similar solvent dielectric constants, have very different selectivity for epoxidation, with sc CO<sub>2</sub> having the highest selectivity, and benzene the lowest of any solvent tested (Table 3). The amount of epoxide produced in each solvent obviously bears a more complex relationship to the reaction conditions than a simple dependence on solvent polarity.

If the products are separated into actual turnovers of epoxide and radical products (Fig. 4), a different dependence is observed. For Fe(TFPP)Cl-catalyzed oxidations, all solvent reactions show similar turnover numbers of radical-based products (**2–5**), suggesting that the solvent, at least in the sub-critical regime, does not affect the amount of radical propagation. The same reaction in sc CO<sub>2</sub>, on the other hand, has a lower turnover number of radical products, suggesting that either free radical propagation reactions are slower, or termination reactions are faster in this medium. In fact, Suppes et al. [28] have observed that cumene oxidation was found to be limited by increased chain termination rates in sc CO<sub>2</sub> relative to a pure cumene solution. The number of epoxide turnovers, on the other hand, varies with sol-



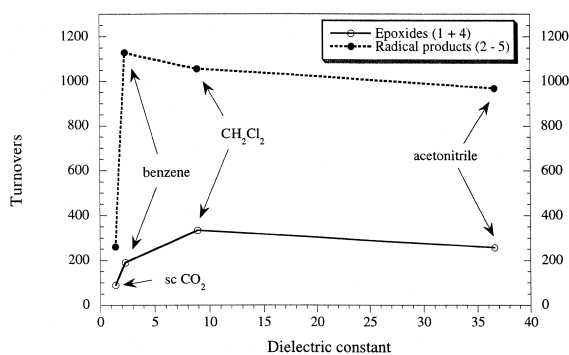
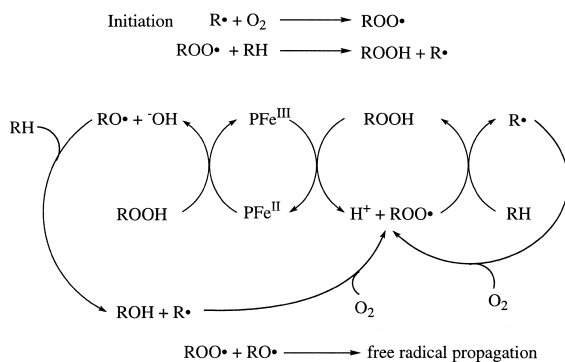


Fig. 4. Turnovers vs. solvent dielectric for Fe(TFPP)Cl-catalyzed oxidation of cyclohexene at 80°C and 500 psig of air. Epoxide turnovers (solid line) = (mol **1** + mol **4**)/mol catalyst. Radical turnovers (dotted line) = (mol **2** + 2 × mol **3** + 2 × mol **4** + mol **5**)/mol catalyst. The activity for radical chemistry is similar for all three organic solvents, and much lower in sc CO<sub>2</sub>.

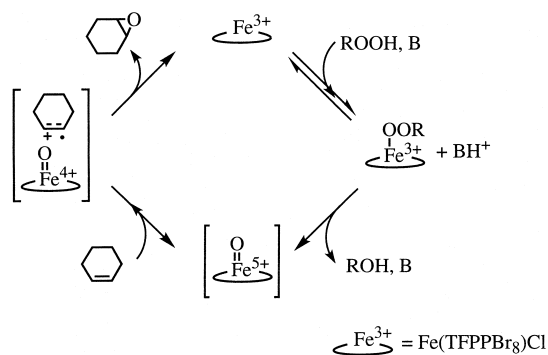
vent. The absence of any trend in these data suggests the potential for different mechanisms to dominate in the various solvents.

### 3.4. Porphyrin-catalyzed oxidation mechanisms

The air oxidation of alkanes and alkenes catalyzed by Fe(TFPPBr<sub>8</sub>)Cl has been studied in detail, and has been shown to occur via an alkyl hydroperoxide decomposition mechanism (Scheme 2) [29,31–33,37]. Alkyl hydroperoxides (ROOH), formed from the reaction of the hydrocarbon with oxygen, are oxidized and reduced by the porphyrin, resulting in formation of alkoxy and alkyl peroxy radicals. These radicals propagate and terminate in free radical



Scheme 2.

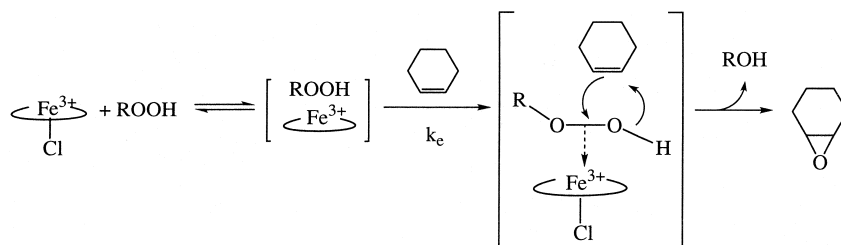


Scheme 3.

reactions to form, in the case of cyclohexene, allylic oxidation products such as **2** and **3**.

The alkyl hydroperoxide decomposition mechanism does not directly address the origin of epoxides, which may be formed via several different mechanisms. Most studies have invoked alternative reactions of the in-situ-formed alkyl hydroperoxides, either on the iron center or on the alkene itself. Some possibilities include: (1) uncatalyzed oxidation of the alkene by ROOH; (2) reaction of ROOH with the iron porphyrin to form a high-valent iron-oxo (ferryl), which then directly epoxidizes the alkene, (3) the iron center may serve as a Lewis acid to catalyze epoxidation via an alkyl hydroperoxide intermediate, or (4) some combination of pathways. In light of the increase in the selectivity towards epoxidation in sc CO<sub>2</sub>, we considered the possibility of a mechanism change from the free radical chemistry that dominates in methylene chloride.

A substantial amount of research has investigated the production of high-valent iron-oxo species in biomimetic catalysts, as this is the proposed active species in several enzymes capable of selective oxidation (i.e., cytochrome *P*-450) [38]. A change from the alkyl hydroperoxide mechanism to increased production of a ferryl intermediate in sc CO<sub>2</sub> is anticipated to be disfavored for several reasons. Previous results [32,39] have shown that the reduced Fe<sup>II</sup> species is unable to bind dioxygen (the first step



Scheme 4.

in enzymatic ferryl generation), prohibiting ferryl generation from dioxygen with these catalysts. However, a high-valent iron-oxo could alternatively be formed from oxidation of the iron by the alkyl hydroperoxide, as described by Traylor et al. [40,41] in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  solution with a variety of porphyrins (Scheme 3). This mechanism depends on the donation of a proton from solvent (represented as  $\text{BH}^+$ ), which is unavailable from carbon dioxide. Without a proton to assist in the heterolytic cleavage of the O–O bond, the barrier for ferryl formation would increase substantially. The charged ferryl species would be further destabilized by the non-polar solvent, and decomposition of the peroxide would be expected to be even more favored over ferryl formation in *sc*  $\text{CO}_2$ . Additional evidence against a high-valent metal-oxo comes from experiments with iodosobenzene (PhIO), a common O-atom donor, as the oxidant. Iodosobenzene is believed to directly form a ferryl with iron(III) porphyrins [42–48], yet with either  $\text{Fe}(\text{TFPP})\text{Cl}$  or  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$  no catalysis is observed.<sup>7</sup> The lack of activity with PhIO would suggest that ferryl formation is disfavored in *sc*  $\text{CO}_2$ , although solubility problems with iodosobenzene cannot be completely precluded.

Uncatalyzed reactions of peroxides and cyclohexene in *sc*  $\text{CO}_2$  (i.e., no porphyrin catalyst) were very slow (Run 28). In control experiments with *tert*-butylhydroperoxide and cyclo-

hexene in *sc*  $\text{CO}_2$ , conversion that would reflect only seventeen turnover equivalents of product were observed after 12 h at  $80^\circ\text{C}$  (were catalyst used). In addition, there was a change in selectivity, as these reactions were found to result in allylic oxidation rather than epoxidation. The only observed products were **2** and **3** in a 1 to 3 ratio. If peroxides are involved in epoxide formation, the catalysis must be porphyrin-mediated.





Epoxidation catalyzed by Lewis acids, on the other hand, would potentially be enhanced in supercritical carbon dioxide. The electron-deficient porphyrins would be additionally destabilized due to the absence of favorable solvent interactions from the completely non-polar solvent. Specifically, this may enable the iron center to behave more like a high-valent early transition metal such as vanadium(V) or molybdenum(VI); complexes of these metals are able to catalyze the epoxidation of alkenes with alkyl hydroperoxides [49] (Scheme 4). A highly electrophilic iron center could enhance the reactivity of a bound peroxide, or even bind olefin in an analogous manner to vanadium catalysts. In fact, traditional Lewis acids such as  $\text{AlCl}_3$  and  $\text{AlBr}_3$  have been found to be very active for alkane isomerization in *sc*  $\text{CO}_2$  [50], suggesting this pathway, if available to the halogenated porphyrins, may be enhanced in this medium.

### 3.5. Oxidation using *tert*-butylhydroperoxide

To further explore the possibility of Lewis acid catalysis by  $\text{Fe}(\text{TFPP})\text{Cl}$  and  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$ , we conducted experiments in a

<sup>7</sup> Some product formation is observed, but the amount of product is identical to a run without any porphyrin catalyst, and consists predominantly of allylic oxidation products **2** and **3**.

Table 4  
Oxidation of cyclohexene with TBHP

Run <sup>a</sup>	Catalyst	Solvent	% product				Turnovers
							
22	F <sub>20</sub>	CO <sub>2</sub>	5.2	35	58	2.2	490
23		Benzene/ N <sub>2</sub>	5.7	31	61	2.2	420
24		CH <sub>2</sub> Cl <sub>2</sub> / N <sub>2</sub>	4.4	43	49	3.6	570
25		Acetonitrile/N <sub>2</sub>	1.2	51	37	11	560
26	Br <sub>8</sub>	CO <sub>2</sub>	4.7	44	43	9.0	760
27		Benzene/ N <sub>2</sub>	5.5	35	60	— <sup>b</sup>	1030
28	none	CO <sub>2</sub>	— <sup>b</sup>	25	75	— <sup>b</sup>	17

<sup>a</sup>Data is the average of multiple reactions. Reactions at 80°C for 4 h with 1 ml cyclohexene, 1 ml 5–6 M TBHP in decane, and 8 ml organic solvent or 5000 psi CO<sub>2</sub>.

<sup>b</sup>No product observed.

series of solvents using *tert*-butylhydroperoxide (TBHP) as the oxidant rather than dioxygen. In a Lewis acid mechanism, the TBHP would take the place of cyclohexenyl peroxide generated from dioxygen in the catalysis described above, and the amount of epoxide formed could be correlated with the strength of the Lewis acid in that solvent. Reactions in the least polar solvent (CO<sub>2</sub>) are predicted to generate the most epoxide, and those in the most polar solvent (acetonitrile) the least. In fact, other work in our group has shown that titanium and vanadium catalysts in dense phase carbon dioxide are quite selective for epoxidation of olefins with TBHP [51].

Net activity in all solvents is much more consistent with TBHP as the oxidant, with the Fe(TFPP)Cl-catalyzed oxidations having approximately 500 turnovers, and the two Fe(TFP-PBr<sub>8</sub>)Cl-catalyzed reactions having a slightly larger difference with 760 and 1030 turnovers in CO<sub>2</sub> and benzene, respectively (Table 4). With a radical source (TBHP) present in high concentration, the solvent has less impact on the radical propagation chemistry.

The selectivity is also very different than with oxygen as the oxidant. Porphyrin-catalyzed decomposition of TBHP, which is reported to be extremely fast [37], dominated the chemistry.

Reactions in both organics and in sc CO<sub>2</sub> move more towards the selectivity observed in liquid methylene chloride, with significant amounts of the allylic oxidation products **2** and **3** observed in all solvents. Minimal amounts of cyclohexene oxide are produced, with no more than 5.7% in any single reaction. Unlike the analogous reactions with dioxygen, epoxide production with TBHP (dotted line) does correlate with solvent dielectric (Fig. 5). Increasing epoxidation is observed with decreasing dielectric, or in

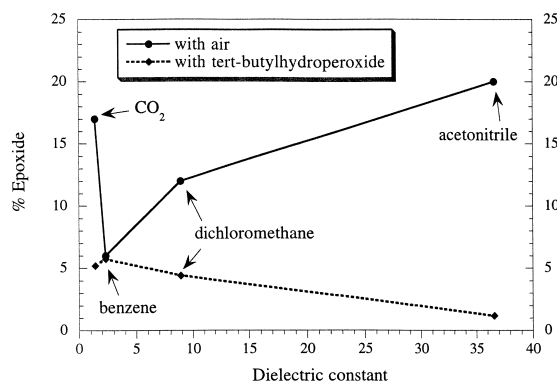


Fig. 5. Percent cyclohexene oxide vs. solvent dielectric for Fe(TFPP)Cl-catalyzed oxidations of cyclohexene with air and TBHP. TBHP results are linear, consistent with an increase in Lewis acidity (and hence epoxidation) in the less polar solvents. The increase in activity in the more polar solvents with air may indicate that a different mechanism begins to dominate under these conditions.

those solvents where the porphyrins would be the strongest Lewis acids. This result is consistent with a Lewis acid-catalysis picture such as shown in Scheme 4. However, with TBHP as the oxidant, this mechanism makes only a minor contribution, as the majority of the peroxide is decomposed by the porphyrins as in Scheme 1 (with subsequent formation of allylic oxidation products). The lack of any linear trend in the amount of epoxidation in the air oxidation reactions (solid line) may indicate a contribution from a third mechanism (i.e., ferryl formation) in a polar, protic solvent such as acetonitrile.

#### 4. Conclusions

The results described above demonstrate that supercritical carbon dioxide serves well as a solvent replacement for methylene chloride for porphyrin-catalyzed oxidation of cyclohexene. Turnover numbers were respectable, with up to 580 turnovers of cyclohexene observed in 12 h. Changes in the reaction selectivity were also noted, specifically the increased epoxidation selectivity for both Fe(TFPP)Cl and Fe(TFPPBr<sub>8</sub>)Cl in reactions at 80°C with 500 psig air. Cyclohexene oxide alone constitutes up to 34% of the product distribution under certain conditions (Run 11). The sensitivity of the reaction to relatively small temperature changes suggests that further tuning to increase the selectivity for epoxidation is possible.

It is not, however, clear if these changes in activity and selectivity are due to the solvent, or simple pressure and temperature effects. Higher temperature and pressure reactions in organic solvents also resulted in substantial changes from room temperature reactions. The assignment of solvent, temperature, and pressure effects could not be clearly determined, perhaps in part due to the number and complexity of porphyrin-catalyzed reactions even in such simple systems. Several advantages for supercritical carbon dioxide were obvious, however: (1)

cleaner chemistry was observed, with no solvent-related products found; (2) less porphyrin decomposition was observed, and (3) less contamination of cell pieces and apparatus was observed with CO<sub>2</sub> than with other high temperature reactions.

Attempts to explain selectivity enhancement in sc CO<sub>2</sub> requires both peroxide decomposition and porphyrin-mediated epoxidation into a single mechanistic picture. Activity depends on a free radical initiation process to generate alkyl hydroperoxides in solution. Presumably, these hydroperoxides can interact with the catalyst by three different routes, oxidation of ROOH ( $k_r$ ), epoxidation of the alkene ( $k_e$ ), or in protic solvents, generation of a ferryl. Reactions in organic solvent at high pressures suffer from the contribution of solvent-generated radicals (as shown for CH<sub>2</sub>Cl<sub>2</sub>), which contribute to the overall amount of radical products formed. Higher activity in organics indicate that the initiation steps are difficult or that the absolute values of  $k_e$  and  $k_r$  may be less in sc CO<sub>2</sub>. The amount of epoxidation indicates that the relative  $k_e/k_r$  is enhanced in sc CO<sub>2</sub>. Experiments on other homogeneous systems are underway in our laboratory to further explore the potential of controlling selectivity with this environmentally benign medium.

#### 5. Experimental

##### 5.1. Materials

Fe(TFPP)Cl was used as received (Aldrich), and Fe(TFPPBr<sub>8</sub>)Cl was synthesized and purified as previously described [52]. Cyclohexene (Aldrich) was distilled under argon before use. Acetone, methylene chloride (EM Science), 3-fluorotoluene, toluene (Aldrich), and iodobenzene (TCI) were used as received. Carbon dioxide (SCF grade) was run through a drying column as well as hydrocarbon and oxygen traps before pressurizing.

## 5.2. Spectroscopy

UV–Vis spectra were obtained in a 20-ml 316 SS cell with sapphire windows. The porphyrin was loaded into the cell, the windows sealed with Teflon and Buna-N O-rings, and the cell placed into a Perkin Elmer Lambda 19 UV–Vis spectrophotometer. The cell was then brought up to 5000 psig CO<sub>2</sub> and 40°C using a high pressure syringe pump (ISCO). The temperature was maintained with heating tape and a thermocouple that connected to the interior of the cell. The cell had a 2-cm path length, and the concentration in solution was estimated based on  $\epsilon$  values in methylene chloride [52].

## 5.3. Reactions

A 316 SS cell without windows was used for catalysis reactions as described previously [4]. The cell had ports for a thermocouple, pressure gauge, and rupture disk, and had a total volume of approximately 18 ml. Catalytic reactions were run in batch as follows: the reactor was charged with catalyst (2–3 mg), cyclohexene (0.5 ml, freshly distilled), and a stir bar, then sealed and attached to the gas manifold. Air (150 or 500 psig) was added next, followed by CO<sub>2</sub>. The CO<sub>2</sub> was added using a high pressure syringe pump (ISCO), and cell temperature was maintained with heating tape. The system was brought up to full CO<sub>2</sub> pressure (5000 psig) and temperature (40 or 80°C) for the duration of the reaction. At the end of the desired time, reactions were let down slowly over a period of 1–2 h into a vial containing 25 ml of cold acetone to trap volatile organics. The reaction vessel was rinsed with acetone to remove residual products, and the solutions were combined for a single let-down solution. Aliquots of this solution were analyzed by GC/MS and/or UV–Vis.

Solvent reactions were conducted in a similar fashion, except that the reactor was charged with 5 ml solvent in addition to the substrate and catalyst. Instead of carbon dioxide, nitrogen

gas was used to pressurize the reactor. Reactions with TBHP had the oxidant (1 ml of a 5–6-M solution in decane) added with the catalyst and substrate (1 ml). For reactions in CO<sub>2</sub> with *tert*-butylhydroperoxide as the oxidant, reactions were set up in a glove bag to exclude air. The organic solvent reactions (8 ml of solvent) were not pressurized, and the solution was deaerated with nitrogen before the cell was sealed.

## 5.4. Analytical procedures

Oxidation products were identified by injection onto an Hewlett Packard GC/MS with an auto injector and a JW Scientific DB-5 30 m column and verified by injection of an authentic sample for cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and 7-oxa-bicyclo-[4.1.0]heptan-2-one (Aldrich). Product concentrations were determined by use of either an external (toluene) or internal (3-fluorotoluene) standard.

All systems were barricaded behind Lexan shielding, and tubing and valves were secured to the work tables to minimize damage in case of a pressure failure. All systems were equipped with vented relief valves or rupture discs for safety purposes.

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