

# Manganeseporphyrin-catalysed heterogeneous and unusually chemoselective oxidations of sulfides by monopersulfate in supercritical CO<sub>2</sub>

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## Abstract

The oxidation of sulfides by Oxone<sup>®</sup> in the presence of catalytic amount of various manganese porphyrins in supercritical CO<sub>2</sub> (scCO<sub>2</sub>) has been studied. The reactions have been carried out in an anhydrous two phase-system (solid Oxone<sup>®</sup>, solid catalyst/scCO<sub>2</sub>). In the experimental conditions employed (40°C, 20 MPa), only the new synthesised 5,10,15,20-tetrakis (heptafluoropropyl)porphyrinate manganese(III) chloride showed a slight solubility in scCO<sub>2</sub>. In the absence of manganese porphyrin and/or of an aromatic nitrogen base a slow stoichiometric sulfide oxidation leading mainly to sulfoxide is observed in spite of the extremely low solubility of Oxone<sup>®</sup> in scCO<sub>2</sub>. Conversely, in the presence of 4-*tert*-butylpyridine and catalytic amount of manganese porphyrins (0.6% with respect to sulfide) enhanced reaction rates are observed. Furthermore, the selectivity of sulfide oxidation reverses and sulfone is formed in larger or comparable amount than sulfoxide even when an excess of sulfide over oxidant is employed. The results collected suggest that the local concentration of the intermediate sulfoxide around the catalyst is higher than that of the bulk supercritical phase thus determining unusual high reaction rates for sulfone formation. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Supercritical CO<sub>2</sub>; Monopersulfate; Porphyrin; Oxidation; Sulfides

## 1. Introduction

Supercritical CO<sub>2</sub> (scCO<sub>2</sub>) represents, among supercritical fluids (scFs), an attractive reaction medium particularly for industrial processes because of some properties, which make it an environmentally and economically profitable solvent [1,2]. In fact, CO<sub>2</sub> is inexpensive, non-flammable, non-toxic and chemically inert under many conditions. One-pot isolation and

purification of products from the reaction mixture, simply by controlling the density of the supercritical phase, allows in principle to recover the capital and operating costs related to high pressures operating plants. Supercritical carbon dioxide has been shown to be a clean and effective reaction medium for many catalytic processes including free radical [3] and cationic polymerizations [4], hydrogenations [5–8], hydroformylations [9] and some enzymatic processes [10–12].

At least in principle, scCO<sub>2</sub> is ideally suited as a reaction medium for oxidation reactions and applications in both homogeneous and heterogeneous catalytic processes. As a matter of fact, CO<sub>2</sub>, being

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fully oxidised, is stable under any oxidative conditions. Moreover, employing gaseous oxygen as primary oxidant, one may take advantage of the great dispersibility of O<sub>2</sub> in scCO<sub>2</sub> and of the much larger concentrations that may be achieved in the supercritical phase than in conventional liquid solvents. Despite the potential advantages offered by scCO<sub>2</sub> only a limited number of catalysed oxidations have been reported in this medium.

Studies of homogeneous epoxidation of alkenes by hydroperoxides in scCO<sub>2</sub> catalysed by Mo(CO)<sub>6</sub> has been recently published [13–15]. In these oxidation processes no particular benefit was obtained by performing the reactions in scCO<sub>2</sub> instead than in an organic solvent other than that related to environmental considerations. On the other hand, one should take into account that at this early stage of the research in the field of scFs, most of the catalysts tested have been simply transferred from the processes usually carried out in organic solvent without any adaptation to the specificity of a supercritical phase. Specifically designed catalysts for homogeneous oxidation in scCO<sub>2</sub> are now attracting much interest. For example, the reactivity of oxygen and *tert*-butylhydroperoxide in the presence of 5,10,15,20-tetrakis(pentafluorophenyl)- $\beta$ -octabromoporphyrinate iron(III) chloride, Fe(Br<sub>8</sub>TFPP)Cl, in the oxidation of alkenes has been recently reported by Tumas [16]. The presence of halogenated substituents on both phenyl rings and  $\beta$ -positions of porphyrin ring increases the solubility of the catalyst in scCO<sub>2</sub> allowing a homogeneous catalytic oxidation. In this case, the activity of the oxidative system in scCO<sub>2</sub> is lower than in conventional organic solvents but the selectivity of epoxidation is higher.

Besides total destructive oxidation of organics, widely studied in scH<sub>2</sub>O, partial oxidation of organic compounds, such as the introduction of an oxygenated functional group into hydrocarbons, can be achieved in scFs by heterogeneous catalysis and partial oxidation in scFs has been checked in order to synthesise chemicals [17].

A scrutiny of studies concerning the oxidation processes in scFs as published by McHugh [18], Gaffney and Sofranko [19], Fan [20], Jiang [21] and their co-workers reveals that interesting results were obtained for the different systems investigated, both in the presence or absence of catalysts and using a

variety of oxidants. In general, although the benefits of the supercritical medium in terms of rates and conversion are far from impressive, in many cases the effects on the selectivity of the reaction are quite relevant. Recently, Rayner and co-workers [22] reported the result of a study that is worth mentioning here being related to the rather impressive effects on selectivity and also to the present study. They found that the process of sulfoxidation of cysteine derivatives using *tert*-butylhydroperoxide in the presence of Amberlite ion exchange resin in scCO<sub>2</sub> leads to a dramatic, pressure dependent increase in diastereoselectivity (up to 95%) when compared to the outcome of the same reaction in conventional solvents where no diastereoselectivity is observed.

On the whole, it appears the regio- and stereoselectivity effects in scFs are the main effects expected in oxidation processes on moving from liquid solvent to supercritical media. However, the studies so far reported being scattered into a variety of systems and conditions do not allow any rationale as for the origin of the observed effects and for the relevant parameters at play and do not allow any prediction for a particular chemical transformation. Moreover, there are apparent serious restrictions concerning the use of scCO<sub>2</sub> as solvent for oxidation processes, as well as other reactions, which are related to the scarce solubility of hydrophilic substances and salts and hence do not stimulate the study of a number and types of transformations under supercritical conditions in the search of rate and conversion benefits. Phase transfer catalysis [23] and reverse micro-emulsions in scCO<sub>2</sub> [24,25] have been indicated as possible solutions to overcome these limitations and try to obtain homogeneous reaction media. However, the possibility of using heterogeneous systems is still largely unexplored.

This paper reports the result of a study addressed to the possibility of carrying out a catalytic oxidation in a heterogeneous system formed by a supercritical phase (scCO<sub>2</sub>) containing the substrate and a solid phase containing the catalyst (manganese porphyrins adsorbed on silica gel) and the oxidant (commercial Oxone<sup>®</sup>: 2KHSO<sub>5</sub>\*KHSO<sub>4</sub>\*K<sub>2</sub>SO<sub>4</sub>). The oxidation of thioethers was chosen as probe reaction in order to evaluate the effect of the nature of organic substrates on the chemoselectivity of the process. The results obtained, in particular the unusual low selectivity for sulfoxide with respect to sulfone formation, suggests

a local higher concentration of the intermediate sulfoxide surrounding the catalyst than that in the bulk conditions.

## 2. Experimental section

### 2.1. Materials

5,10,15,20-Tetrakis(mesityl)porphyrin (TMPH<sub>2</sub>) and 5,10,15,20-tetrakis(octyl)porphyrin (TOPH<sub>2</sub>), were synthesised following a slightly modified Lindsay Smith method [26,27]. 5,10,15,20-Tetrakis(mesityl)- $\beta$ -octabromoporphyrin (Br<sub>8</sub>TMPH<sub>2</sub>) was obtained by *N*-bromosuccinimide (NBS) bromination of the pyrrole  $\beta$ -positions of TMPH<sub>2</sub> [28]. 5,10,15,20-Tetrakis(heptafluoropropyl)porphyrin (THEFPPH<sub>2</sub>) was obtained through the procedure reported by DiMugno and Therien [29]. 5,10,15,20-Tetrakis(pentafluorophenyl) porphyrin (TFPPH<sub>2</sub>) was purchased from Aldrich. The metallation of free base ligand porphyrins with Mn(II)(OAc)<sub>2</sub> was performed by conventional methods [30,31]. Metallation of 5,10,15,20-tetrakis(heptafluoropropyl) porphyrin (THEFPPH<sub>2</sub>) with Mn(II)(OAc)<sub>2</sub> followed by treatment with HCl lead to the new synthesised Mn(THEFPP)Cl, UV–VIS (CHCl<sub>3</sub>): 350 ( $\epsilon = 18789 \text{ M}^{-1} \text{ cm}^{-1}$ ), 410 ( $\epsilon = 19283 \text{ M}^{-1} \text{ cm}^{-1}$ ), 448 ( $\epsilon = 21147 \text{ M}^{-1} \text{ cm}^{-1}$ ). Oxone<sup>®</sup>, tricaprilmethylammonium chloride (Aliquat 336), *n*-decane (GLC internal standard), 4-*tert*-butylpyridine, *p*-tolylmethylsulfide, diphenylsulfide, were all commercially available, high purity products (Aldrich) used as received.

### 2.2. Instruments

The apparatus employed for catalytic oxidations in scCO<sub>2</sub> is a modified SFC 3000 series 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 (10,000 psig) connected to a restrictor (1/16 in. o.d., 0.005 in. i.d.) through a six-way HPLC valve (Rheodyne 7125) for reaction samples withdrawing. The apparatus consists of a 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  $\mu\text{l}/\text{min}$ . The pump cylinder is thermostated 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 products concentration in sulfides oxidation were determined by GLC analysis with the internal standard method on the basis of previously calculated response factors. The analyses were performed on a 30 m SE-30 capillary column (0.25 mm i.d.). The GC was a HP 6890 series equipped with a Shimadzu C-R4 A data processor. The identification of the reaction products was performed by comparison of the GLC data with those of authentic samples and/or by GC–MS analysis carried out with a Hewlett-Packard 5890 gas chromatograph, connected with a Hewlett-Packard 5970 mass selective detector, using a 15 m SE-30 capillary column, 0.25 mm i.d.

### 2.3. Preparation of manganese porphyrin complexes supported on silica gel

A 500 mg sample of silica gel (70–230 mesh ASTM, 0.063–0.2 mm) was added to a solution of 26 mg of Mn(THEFPP)Cl in 20 ml of methanol. After 24 h of gentle magnetic stirring, the solvent was eliminated by evaporation and the solid residue was dried under vacuum. Aliquots of 53 mg of this supported catalyst, each containing 2.6 mg of manganese porphyrin (2.4 mmol), were used in catalytic oxidations.

### 2.4. Oxidation procedure in conventional organic solvents

Catalytic oxidations of *p*-tolyl-methylsulfide in hexane and methanol were initiated by suspending under magnetic stirring 0.100 g of Oxone<sup>®</sup> (0.32 mmol of KHSO<sub>5</sub>) in 10 ml of a solution (methanol or hexane) containing the sulfide (0.74 mmol), the 4-*tert*-butylpyridine acting as axial ligand of the catalyst (0.17 mmol), *n*-decane as GLC internal standard (0.24 mmol), and Mn(TFPP)Cl (2.4  $\mu\text{mol}$ ) in a jacketed reactor thermostated at 40°C. At various time

intervals, the stirring was suspended and 100  $\mu$ l of the supernatant solution were withdrawn, quenched with an equivalent volume of a 1.0 M solution of PPh<sub>3</sub> in DCE and analysed by GLC. The concentration of the oxygenation products was measured on the basis of previously determined response factors.

### 2.5. Oxidation procedure in scCO<sub>2</sub>

Catalytic oxidations of *p*-tolyl-methylsulfide in scCO<sub>2</sub> were carried out in a 10 ml cylindrical high pressure vessel, originally designed for extraction operations. At the two bases of the vessel were placed two 5  $\mu$ M pores frits. At the vessel bottom was placed a Teflon dish containing a mixture of Oxone<sup>®</sup> and manganese porphyrin adsorbed on silica gel. A small glass cylinder (about 0.8 ml volume) was loaded with the sulfide, the nitrogen base acting as axial ligand of the catalyst (4-*tert*-butyl pyridine), the internal GC standard (*n*-decane) and, if the case, with a solvent modifier (acetone) and/or a phase transfer catalyst (Aliquat 336). The glass cylinder was placed upright into the Teflon dish inside the vessel. In this way, the mixture of oxidant and catalyst is separated from the substrate. After sealing, the vessel was placed into the SFC oven and thermostated at 40°C. Finally, pressurisation was achieved in about three minutes time interval by pumping liquid carbon dioxide to the desired final pressure (20.0 MPa). After pressurisation, the content of the glass cylinder diffuses into the supercritical phase and enters in contact with the solid oxidant and catalyst. Stirring was not possible with this reaction vessel. Control experiments showed that a complete dissolution of sulfide and *n*-decane into scCO<sub>2</sub> occurs during a 40–60 min time interval. At appropriate time intervals, reaction samples were withdrawn through the stainless steel restrictor maintained at 90°C, by means of a six-way valve and trapped in methylene chloride. The samples were then analysed by GLC. The concentration of the oxygenation products was measured on the basis of previously determined response factors.

## 3. Results and discussion

First, we checked that the components used (see *infra*) in the oxidative system were soluble

in the supercritical phase under the experimental conditions adopted. GLC analysis of a standard mixture of *n*-decane, *p*-tolyl-methylsulfide, *p*-tolyl-methylsulfoxide, *p*-tolyl-methylsulfone and 4-*tert*-butylpyridine gave essentially the same peak-area ratios in methylene chloride and in scCO<sub>2</sub>, provided that a small amount of acetone was present in the supercritical phase. The presence of 1% acetone w/w in the scCO<sub>2</sub> ensures the solubility even of the most polar substrates, namely sulfoxide and the nitrogen base, and a relatively rapid dissolution of all these species; complete dissolution in the supercritical phase is normally achieved 1 h after pressurisation.

Preliminary experiments were addressed to the oxidation of diphenylsulfide with potassium monopersulfate (used as triple salt, 2KHSO<sub>5</sub>\*KHSO<sub>4</sub>\*K<sub>2</sub>SO<sub>4</sub>) in the presence of 5,10,15,20-tetrakis(pentafluorophenyl) porphyrinate manganese(III) chloride (Mn(TFPP)Cl) (see Fig. 1), in scCO<sub>2</sub> at 20 MPa and 40°C.

The amount of catalyst employed (2.5 mg, 0.8% molar ratio with respect to the substrate) was previously adsorbed on 50 mg of silica gel in order to facilitate reactor loading. The perfluorinated manganese porphyrin, Mn(TFPP)Cl, and 1% w/w acetone as solvent (scCO<sub>2</sub>) modifier were used in the attempt to solubilize the catalyst. However, partitioning of the catalyst in scCO<sub>2</sub> was negligible as revealed by colourless reaction samples withdrawn in the course of experiments. Therefore, this oxidising system has a definite heterogeneous character, being both oxidant and catalyst virtually insoluble in scCO<sub>2</sub>. Nevertheless, the oxidative process was found to occur, in opportune conditions, and the reaction course was monitored by measuring the sulfoxide and sulfone concentrations by GLC analysis of reaction samples withdrawn through a six-way HPLC valve and trapped in methylene chloride.

Table 1 reports the analysis data indicating that a heterogeneous catalytic oxidative process is operating under the appropriate conditions employed.

Control experiment (run 1) indicate that a slow, non-catalytic reaction leading to diphenylsulfoxide and diphenylsulfone occurs between monopersulfate and diphenylsulfide; after 24 h, a 5% conversion of the substrate is observed with a sulfoxide:sulfone ratio of 4. This ratio is expected on the basis of the relative nucleophilicity of the starting sulfide and the sulfoxide produced in the course of the reaction. In

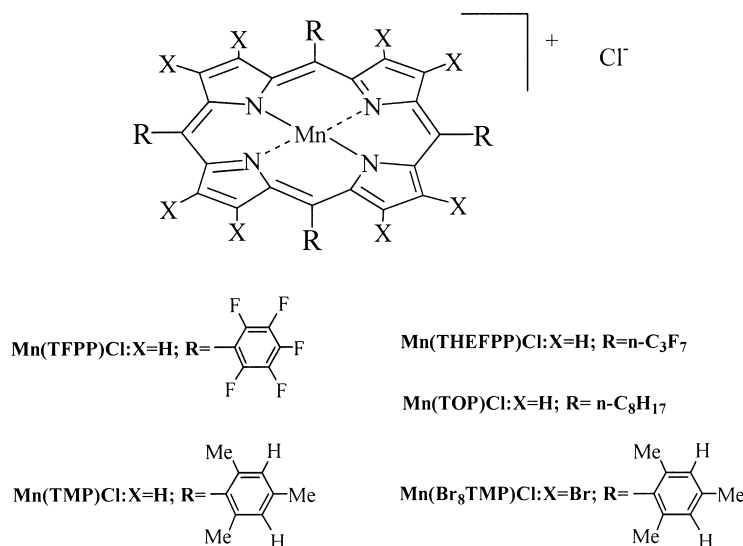


Fig. 1. Manganese porphyrines utilised in this study.

fact, the oxygen transfer from peracids or hydrogen peroxide to organic substrates has been shown [32] to proceed through a simple, bimolecular mechanism in which the peroxidic species is the electrophilic partner and the organic substrate the nucleophilic partner of the process. Addition of a lipophilic salt, tricaprylmethyl ammonium chloride (Aliquat 336), as a phase transfer promoter, in 17% molar ratio with respect to the monopersulfate (run 2) increases the sulfide conversion to 14% after 24 h with a products ratio of 3.7 still favouring the sulfoxide. The effect of addition of Aliquat 336 suggests that phase transfer takes place. Under the phase transfer conditions, addition of Mn(TFPP)Cl adsorbed on silica gel in 0.8% molar ratio with respect to the sulfide (run 3) leads to a rather unexpected drop to 1.3% sulfide conversion while a products ratio of 3.3 still fits the range ob-

served in previous experiments. This outcome may be explained by assuming that the manganese porphyrin decomposes the monopersulfate and hence inhibits the uncatalysed sulfide oxidation. On the other hand, when 4-*tert*-butylpyridine is present together with the manganese porphyrin (run 4) a completely different picture is observed. In fact, in the presence of the nitrogen base, which presumably acts as axial ligand of the catalyst, a much faster production of sulfoxide and sulfone is observed. Furthermore, the selectivity of oxidative process changes and sulfone is formed in twice the amount of sulfoxide. The sulfide conversion after 24 h is 31% in run 4 and is limited by the concomitant parasite oxidation of the axial ligand. In fact, nitrogen bases are oxidizable substrates and consume part of the monopersulfate thus reducing the efficiency of the process leading to sulfoxide and

Table 1

Oxidation of diphenylsulfide (0.3 mmol) by Oxone<sup>®</sup> (0.65 mmol active oxygen) in scCO<sub>2</sub> at 20 MPa and 40°C, in the presence of 1.0% w/w acetone

Run	Catalyst (mol × 10 <sup>6</sup> )	Phase transfer (mol × 10 <sup>3</sup> )	Axial ligand (mol × 10 <sup>3</sup> )	Ph <sub>2</sub> SO yield <sup>a</sup> (%)	Ph <sub>2</sub> SO <sub>2</sub> yield <sup>a</sup> (%)
1	–	–	–	4	1
2	–	Aliquat 336 (0.11)	–	11	3
3	Mn(TFPP)Cl (2.4)	Aliquat 336 (0.11)	–	1	0.3
4	Mn(TFPP)Cl (2.4)	Aliquat 336 (0.11)	4- <i>tert</i> -butylpyridine (0.17)	9	22

<sup>a</sup> As determined after 24 h relative to the starting diphenylsulfide.

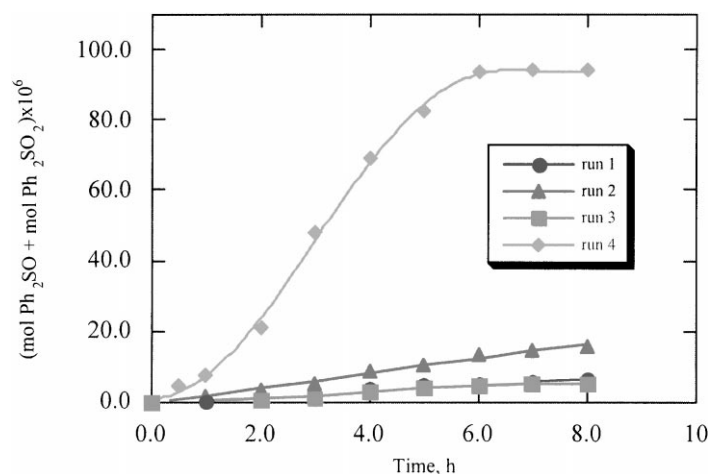


Fig. 2. Dependence of products concentration (sulfoxide + sulfone) vs. time in the experiments (runs 1–4) of Table 1.

sulfone formation. Therefore, the efficiency of the overall oxidative process may be improved by tuning basicity and concentration of the base acting as catalyst's axial ligand.

The effect of the addition of phase transfer agent, manganese porphyrin and axial ligand on sulfide conversion is shown in Fig. 2.

The fast catalytic sulfide oxidation (run 4) which takes place only when both catalyst and nitrogen base are present may be taken as an indication that 4-*tert*-butylpyridine co-ordinates to manganese and makes the metal centre prone to oxidation by the monopersulfate. The consequence of such interaction is the formation of an oxo-manganese porphyrin intermediate which, in a subsequent step, oxidises sulfide to sulfoxide and then to sulfone. The crucial point is that while the oxo-manganese derivative is known to act as an electrophilic oxidant [33,34], the chemoselectivity indicates that the oxidative process apparently favours the sulfoxide which is less nucleophilic than its precursor sulfide.

In order to minimise the competitive axial ligand oxidation and enhance the yields of sulfoxide and sulfone, we studied the oxidation of a more nucleophilic substrate than diphenylsulfide. Table 2 shows the results of the oxidation of *p*-tolyl-methylsulfide with Oxone<sup>®</sup> in the presence of various manganese porphyrins in scCO<sub>2</sub> at 20 MPa and 40°C.

The oxidation of *p*-tolyl-methylsulfide under the experimental conditions of run 4 in Table 1 affords a

considerable conversion of sulfide (82%), thus, confirming that the oxidative process proceeds faster with a more nucleophilic substrate (run 5). Nevertheless, under the experimental conditions of run 5, the only oxidation product is the sulfone and this indicates that sulfoxide oxidation is being favoured by some mecha-

Table 2

Oxidation of *p*-tolyl-methylsulfide (0.37 mmol) by Oxone<sup>®</sup> (0.65 mmol active oxygen), in the presence of  $2.4 \times 10^{-6}$  mol of manganese porphyrin, 0.17 mmol of 4-*tert*-butylpyridine, 0.11 mmol of Aliquat 336, in scCO<sub>2</sub> at 20 MPa and 40°C containing 1.0% w/w acetone

Run	Catalyst	<i>p</i> -TolSOMe yield <sup>a</sup> (%)	<i>p</i> -TolSO <sub>2</sub> Me yield <sup>a</sup> (%)
5	Mn(TFPP)Cl	0	82
6	Mn(TFPP)Cl	7 <sup>b</sup>	11
7	Mn(TFPP)Cl	14 <sup>c</sup>	27
8	Mn(TFPP)Cl	14 <sup>d</sup>	24
9		0 <sup>e</sup>	2
10	Mn(TMP)Cl	13 <sup>c</sup>	26
11	Mn(TOP)Cl	11 <sup>c</sup>	29
12	Mn(Br <sub>8</sub> TMP)Cl	15 <sup>c</sup>	35
13	Mn(THFPP)Cl	14 <sup>c</sup>	29
14	Mn(THFPP)Cl	14 <sup>c, f</sup>	30

<sup>a</sup> As determined after 24 h relative to the starting *p*-tolyl-methylsulfide.

<sup>b</sup> Oxone<sup>®</sup> (0.32 mmol active oxygen).

<sup>c</sup> In the absence of phase transfer.

<sup>d</sup> In the absence of phase transfer and acetone.

<sup>e</sup> In the absence of phase transfer and axial ligand.

<sup>f</sup> At 30 MPa.

nistic aspects of the overall catalytic process. Employing equimolar amounts of monopersulfate and sulfide (run 6), the conversion drops to 18% and sulfoxide is formed together with sulfone although in a 1:2 ratio. Run 7 indicates that the presence of a phase transfer agent is not an essential requisite for the occurrence of the oxidative process. In fact, even in the absence of Aliquat 336, the sulfide conversion (41%) is still much higher than that observed in the blank experiment in the absence of the nitrogen base (run 9, 2% conversion). Even the presence of acetone as  $scCO_2$  modifier appears ineffective for the occurrence of the oxidative process (run 8). In its absence however, dissolution of the starting reagents into the supercritical phase is slower and less effective so that *p*-tolyl-methylsulfide is not completely solubilised.

The effect of the nature of manganese porphyrin has been also examined (runs 7, 10–14). 5,10,15,20-Tetrakis(mesityl)porphyrinate manganese(III) chloride,  $Mn(TMP)Cl$ , (run 10) in spite of the twelve methyl groups present on the phenyls turned out to be insoluble in  $scCO_2$  under the experimental conditions adopted and gave essentially the same results of  $Mn(TFPP)Cl$ . The use of 5,10,15,20-tetrakis(mesityl)- $\beta$ -octabromoporphyrinate manganese(III) chloride,  $Mn(Br_8TMP)Cl$  (run 12) in spite of its low, if any, solubility in  $scCO_2$ , leads to a remarkable improvement in sulfoxide and sulfone yields. The high yield obtained with this catalyst is probably related to a more pronounced electrophilic character of the oxo-manganese intermediate due to the electron-withdrawing effect of the bromine substituents. In general, among metal complexes with hydrocarbon ligands, those bearing aliphatic substituents are more soluble in  $scCO_2$  than those with aromatic ligands [35]. Therefore, the activity as catalyst of a potentially soluble 5,10,15,20-tetrakis(octyl)porphyrinate manganese(III) chloride,  $Mn(TOP)Cl$ , has been tested (run 11). However, even in this case the solubility is negligible whereas both activity and selectivity in sulfide oxidation are comparable to those observed in the presence of  $Mn(TFPP)Cl$ . Among the various manganese porphyrins tested, only the new synthesised 5,10,15,20-tetrakis(heptafluoropropyl)porphyrinate manganese(III) chloride,  $Mn(THEFPP)Cl$ , featured a detectable, although slight, solubility in  $scCO_2$ . In fact, reaction samples of the reaction mixture with

$Mn(THEFPP)Cl$  trapped in methylene chloride show a distinct green colour and their UV–VIS spectra confirmed the presence of the catalyst in solution. The results obtained in the presence of such perfluoroalkylporphyrin are in line with those obtained with the insoluble catalysts, in particular the chemoselectivity with a sulfone:sulfoxide ratio of 2 (run 13). These results were also confirmed at 30 MPa (run 14) where the catalyst solubility is expected to increase.

A first significant indication, which stems out from the results here reported, is that an efficient catalytic process in  $scCO_2$  can be achieved even if the solubility of both, catalyst and primary oxidant, is remarkably low. As said above, many efforts in implementing catalytic processes in  $scCO_2$  are devoted to the synthesis of soluble catalysts or to the development of techniques, which allow to realise physically homogeneous systems. In fact, it was perceived that to ensure the success of a chemical reaction in  $scCO_2$  the reagents must be present in appreciable concentrations in the same phase. On the other hand, many primary oxidants commonly used in catalytic processes carried out in conventional solvents exhibit negligible solubilities in  $scCO_2$  owing their ionic or polar character ( $KHSO_5$ ,  $NaOCl$ ,  $NaIO_4$ ,  $H_2O_2$ , etc.) and, therefore, were deemed valueless for use in  $scCO_2$ . The results here reported show that catalytic oxidation in  $scCO_2$  may be achieved even if the solubility of the catalyst is below  $10^{-5}$  M [16] and that of the primary oxidant still lower. We are keen that the formation of the oxo-manganese derivative takes place because of the exceptionally high reactivity of the catalyst activated by 4-*tert*-butylpyridine co-ordination and, hence, the formation of the oxo-manganese derivatives occurs even if the oxidant concentration in  $scCO_2$  is low. More to the point, such low oxidant concentration in the supercritical phase is likely to preserve the manganese complex from reactions occurring at the porphyrin ring which cause catalyst damages and deactivation. The overall oxidative process here studied includes several consecutive steps the main one being: (i) the transport of the oxidant into the supercritical fluid; (ii) the heterogeneous reaction between the oxidant in the supercritical phase and the catalyst in the solid one; (iii) the heterogeneous reaction between the oxo-manganese derivative in the solid phase and the organic substrate in the supercritical one. In conventional organic solvents,

transport through the liquid is relatively slow and may limit the formation of the oxo-manganese derivative. Conversely, the mass transport through  $scCO_2$  is always very fast and the equilibrium concentration of oxidant, although low, is smoothly reached and maintained. Therefore, in  $scCO_2$ , the formation of the oxo-manganese derivative could be the rate-limiting step.

A second relevant indication concerns the peculiar selectivity observed in sulfide oxidation. In fact, the oxidation of both sulfides tested leads to sulfone and sulfoxide in a 1–3:1 ratio even when sulfide conversion reaches moderate values. This outcome does not appear to fit the reactivity of the oxo-manganese species, which normally behaves as an electrophilic oxidant thus favouring the oxidation of the more nucleophilic substrate, namely, the sulfide, thus, leading preferentially to sulfoxide formation. In order to gain insight on this issue, a series of catalytic oxidations have been carried out using an excess of sulfide relative to the oxidant. Furthermore, the effect of the reaction medium on the selectivity was investigated by carrying out the catalytic processes in  $scCO_2$  and in two conventional liquid solvents of remarkably different polarity, namely, hexane and methanol. The pertinent results are reported in Table 3.

The kinetic profile of the reaction carried out in  $scCO_2$  in the presence of 1% acetone w/w as solvent

Table 3

Oxidation of *p*-tolyl-methylsulfide (0.74 mmol) by Oxone® (0.32 mmol active oxygen), in the presence of  $2.4 \times 10^{-6}$  mol of Mn(TFPP)Cl, 0.17 mmol of 4-*tert*-butylpyridine, in various solvents at 40°C

Run	Solvent	<i>p</i> -TolSOMe yield <sup>a</sup> (%)	<i>p</i> -TolSO <sub>2</sub> Me yield <sup>a</sup> (%)
15	$scCO_2$ <sup>b</sup>	26.3	23.0
16	$scCO_2$	16.0	18.3
17	Methanol	53.2	16.6
18	Hexane	14.3	29.4

<sup>a</sup> As determined after 24 h relative to the starting monopersulfate.

<sup>b</sup> In the presence of 1% acetone w/w.

modifier (run 15), shown in Fig. 3, does not exhibit the typical trend of two consecutive reactions.

In fact, if the sulfone is formed by oxidation of sulfoxide initially produced through a reaction occurring at a rate comparable to that of sulfoxide formation, a bell shaped curve for the intermediate sulfoxide formation and a sigmoidal one for sulfone formation should be observed. The steady increase of sulfone concentration, shown in Fig. 3, is observed from the beginning of the reaction while the sulfoxide formation shows an induction period. A kinetic profile of this kind could be observed if the specific rate constants of the two consecutive processes are quite different, i.e. if the oxidation of sulfide to sulfoxide is much slower than the

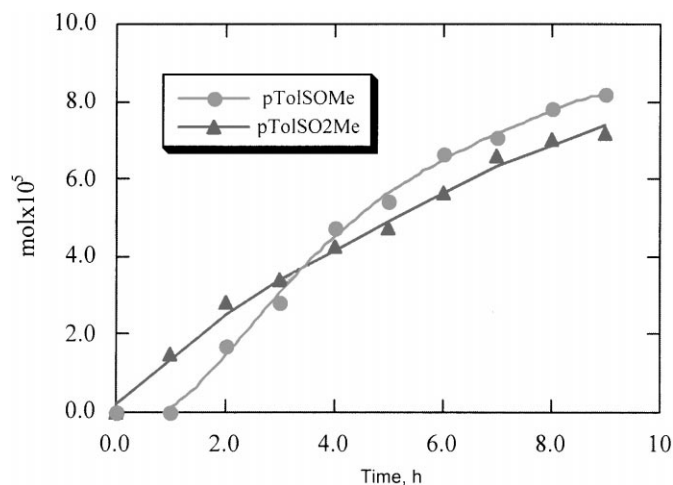


Fig. 3. Dependence of sulfoxide and sulfone concentrations vs. time in the oxidation of *p*-tolyl-methylsulfide in  $scCO_2$  at 40°C and 20 MPa (run 15 of Table 3).



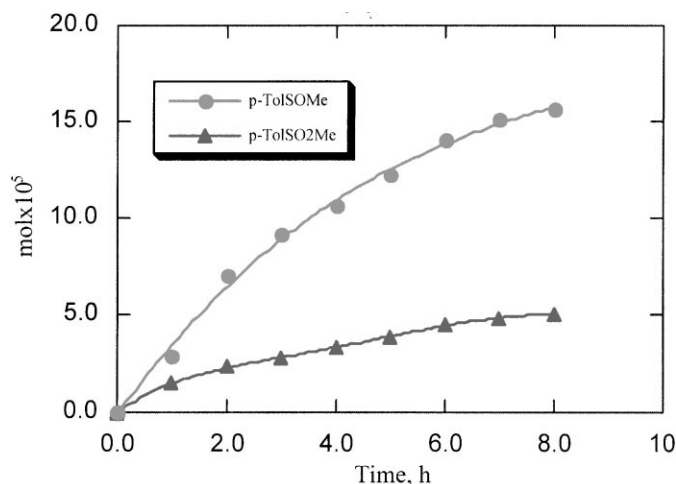


Fig. 4. Dependence of sulfoxide and sulfone concentrations vs. time in the oxidation of *p*-tolyl-methylsulfide in methanol at 40°C (run 17 of Table 3).

oxidation of sulfoxide to sulfone. However, this has been ruled out on the basis of direct experiments. In fact, we verified that the oxidation of sulfoxide to sulfone occurs at a rate comparable to that of the oxidation of sulfide. The presence of the modifier in *scCO*<sub>2</sub> has little effect on the reaction products distribution. In fact, in the absence of acetone (run 16) only a slight excess of the sulfone over the sulfoxide is observed.

Conversely, the reaction picture in a conventional polar liquid solvent (methanol) shows an opposite trend with respect to that observed in *scCO*<sub>2</sub>, as shown in Fig. 4. In fact, in this case a steady formation of sulfoxide is observed whereas sulfone production shows a small but detectable induction period.

Moreover, the final products distribution reflects the well-established reactivity of the oxo-manganese species and sulfoxide is formed in a more than three-fold larger amount than sulfone (run 17). Interestingly, the chemoselectivity observed in liquid *n*-hexane, a solvent exhibiting an  $E_t$  polarity parameter according to Dimroth and Reichard ( $E_t = 31$ ) similar to that of *scCO*<sub>2</sub> ( $E_t = 28$ – $30$  depending on pressure) [36], favours sulfone formation even more than *scCO*<sub>2</sub> (run 18). All the above observations can be interpreted by assuming that the sulfoxide formed in the first step of the oxidative process

remains co-ordinated to the positively charged catalyst by virtue of its marked dipole moment. Thus, sulfoxide clustering around the catalyst induces a preferential over-oxidation to sulfone which occurs faster than the oxidation of sulfide in liquid *n*-hexane in spite of the electrophilic character of the oxo-manganese derivative. On the other hand, in methanol, a solvent of remarkable polarity ( $E_t = 55.5$ ), the sulfoxide-catalyst clustering is much less relevant due to strong solute-solvent interactions. Therefore, in methanol, the sulfoxide concentration in the proximity of the catalyst is likely to be similar to that in the bulk phase and the chemoselectivity is determined only by the relative rate constants for sulfide and sulfoxide oxidation, which favours sulfoxide production.

Thus, a possible rationale for the difference in chemoselectivity observed in the two media of similar polarity, namely, *scCO*<sub>2</sub> and liquid hexane takes into account the different clustering effects experienced in the two phases. In fact, clustering of sulfoxide intermediate on the catalyst surface could be depressed in supercritical conditions due to the severe constraints imposed on the sulphoxide by the surrounding *CO*<sub>2</sub> molecules. In other words, solute-solute clustering would be favoured in *scCO*<sub>2</sub> whereas solute-catalyst clustering would be predominating in a liquid apolar solvent.

#### 4. Conclusion

The results reported in this paper show the importance of solute–solute and catalyst–solute clustering in determining the chemoselectivity of an oxidative process. The tuning of such interactions provides a further tool for controlling reaction selectivities, in addition to the well-explored pressure effect on the individual rate constants.

The catalytic procedure described in this paper is not limited to the oxidation of sulfides and sulfoxides. In fact, as we mentioned above, even aromatic nitrogen bases are smoothly converted into the corresponding N-oxides. Moreover, preliminary experiments revealed that alkenes may be converted into the corresponding epoxides although at slower rates than sulfides. Further work is now in progress in our laboratory on this issue.

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#### References

- [1] P.G. Jessop, W. Leitner (Eds.), *Chemical Synthesis Using Supercritical Fluids*, Wiley-VCH, New York, 1999.
- [2] P.T. Anastas, T.C. Williamson (Eds.), *Green Chemistry—Designing Chemistry for the Environment*, American Chemical Society, Washington, DC, 1996.
- [3] J.M. DeSimone, E.E. Maury, Y.Z. Meneceloglu, J.B. Mc-Clain, T.J. Romack, J.R. Combes, *Science* 265 (1994) 356.
- [4] M.R. Clark, J.M. DeSimone, *Macromolecules* 28 (1995) 3002.
- [5] J.W. Rathke, R.J. Klinger, T.R. Krame, *Organometallics* 10 (1991) 1350.
- [6] M.J. Burk, S. Feng, M.F. Gross, W. Tumas, *J. Am. Chem. Soc.* 117 (1995) 8277.
- [7] P.G. Jessop, T. Kariya, R. Noyori, *Science* 269 (1995) 1065.
- [8] S. Kainz, A. Brinkmann, W. Leitner, A. Pfalz, *J. Am. Chem. Soc.* 121 (1999) 6421.
- [9] R.J. Klinger, J.W. Rathke, *J. Am. Chem. Soc.* 116 (1994) 4772.
- [10] J.W. Randolph, D.S. Clark, H.W. Blanch, J.M. Prausnitz, *Science* 238 (1988) 387.
- [11] E. Cernia, C. Palocci, F. Gasparini, D. Misiti, N. Fagnano, *J. Mol. Catal. A* 89 (1994) L11–L18.
- [12] E. Catoni, E. Cernia, C. Palocci, *J. Mol. Catal. A* 105 (1996) 79.
- [13] P.G. Jessop, *Top. Catal.* 5 (1998) 95.
- [14] U. Kreher, S. Schebesta, D. Walther, *Z. Anorg. Allg. Chem.* 624 (1998) 602.
- [15] D.R. Pেসisi, D.K. Morita, W. Glaze, W. Tumas, *J. Chem. Soc., Chem. Commun.* (1998) 1015.
- [16] E.R. Birnbaum, R.M. Le Lacheur, A.C. Horton, W. Tumas, *J. Mol. Catal. A* 139 (1999) 11.
- [17] K.M. Dooley, F.C. Knopf, *Ind. Eng. Chem. Res.* 6 (1987) 1910.
- [18] G.J. Suppes, R.N. Occhiogrosso, M.A. McHugh, *Ind. Eng. Chem. Res.* 28 (1989) 1152.
- [19] A.M. Gaffney, J.A. Sofranko, *ACS Div. Pet. Chem. Prep.* 37 (1992) 1273.
- [20] L. Fan, Y. Nakayama, K. Fujimoto, *J. Chem. Soc., Chem. Commun.* (1997) 1179.
- [21] L. Jia, H. Jiang, J. Li, *J. Chem. Soc., Chem. Commun.* (1999) 985.
- [22] R.S. Oakes, A.A. Clifford, K.D. Bartle, M.T. Pett, C.M. Rayner, *J. Chem. Soc., Chem. Commun.* (1999) 247.
- [23] A.K. Dollow, S.L.J. Yun, D. Suleiman, D.L. Boatright, C.L. Liotta, C.A. Eckert, *Ind. Eng. Chem. Res.* 35 (1996) 1801.
- [24] G.B. Jacobson, C.T. Lee, S.R.P. daRocha, K.P. Johnston, *J. Org. Chem.* 64 (1999) 1207.
- [25] G.B. Jacobson, C.T. Lee, K.P. Johnston, *J. Org. Chem.* 64 (1999) 1201.
- [26] J.R. Lindsay Smith, R.W. Wagner, *J. Org. Chem.* 54 (1989) 828.
- [27] P. Hoffmann, A. Robert, B. Meunier, *Bull. Soc. Chim. Fr.* 129 (1992) 85.
- [28] P. Hoffmann, G. Labat, A. Robert, B. Meunier, *Tetrahedron Lett.* 31 (1990) 1991.
- [29] S.G. DiMagno, R.A. Williams, M.J. Therien, *J. Org. Chem.* 59 (1994) 6943.
- [30] A.D. Adler, F.R. Longo, F. Kampes, J. Kin, *J. Inorg. Nucl. Chem.* 32 (1970) 2443.
- [31] A. Robert, M. Momenteau, B. Looock, B. Meunier, *Inorg. Chem.* 30 (1991) 706.
- [32] R. Curci, J.O. Edwards, in: D. Swern (Ed.), *Organic Peroxides*, Vol. I, Wiley, New York, 1970, p. 199, and references therein.
- [33] J.T. Groves, T.E. Nemo, R.S. Meyers, *J. Am. Chem. Soc.* 101 (1979) 1032.
- [34] B. Meunier, *Chem. Rev.* 92 (1992) 1411.
- [35] N.G. Smart, T. Carleson, T. Kast, A.A. Clifford, M.D. Burford, C.M. Wai, *Talanta* 44 (1997) 137.
- [36] R. Eberhardt, S. Loblecke, B. Neidhart, C. Reichardt, *Liebigs Ann./Recl* (1997) 1195.