Catalytic Olefin Epoxidation With H_2O_2 in Supercritical CO_2. Synergic Effect by Hexafluoroacetone and Manganese-Porphyrins

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Abstract: The heterogeneous oxidation of cyclooctene with hydrogen peroxide catalyzed by manganese 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrinate, in the presence of hexafluoroacetone hydrate as co-catalyst, has been studied in supercritical carbon dioxide, at 40 °C and 20 MPa. Under proper conditions, a complete olefin conversion may be obtained with the formation of cyclooctene oxide as the sole product. Fixation by hexafluoroacetone into its perhydrate derivatives provides a useful system to solubilize hydrogen peroxide in supercritical carbon dioxide, and to hamper catalyst bleaching and oxidant decomposition. Moreover, in the presence of both manganese-porphyrin and hexafluoroacetone, the reaction rates are enhanced. Among the factors that may increase yields and rate of conversion, the use of a Teflon-coated steel reactor rather than an uncoated one proved to be quite relevant, thus indicating the occurrence of a parasite radical decomposition of hydrogen peroxide promoted by steel reactor walls.

Keywords: carbon dioxide (supercritical); hexafluoroacetone; hydrogen peroxide; oxidation; porphyrin

Introduction

Among the various substances that can be employed at supercritical conditions, carbon dioxide ($scCO_2$) is a particularly attractive reaction medium as it is environmentally and economically convenient,[1,2] non-flammable, non-toxic, and chemically inert under many conditions. $ScCO_2$ has already been shown to be a clean and effective reaction medium for many catalytic processes including free radical[3] and cationic[4] polymerization, hydrogenations,[5–8] hydroformylations,[9] and enzymatic processes.[10–12]

In the case of oxidation processes, $scCO_2$ is particularly well suited being fully oxidized and hence quite stable under any conditions. As a matter of fact, the major part of the reports concerning oxidation under supercritical conditions deal with unselective oxidation by molecular oxygen promoted by both homogeneous[13] and heterogeneous[14] catalysts. Conversely, only a limited number of reports deal with selective oxidations carried out by other primary oxidants such as hydrogen peroxide, alkyl peroxides, hydroperoxides, monopersulfate, hypochlorite, etc. The most investigated primary oxidants in selective catalytic oxidations are low molecular weight hydroperoxides because of their fair solubility in $scCO_2$. These were employed in the epoxidations of olefins[15–19] and in the sulfoxidation of cysteine derivatives[20] using a variety of catalysts and also of chiral additives under conditions that, in a few cases, led to interesting stereochemical results.[17,19]

Reports on the utilization of primary oxidants other than hydroperoxides are particularly scarce.[21] We recently reported a study on the oxidation of thioethers with Oxone® ($2\ KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) catalyzed by various manganese porphyrins in $scCO_2$ at 40 °C and 20 MPa.[22] The oxidizing system had a definite heterogeneous character, both oxidant and catalyst being virtually insoluble in $scCO_2$. Nevertheless, under proper conditions, the oxidative process was found to take place to yield the corresponding sulfoxides and sulfones.

These encouraging results prompted us to realize a catalytic oxidative process in $scCO_2$ employing hydrogen peroxide (H_2O_2) as primary oxidant. In fact, its low molecular weight and non-ionic character should allow a fair solubility in $scCO_2$. In spite of all these ideal properties, two major drawbacks may hamper the use of H_2O_2, unlike that of other peroxides. The first one is related to the presence of water, which may cause the hydrolysis of the reaction products. The second disadvantage is the free radical decomposition of H_2O_2 in transition metal-catalyzed oxidations.[23–26] For these reasons, only relatively few oxygenation reactions have been reported using H_2O_2 as a source of oxygen using metalloporphyrins as catalyst.[27–34]

In this study we utilized hexafluoroacetone hydrate (HFAH) for the oxygen transfer from H_2O_2 to cyclooctene mediated by an activated manganese porphyrin in $scCO_2$ under mild conditions (40 °C, 20 MPa). Although HFAH is known to act as a catalyst via formation of its perhydrate derivative (HFAPH) in the epoxidation of reactive olefins by H_2O_2,[35–37] it is here reported that its utilization in the presence of an appropriate metalloporphyrin in $scCO_2$, speeds up the reaction and effectively converts the olefin employing only a moderate excess of H_2O_2.

Results and Discussion

The Oxidation of Cyclooctene using H_2O_2, HFAH and Mn(TDCPP)Cl in Chloroform and in *n*-Hexane

Preliminary experiments were carried out to check the effect of HFAH on the oxidation of cyclooctene with H_2O_2 promoted by manganese 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrinate [Mn(TDCPP)Cl] in two conventional liquid solvents, namely chloroform and *n*-hexane. Cyclooctene was the substrate of choice since it was proven that its epoxide is perfectly stable under the experimental conditions adopted in both liquid and supercritical reaction media. Mn(TDCPP)Cl was chosen because it is known as one of the most robust porphyrinic catalyst in the oxidations with H_2O_2. In these experiments, the catalyst employed [Mn(TDCPP)Cl, 1.2 mg] was previously adsorbed on 50 mg of silica gel in order to facilitate reactor loading and the oxidation reactions were carried out in a jacketed reactor maintained at 40 °C, under magnetic stirring, in the presence of H_2O_2 (70% w/w aqueous solution), HFAH and 4-*tert*-butylpyridine, in a biphasic 1/0.1 v/v organic solvent/water medium. The molar ratios of the components (when present) of the reaction mixture were approximately the following: substrate/HFAH/H_2O_2/catalyst/4-*t*-BuPy = 1/1/5.8/0.0034/0.09. The excess of H_2O_2 was used to ensure a complete conversion of cyclooctene. The progress of the reaction was monitored by GLC analysis of organic solution samples taken at appropriate times to determine the concentration of cyclooctene epoxide formed as the sole product. Figure 1 shows the kinetic profile of cyclooctene oxidation with H_2O_2 in $CHCl_3$ at 40 °C promoted by HFAPH and by its association with Mn(TDCPP)Cl in the presence of 4-*tert*-butylpyridine.

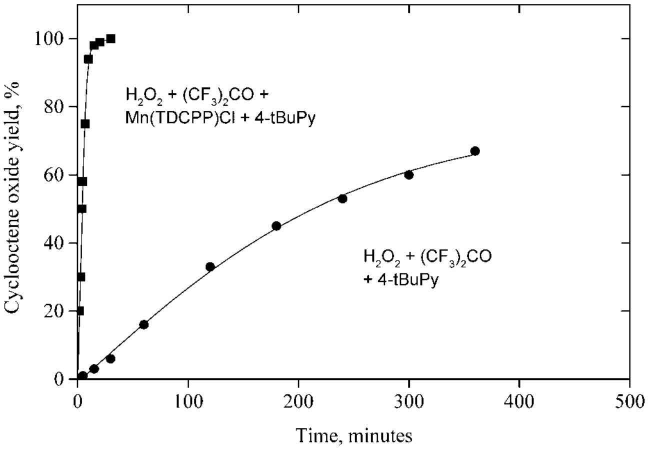


Figure 1. Cyclooctene (3.80×10^{-2} M) oxidation by H_2O_2 (formally 0.22 M) in the presence of $(CF_3)_2CO \cdot 3\,H_2O$ (3.60×10^{-2} M), 4–*tert*-butylpyridine (3.38×10^{-3} M), in the absence (●) and presence (■) of Mn(TDCPP)Cl (1.28×10^{-4} M), in $CHCl_3$ at 40 °C.

In the absence of the porphyrinic catalyst (●), a relatively slow but clean epoxidation is observed. The initial rate of cyclooctene oxide formation (here and hereafter expressed as molarity per minute, M min^{-1}) is 1.0×10^{-4} M min^{-1}, whereas the substrate conversion is complete (>99%) after 29 hours. In the presence of both Mn(TDCPP)Cl and HFAH (■), the reaction rate is remarkably higher and reaches a value of 4.8×10^{-3} M min^{-1}, whereas a total substrate conversion is obtained in 30 minutes. It should be noticed that in this case the catalytic oxidation occurs essentially in a homogeneous phase since substrate, catalyst and axial ligand are all soluble in $CHCl_3$ while it may be assumed that HFAPH is partitioned between the two phases.

In *n*-hexane, a solvent with a polarity very close to that of $scCO_2$, the catalyzed oxidation occurs in a heterogeneous system since the catalyst Mn(TDCPP)Cl is not soluble in the organic phase and the outcome is predictably different as shown in Figure 2.

In the absence of the porphyrinic catalyst (●) the oxidation proceeds as well as in $CHCl_3$. In fact, the initial rate is 1.6×10^{-4} M min^{-1}, somewhat higher than in $CHCl_3$, and an almost quantitative conversion of substrate (>93%) is observed after 24 hours. In the presence of both Mn(TDCPP)Cl and HFAH (■) the kinetic profile differs from that found in $CHCl_3$ as an initial burst is followed by a much slower reaction. The initial rate is 9.5×10^{-4} M min^{-1}, lower than that in $CHCl_3$ and the maximum olefin conversion is 32% after 24 hours. The lower initial rate can be ascribed to the heterogeneous system in which the catalyzed oxidation occurs. The relatively low conversion is likely due to the fact that the aqueous solution of H_2O_2 is adsorbed by the catalyst support, namely sili-

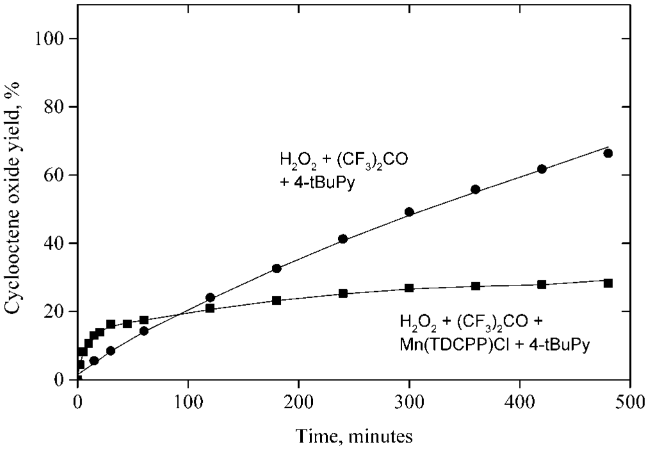


Figure 2. Cyclooctene (3.80×10^{-2} M) oxidation by H_2O_2 (formally 0.22 M) in the presence of $(CF_3)_2CO \cdot 3\ H_2O$ (3.60×10^{-2} M), 4-*tert*-butylpyridine (3.38×10^{-3} M), in the absence (●) and presence (■) of Mn(TDCPP)Cl (formally 1.28×10^{-4} M), in *n*-hexane at 40 °C.

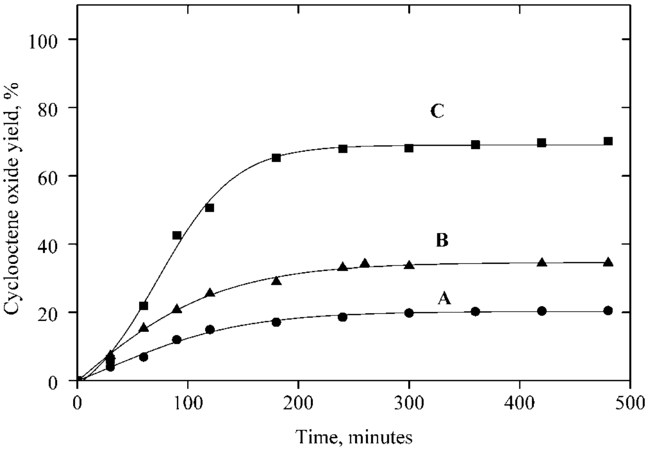


Figure 3. Cyclooctene (3.80×10^{-2} M) oxidation by H_2O_2 (formally 0.22 M) in $scCO_2$ at 40 °C and 20 MPa in the presence of 4-*tert*-butylpyridine (3.38×10^{-3} M) and: in the presence of $(CF_3)_2CO \cdot 3\ H_2O$ (3.60×10^{-2} M) (●); in the presence of Mn(TDCPP)Cl (formally 1.28×10^{-4} M) (▲); in the presence of Mn(TDCPP)Cl (formally 1.28×10^{-4} M) and of $(CF_3)_2CO \cdot 3\ H_2O$ (3.60×10^{-2} M) (■).

ca gel, and quickly decomposed by the catalase activity of the manganese porphyrin. In fact, an evident gas evolution was observed in this case.

Two indications may be drawn from the results of the experiments carried out in the two liquid solvents examined. The first one is that cyclooctene epoxidation is effectively promoted by HFAH alone independently by the reaction medium. It follows that this should occur also in $scCO_2$, where cyclooctene and HFAPH, under the experimental conditions adopted, are fairly soluble. The second point is that Mn(TDCPP)Cl further on increases the oxidative efficiency of the catalytic process, at least in terms of reaction rates. On the other hand, this advantage is overcome in *n*-hexane by a remarkable H_2O_2 decomposition. However, this problem could be bypassed by operating in $scCO_2$. In fact, the adsorption of H_2O_2 on the catalyst's surface can be greatly limited by compartmentalizing the reagents inside the high-pressure vessel used for reactions carried out in $scCO_2$.

The Oxidation of Cyclooctene using H_2O_2, HFAH and Mn(TDCPP)Cl in $scCO_2$

The oxidation reactions hereafter described were carried out in a 10-mL stainless steel reactor, maintained at 40 °C. The reactants were placed separated inside the vessel. In particular, the substrate, catalyst, axial ligand and internal GC standard were placed at the bottom of the reactor while H_2O_2 and HFAH were placed together in a glass container positioned in the upper part of the reactor (see Figure 6). Stirring of the reaction mixture was obtained with one or two magnetic bars located in one or both the containers. The catalytic process was started by pressurizing the system with CO_2 so that the reactants could diffuse inside the reactor. Figure 3 shows the kinetic profile for cyclooctene oxidation with H_2O_2 in $scCO_2$, promoted by three different catalyst associations, employing only one magnetic bar positioned in the upper container.

Curve **A** (●) shows the cyclooctene oxidation catalyzed by HFAH in the presence of 4-*t*-BuPy. The initial rate of epoxide formation is 4.4×10^{-5} M min^{-1}, a value very close to those measured in liquid solvents. However, the olefin conversion stops at 20%, thus suggesting a much more pronounced decomposition of H_2O_2 in $scCO_2$ than in the two liquid solvents examined. Curve **B** (▲) shows the oxidation catalyzed by Mn(TDCPP)Cl in the presence of 4-*t*-BuPy. The initial rate is 9.8×10^{-5} M min^{-1} and an olefin conversion of 35% is observed. The association of Mn(TDCPP)Cl with HFAH allows us to improve reaction rate and conversion, as shown by curve **C** (■). In this case the olefin conversion approaches 70% with an initial rate of 1.4×10^{-4} M min^{-1}.

It should be noticed that, to the best of our knowledge, there is only one literature precedent concerning epoxidation with H_2O_2 in $scCO_2$. Walther reported cyclooctene epoxidation in $scCO_2$ with a 21-fold excess H_2O_2 catalyzed by methylrhenium trioxide.[16] In this case however, the substrate conversion was only 13% with an epoxide selectivity of 98%.

Figure 4 shows the results of some experiments aimed at establishing the effect of 4-*t*-BuPy concentration on the oxidative process catalyzed by the association of Mn(TDCPP)Cl and HFAH.

Curves **C–F**, recorded at increasing nitrogen base concentration, indicate that reaction rates and sub-

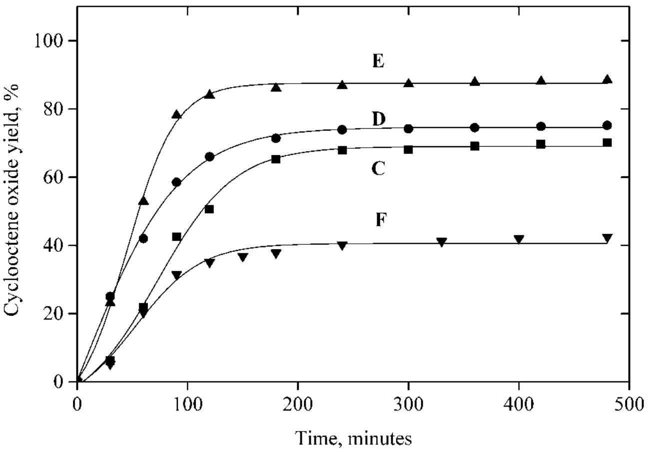


Figure 4. Effect of 4-*tert*-butylpyridine concentration on the cyclooctene (3.80×10^{-2} M) oxidation by H_2O_2 (formally 0.22 M) in $scCO_2$ at 40 °C and 20 MPa in the presence of Mn(TDCPP)Cl (formally 1.28×10^{-4} M) and of $(CF_3)_2CO \cdot 3\ H_2O$ (3.60×10^{-2} M): 4-*t*-BuPy 3.38×10^{-3} M (■); 4-*t*-BuPy 6.76×10^{-3} M (●); 4-*t*-BuPy 1.69×10^{-2} M (▲); 4-*t*-BuPy 3.38×10^{-2} M (▼).

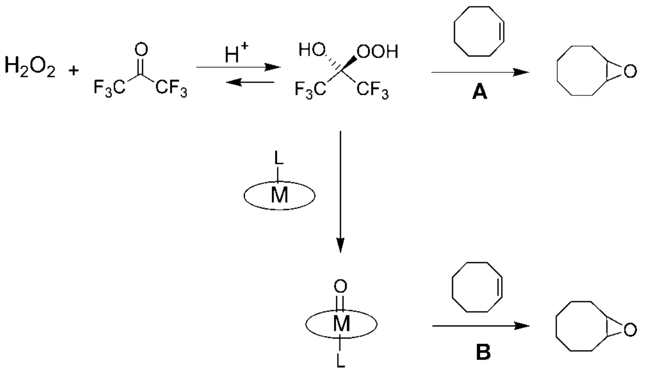
strate conversions depend on the 4-*t*-BuPy concentration in a non-monotonous way. In fact both velocities and conversions increase until a ratio base/catalyst of 130 is reached (curve **E**) and then drop as the ratio increases (curve **F**).

The resulting bell-shaped olefin conversion-[base] profile may be the result of two effects acting in opposite ways as the concentration of base increases. The first one, leading to a rate increase, is the expected result of the larger concentration of the "effective catalyst", namely the manganese complex bearing the nitrogen axial ligand.[34] The second effect, responsible for the rate and conversion drop, is likely the consequence of a parasite reaction involving the nitrogen base. In fact, 4-*t*-BuPy not only acts as an axial ligand of the catalyst, but also competes with olefin for the oxidant. Table 1 shows the results of experiments aimed at establishing the effect of other relevant parameters such as H_2O_2 and co-catalyst concentration, on reaction rate and substrate conversion.

Table 1. Oxidation of cyclooctene (3.80×10^{-2} M), with H_2O_2, catalyzed by Mn(TDCPP)Cl (formally 1.28×10^{-4} M) and HFAH, in the presence of 4-*tert*-butylpyridine (1.69×10^{-2} M), in $scCO_2$ at 40 °C and 20 MPa.

Run	$[H_2O_2]$ M	[HFAH] × 10^2 M	$T_{50\%}$ [a] min	Cyclooctene oxide yield [%]
1	0.11	3.6	70	49
2	0.22	"	50	89
3	0.44	"	140	97
4	0.22	0.72	50	32
5	"	1.8	55	43
6	"	7.2	60	91
7	"	14.4	65	92

[a] Time required for reaching 50% of the maximum epoxide yield in each run.



Scheme 1. Alternative mechanistic pathways for cyclooctene oxidation with H_2O_2 catalyzed by manganese porphyrin and hexafluoroacetone.

The concentration of H_2O_2 appears to play an intricate role in determining the efficiency of the overall oxygen transfer process. In fact, by increasing the H_2O_2 concentration (runs 1–3) the epoxide yield steadily increases while the rate ($T_{50\%}$) first decreases and then increases. The increasing epoxide yields with increasing H_2O_2 concentrations reflects the fact that an appreciable amount of primary oxidant is being decomposed under the experimental conditions adopted. Thus, larger amounts of H_2O_2 are needed to convert more substrate. The change in reaction rates could be related to the main oxidative pathway followed. In fact, at least two possible pathways may be envisaged. The first one, path A of Scheme 1, involves the perhydrate HFAPH as the primary oxidizing reagent.

The second one, path B, again involves HFAPH but as a precursor of an oxo-manganese derivative, which is the ultimate oxygen-transferring agent for the olefin. At high H_2O_2 concentration, the large amount of hydroxyl radicals arising from its decomposition may induce a fast catalyst bleaching. This, in turn, directs the reaction through path A. The cocatalyst concentration also plays an important role in determining the efficiency of the oxidative process. In fact, an increase in HFAH concentration, all other parameters being unchanged, produces a constant rise in epoxide yields and reaction rates (runs 4–7). This outcome is probably the result of a shift of the pre-equilibrium (see Scheme 1) to HFAPH with a consequent fixation of H_2O_2 and reduction of its radical decomposition.

Comparison of the data in Table 1 with those represented in Figure 1 clearly indicates that H_2O_2 decomposition in $scCO_2$ is much more relevant than in the two liquid solvents examined. Since it has been reported that stainless steel may promote radical formation in $scCO_2$, for instance in the aldehydes auto-

Table 2. Oxidation of cyclooctene (3.80×10^{-2} M), with H_2O_2, catalyzed by Mn(TDCPP)Cl (formally 1.28×10^{-4} M) and HFAH (3.60×10^{-2} M), in the presence of 4-*tert*-butylpyridine, in $scCO_2$ at 40 °C and 20 MPa, in a Teflon-lined reactor.

Run	$[H_2O_2]$ M	[4-*t*-BuPy] $\times 10^2$ M	$T_{50\%}$ [a] min	Epoxide yield [%]
8[b]	0.22	0	180	66
9[b]	"	0.34	360	66
10	"	"	50	66
11	"	1.7	45	83
12[c]	"	"	15	98
13[c]	0.11	"	15	98
14[c]	0.055	"	25	72

[a] Time required for reaching 50% of the maximum epoxide yield in each run.

[b] In the absence of Mn(TDCPP)Cl.

[c] In the presence of double magnetic stirring.

oxidation,[38] we have carried out some experiments aimed at evaluating the possibility of H_2O_2 decomposition induced by the metal surface of the reactor. To this purpose, the same cylindrical reactor utilized in previous experiments was loaded with a 1-mm thick cylindrical Teflon vessel with an external diameter very close to that internal of the reactor. By this means, still aware that the supercritical phase may get into the interspace between steel and Teflon, we assumed that the contact of the oxidant with steel is greatly reduced, as confirmed by the results reported in Table 2 of experiments carried out using the "Teflon-coated reactor" (see Figure 6).

First, cyclooctene oxidation with H_2O_2 and catalyzed by HFAH was examined in the absence and in the presence of 4-*t*-BuPy (runs 8,9). In both experiments the epoxide yield reaches 66%, but the reaction is faster in the absence of nitrogen base. This outcome confirms the hypothesis of a left shift in the equilibrium constant related to the formation of HFAPH, which is, very likely, pH dependent. The Teflon coating of reactor walls effectively prevents H_2O_2 decomposition. In fact, the epoxide yields are significantly higher with respect to that measured in the uncoated reactor (see curve **A** of Figure 3 in which epoxide yield is 20%). In spite of the diminished H_2O_2 decomposition, the reaction performed in the presence of both Mn(TDCPP)Cl and HFAH (run 10) does not lead to higher epoxide yield, even when compared with the analogue reaction carried out in a steel reactor (66% vs. 69% of curve **C** in Figure 4). The catalytic process in run 10 probably stops because of axial ligand exhaustion. In fact, by carrying out the reaction in the presence of a larger amount of axial ligand (run 11), an epoxide yield of 83% is reached.

Runs 12 – 14 highlight another important factor in determining the efficiency of the catalytic process. Run 12 shows the effect on the oxidative process of an additional magnetic stirring bar positioned (see Figure 6) at the vessel bottom, directly in contact with the supported catalyst. Under these experimental conditions an almost complete cyclooctene conversion is obtained in a remarkably short time. Finally, runs 13, 14 show that under the "best" conditions employed a near quantitative substrate epoxidation may be obtained employing only a 2.9-fold excess of H_2O_2 over the olefin.

Conclusions

In conclusion, we have demonstrated the feasibility of an efficient oxidative catalytic process exploiting H_2O_2 in $scCO_2$. HFAH plays a synergic role together with Mn(TDCPP)Cl in determining the efficiency of the cascade oxygen transfer process. The role of HFAH in the catalytic process here reported is manifold. Firstly, it allows us to better exploit the oxidative properties of H_2O_2 *via* the formation of HFAPH, which is soluble in the supercritical phase. Secondly, H_2O_2 fixation by HFAH provides a useful tool to preserve H_2O_2 from decomposition induced by the catalase activity of the manganese porphyrin. Furthermore, a low level of hydroxyl radicals, as result of a diminished homolytic decomposition of free H_2O_2, reduces the possibility of catalyst bleaching. Finally, the formation of HFAPH, which is a much better electrophilic oxidant than free H_2O_2, leads to a fast and clean formation of an oxomanganese porphyrin, which is the ultimate oxidizing agent able to epoxidize the olefin.

The recognition of the main parameters governing the oxidative process and of the mode of action is of paramount importance for further improvements which will be reached by the proper modulation of both chemical and physical factors which have been brought to light in this study. Among these parameters the specific inertness of the reactor walls and the efficiency of stirring of the supercritical fluid must be duly considered in the design of the reactor for possible applications.

Experimental Section

Materials

5,10,15,20-Tetrakis(2′,6′-dichlorophenyl)porphyrin ($TDCPPH_2$) was synthesized following a slightly modified Lindsay Smith procedure.[39,40] The metallation of free base ligand porphyrin with $Mn(II)(OAc)_2$ was performed by conventional methods.[41,42] Cyclooctene, cyclooctene oxide, *n*-decane (GLC internal standard), *n*-hexane, chloroform, 4-*tert*-butylpyridine, hexafluoroacetone trihydrate, hydrogen peroxide, were all commercially available, high purity products used as received.

Instruments

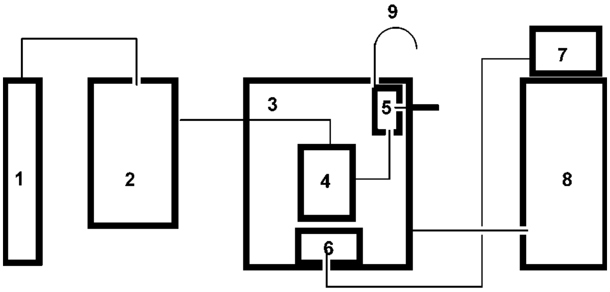
The apparatus employed for catalytic oxidations in $scCO_2$ (see Figure 5) is a modified SFC 3000 series from Carlo Erba Instruments originally designed for capillary supercritical fluid chromatography. Capillary column and splitting valve were replaced by a 316 stainless steel 10-mL high pressure vessel (10000 psig) connected to a restrictor (1/16, o.d., 0.005, i.d.) through a 6-way HPLC valve (Rheodyne 7125) for reaction samples withdrawing. The apparatus consists of an SFC 300 Carlo Erba Instruments pump, a chromatographic SFC 3000 Carlo Erba Instruments oven containing the reaction vessel and an ICU 600 Carlo Erba Instruments for the temperature control of the oven and restrictor. SFC 300 is a 150-mL capacity, pulse-free syringe pump developed for pressures ranging up to 50 MPa and flow rates from 1 to 7000 μL/min. The pump cylinder is thermostatted at 7 °C by an external liquid circulation thermostat (Haake GH refrigerator controlled by a Haake D8 head) thus permitting the syringe to be easily refilled with liquid carbon dioxide. The product concentration in cyclooctene oxidation was determined by GLC analysis with the internal standard method on the basis of a previously calculated response factor. The analyses were performed on a 30 m SE-30 capillary column (0.25 mm ID). The GC was a HP 6890 series equipped with a Shimadzu C-R4A data processor. The identification of the reaction product was performed by comparison of the GLC data with those of an authentic sample and by GC-MS analysis carried out with a Hewlett-Packard 5890 gaschromatograph, connected with a Hewlett-Packard 5970 mass selective detector, using a 15 m SE-30 capillary column, 0.25 mm i.d.

Preparation of Manganese Porphyrin Supported on Silica Gel

A 400 mg sample of silica gel (70 – 230 mesh ASTM, 0.063 – 0.2 mm) was added to a solution of 10 mg of Mn(TDCPP)Cl in 20 mL of methanol. After 24 hours of gentle magnetic stirring, the solvent was eliminated by evaporation and the solid residue was dried under vacuum. Aliquots of 50 mg of this supported catalyst, each containing 1.22 mg of manganese porphyrin (1.25 μmol), were used in the catalytic oxidations.

Oxidation Procedure in Conventional Organic Solvents

Catalytic oxidations of cyclooctene in *n*-hexane and chloroform were initiated by suspending under magnetic stirring 100 μL of H_2O_2 (70% w/w) in 10 mL of a solution (chloroform or *n*-hexane) containing cyclooctene (3.84×10^{-4} mol), 4-*tert*-butylpyridine acting as axial ligand of the catalyst (3.38×10^{-5} mol), *n*-decane as GLC internal standard (2.4×10^{-4} mol), Mn(TDCPP)Cl (1.25×10^{-6} mol) adsorbed on 50 mg of silica gel, and 50 μL of HFAH, in a jacketed reactor thermostatted at 40 °C. At various time intervals, the stirring was suspended and 100 μL of the organic solution were withdrawn, quenched with an equivalent volume of a 1.0 M solution of PPh_3 in DCE and analyzed by GLC. The concentration of the product was measured on the basis of a previously determined response factor.



1: CO_2 Reservoir
2: Cryogenic Pump Carlo Erba SFC 300
3: Termosthatic Oven Carlo Erba SFC 3000
4: Reactor
5: Six Way Valve
6: Alternating Field Magnetic Stirrer
7: Magnetic Stirrer Control Unity
8: Restrictor and Oven Temperature Control Unity Carlo Erba ICU 600
9: Restrictor

Figure 5. Block scheme of the high-pressure apparatus employed in this work.

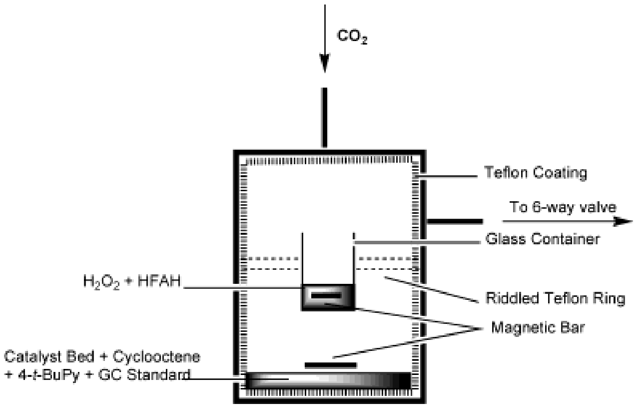


Figure 6. Details of the batch reactor employed in this work.

Oxidation Procedure in $scCO_2$

Catalytic oxidations of cyclooctene in $scCO_2$ were carried out in a 10-mL cylindrical, high-pressure vessel (see Figure 6). At the entrance and exit of the vessel were placed two 5 μM pore frits. At the vessel bottom was placed a mixture of catalyst, substrate, axial ligand and internal standard. A small glass cylinder (about 0.8 mL volume) was loaded with H_2O_2 and HFAH. The glass cylinder was suspended upright by means of a riddled Teflon ring inside the vessel. In this way, the mixture of oxidant and co-catalyst is separated from the remaining reagents. After sealing, the vessel was placed into the SFC oven and thermostatted at 40 °C. Finally, pressurization was achieved in about three minutes time interval by pumping liquid carbon dioxide to the desired final pressure (20.0 MPa). After pressurization, the content of the glass cylinder diffuses into the supercritical phase and enters in contact with the others reagents. Stirring was obtained by one or two magnetic bars, positioned inside the two containers, dragged by an alternating field magnetic stirrer. Control experiments showed that a complete dissolution of cyclooctene and *n*-decane into $scCO_2$ occurs during a 10–15 minute time interval. At appropriate time intervals, reaction samples were withdrawn through the stainless steel restrictor maintained at 80 °C, by means of a 6-way HPLC valve and trapped in dichloromethane. The samples were then analyzed by GLC. The concentration of the product was measured on the basis of a previously determined response factor.

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