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Biomimetic oxidation of organosulfur compounds with hydrogen peroxide catalyzed by manganese porphyrins

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ABSTRACT

A biomimetic and environmentally benign approach, with potential application in the oxidative desulfurization procedure for several organosulfur compounds (thioanisol, diphenylsulfide, benzothiophene, 2-methylbenzothiophene, 3-methylbenzothiophene, benzothiophene-2-methanol and dibenzothiophene), is presented. The current methodology involves manganese porphyrins as catalysts, which are well-known biomimetic models of cytochrome P450 enzymes, and hydrogen peroxide as the oxygen source. [Mn(TDCPP)CI] and [Mn(TPFPP)CI], the manganese porphyrin complexes used in this study, proved to be very efficient catalysts, affording high conversions of all the substrates tested into the corresponding sulfones. The conversion of benzothiophene reaches 99.9% in 90 min, whereas the conversion of dibenzothiophene attains 99.9% after 120 min of reaction, both for a catalyst/substrate molar ratio of 150. The substituted benzothiophenes give rise to similar results, being the best conversions obtained for a catalyst/substrate molar ratio of 150. The oxidation of a model fuel (solution of benzothiophene, 3-methylbenzothiophene, 2-methylbenzothiophene, and dibenzothiophene in hexane) was performed using hydrogen peroxide and [Mn(TDCPP)CI] as catalyst, achieving total conversion into the corresponding sulfones.

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1. Introduction

The growing concern with problems associated to a sustainable development and the urgent need for clean technologies had indubitably contributed to the development and dissemination of catalytic processes, namely those related with oxidative transformations. In this context, metalloporphyrins, perhaps the best understood and well studied biomimetic or bio-inspired catalysts, have emerged due to their ability to mimic the catalytic activity of the cytochrome P450 enzymes in the presence of several oxygen donors [1,2]. Since the first report by Groves et al. [3], concerning the use of an iron complex of tetraphenylporphyrin (TPP) as catalysts in the oxidation of alkanes and alkenes, huge improvements have been observed. The amount of work meanwhile disclosed, regarding mainly the use of manganese and iron porphyrin complexes, led to the development of the so-called second and third generation of porphyrin based catalysts, containing electron-withdrawing

** Corresponding author. Tel.: +351 234370710; fax: +351 234370084. *E-mail addresses*: msimoes@ua.pt (M.M.Q. Simões), gneves@ua.pt (M.G.P.M.S. Neves). substituents at the *meso*- and/or β -pyrrolic positions [4,5]. These enhanced porphyrin complexes proved to be highly efficient and much more resistant to oxidative conditions, affording excellent conversions in several oxidation reactions of an enormous plethora of substrates using several oxygen donors. Chloro[5,10,15,20tetrakis(2,6-dichlorophenyl)porphyrinato]manganese(III), abbreviated as [Mn(TDCPP)Cl] or (I), and chloro [5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato]manganese(III), [Mn(TPFPP) Cl] or (II), are good examples of high efficient porphyrin based catalysts, which have been tested in the oxidation of a range of substrates [6–8].

Several oxygenase enzymes are known to selectively produce sulfones, sulfoxides, and even chiral sulfoxides, under very mild conditions [9,10]. Since metalloporphyrins can be considered as the best models of cytochrome P450 monooxygenases, sulfoxidation catalyzed by metalloporphyrins has been explored, almost exclusively with sulfides as substrates [11–17].

Nowadays, the negative impact induced by the presence of sulfur-containing compounds (thiols, sulfides, disulfides, and thiophenes) in petroleum products is well established, both from industrial and environmental reasons [18,19]. Firstly, they are responsible for the poisoning of the catalysts and for the corrosion of parts of the internal combustion engines in petrochemical

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industries. Secondly, the SO_x emissions from their combustion pollute air, water, and soil, being harmful to health, besides promoting acid rains [20,21]. Therefore, deep desulfurization of liquid fuels has become a worldwide challenge [19,22]. In recent years, oxidative desulfurization (ODS) has become a promising and emerging alternative to the conventional hydrodesulfurization (HDS) technology used by most of the oil refineries all over the world [21,23,24]. Besides being arduous and very costly, HDS presents limited performance and do not allow the achievement of ultralow sulfur levels [25,26], mostly due to the presence of the so-called refractory Scontaining aromatic compounds, predominantly alkyl-substituted benzothiophenes (BTs) and dibenzothiophenes (DBTs). In contrast, ODS not only allows moderate process conditions, without employing hydrogen consumption, but it is also efficient in the treatment of BTs and DBTs [20]. The oxidation of these thiophenic compounds to the corresponding sulfoxides and sulfones, more polar products, permits an easier separation from the fuel product by extraction, distillation, decomposition, or adsorption on activated carbon, alumina or silica [20,27–31]. Furthermore, sulfoxides and sulfones have received much attention since they are known as intermediates of biologically significant molecules, ligands in asymmetric catalysis, and oxo-transfer reagents [32-34].

Many oxidants have been tested in several ODS methodologies such as peroxyacids, NaIO₄, MnO₂, CrO₃, SeO₂, *t*-butyl hydroperoxide, cumene hydroperoxide, PhIO, O₃ and O₂, being H₂O₂ the most commonly used, by efficiency and environment protection reasons [35,36]. So, using H₂O₂ as oxidant, several catalytic systems have been reported, namely heterogeneous and homogeneous systems [36–49], organic acid catalysts [50–52], and polyoxometalates [53–57]. However, the narrow applicability to a limited number of BTs and DBTs, observed for several of these procedures, associated with the necessity to meet more and more stringent environmental regulations, makes the development of alternative ODS processes a matter of crucial significance.

There are some reports concerning the use of tetrapyrrolic macrocycles such as porphyrins [11–17], phthalocyanines [58], and corroles [59] in oxidative desulfurization, involving the corresponding Fe(III), Mn(III) or Ru(III) complexes, and oxidants such as O_2 , H_2O_2 , PhIO and Oxone (as TBA or K salts). Now we disclose the high potentiality of manganese porphyrins (I) and (II) (Scheme 2) as catalysts in *S*-oxidation of sulfides, and more significantly, of benzothiophenes and dibenzothiophene, under very mild conditions. As far as we know, this is the first application of manganese porphyrins in the oxidation of recalcitrant dibenzothiophenes, using hydrogen peroxide as oxidant.

2. Results and discussion

The results obtained for the oxidation of substrates (1-7) (Scheme 1) with H₂O₂ using porphyrin catalysts [Mn(TDCPP)Cl] (I) and [Mn(TPFPP)Cl] (II) (Scheme 2) show that the approach is



an easy, high efficient, green, and sustainable procedure to oxidize sulfides (1–2), benzothiophenes (3–6), and dibenzothiophene (7).

Taking into account the amount of work performed in our laboratory in the field of oxidative catalysis with metalloporphyrins [60–70], the methodology, as pointed out in Scheme 3, consists on the use of CH₃CN as the reaction solvent, ammonium acetate as the co-catalyst, and H_2O_2 as the oxidant. This one is progressively added to the reaction mixture, at each 15 min, in aliquots corresponding to half-substrate amount. All the reactions were performed at room temperature, in the absence of light and were followed by GC–FID. The conversion values presented in Table 1 were determined based on the GC–FID results and chlorobenzene was used as the internal standard.

For both catalysts, (I) and (II), and for all the substrates tested, the resultant sulfones were obtained as the only products at the end of the oxidation reactions, corresponding to moderate to high substrate conversion values, depending on the catalyst and on the substrate/catalyst molar ratio. To confirm that metalloporphyrins are in fact catalyzing the oxidation of substrates (1-7), blank experiments were performed, without catalyst, for all the substrates, and no significant conversions were registered (always <5%). In the GC-FID and GC-MS analyses for all the substrates, two products were detected at the beginning of the reactions. The peaks with lower retention times were identified by GC-MS as the resulting sulfoxides, whereas the peaks with higher retention times were attributed to the corresponding sulfones. As exemplified for 3methylbenzothiophene (Fig. 1), after the initial 30 min of reaction the sulfoxide decreases until its total disappearance whereas the sulfone increases until the end of the reaction. So, the manganese porphyrin catalyzed oxidation reactions seem to involve a two step process: first the oxidation to the sulfoxide, followed by its oxidation to the respective sulfone.



Fig. 1. 3-Methylbenzothiophene (**4**) oxidation reaction profile with H_2O_2 in the presence of catalyst (**I**) for a sub/cat molar ratio of 150.

S.M.G. Pires et al.	/ Applied	Catalysis A:	General	439-440	(2012)	51-5	6
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Substrate	Catalyst	Sub/cat molar ratio	Conversion (%)	Product	Time (min)
1	I	300	99.9	0	90
		150	99.9	S	60
	11	300	92.1	CH3	180
		150	99.9		120
2	I	300	99.7		120
		150	99.9		90
	II	300	92.5		240
		150	99.9		150
3	I	300	97.0		180
		150	99.9		90
	11	300	87.4		180
		150	97.8		150
				Ŭ	
4	I	300	95.1	/	120
		150	99.7		90
	п	300	85.9		180
		150	98.8		120
		150	50.0		120
				ő	
5	I	300	96.1		150
		150	99.8		120
	П	300	81.9		180
		150	96.5		180
				ö	
6	I	300	99.4	~ ~ ~	180
U	1	150	99.4 00.7		120
	п	200	55.7 66.1		120
	п	150	05.0	S	150
		150	53.5		150
_					
7	I	300	90.9		180
		150	99.9	NS N	120
	Ш	300	50.9		120
		150	92.4	()()	120

 Table 1

 Results obtained for the oxidation of substrates (1–7) with H₂O₂ catalyzed by manganese porphyrins (I) and (II).^a

^aThe substrate (0.3 mmol) was dissolved in 2.0 mL of CH₃CN and kept under magnetic stirring at 22–25 °C in the presence of Mn–Porph (for sub/cat molar ratio of 150, the catalyst amount was 2.0×10^{-3} mmol; for sub/cat molar ratio of 300, the catalyst amount was 1.0×10^{-3} mmol; for sub/cat molar of 600, the catalyst amount was 0.5×10^{-3} mmol). The co-catalyst used was NH₄CH₃CO₂ (0.12 mmol). The oxidant was progressively added at regular intervals of 15 min in small aliquots, each corresponding to a half-substrate amount. The conversion values are the result of at least two essays.

As clearly evidenced by the results presented in Table 1 and in Fig. 2, generally [Mn(TDCPP)Cl] affords the best results, giving higher conversions in lower reaction times, under similar conditions. The conversion values obtained after 90 min of reaction using a substrate/catalyst molar ratio of 300 (Fig. 2i) or of 150 (Fig. 2ii), also put in evidence the better performance of both catalysts in the oxidation of sulfides (1) and (2), comparatively to the so-called refractory substrates 3-7, probably due to the sulfur unshared electrons involvement in the aromatic system of 3-7. Besides that, in the presence of catalyst (I), a substituent at positions 2 or 3 of benzothiophene does not seem to affect the efficiency of the reaction (substrates 4-6). In general, the substrates tested give rise to lower conversions in the presence of catalyst (II), with special emphasis on 6 and 7. As referred previously, this behavior can be understood by considering the electron-withdrawing capabilities of [Mn(TPFPP)Cl] relatively to [Mn(TDCPP)Cl], thus suggesting a more difficult formation of the active oxo-species for [Mn(TPFPP)Cl] [65].

The catalytic system was evaluated for the removal of refractory S-containing compounds in a model fuel, consisting on a mixture of benzothiophene (3), 3-methylbenzothiophene (4), 2methylbenzothiophene (5), and dibenzothiophene (7) in hexane, using the more efficient catalyst [Mn(TDCPP)Cl], as demonstrated above. GC-MS analyses were used to follow the oxidation reactions of the model fuel. The chromatograms obtained before (Fig. 3A) and after (Fig. 3D) the catalytic oxidation of the model fuel were used to confirm that all the S-containing compounds had been completely oxidized to the corresponding sulfones **10** (R_t = 10.23), **11** $(R_t = 10.84)$, **12** $(R_t = 11.93)$, and **14** $(R_t = 15.68)$. After 60 min of reaction (Fig. 3B) is possible to observe the four chromatographic peaks corresponding to the substrates, four new peaks corresponding to the sulfones and two additional peaks identified by GC-MS as the sulfoxides (R_t = 10.04 for the benzothiophene oxide and R_t = 11.68 for the 2-methylbenzothiophene oxide). After 120 min of reaction almost complete conversion of the model fuel is achieved, as can be observed in Fig. 3C.





Fig. 2. Conversion values obtained for substrates (1–7) after 90 min of oxidation reaction with H_2O_2 , using (A) a sub/cat molar ratio of 300 and (B) a sub/cat molar ratio of 150.

3. Experimental

The syntheses of manganese porphyrin catalysts were accomplished according to already established procedures [71,72]. For the catalytic studies, in a typical experiment, the substrate (0.3 mmol), the catalyst $(2.0 \times 10^{-3} \text{ mmol}, 1.0 \times 10^{-3} \text{ mmol or } 0.5 \times 10^{-3} \text{ mmol},$ depending on the sub/cat molar ratio employed, 150, 300 or 600, respectively), the co-catalyst (ammonium acetate, 0.2 mmol) and the internal standard (chlorobenzene, 0.3 mmol) were dissolved in CH₃CN (2.0 mL). For the model fuel catalytic studies, the substrates 3-5 and 7 (0.03 mmol each in hexane), the catalyst (I) $(1.7 \times 10^{-3} \text{ mmol in } 475 \,\mu\text{L of CH}_3\text{CN})$, and the co-catalyst (ammonium acetate, 0.1 mmol) were dissolved in hexane for a total volume of 2.0 mL. The reaction mixtures were kept under magnetic stirring and in the absence of light at 22-25 °C. The oxidant, 30% H₂O₂ (w/w, aqueous solution), was diluted in CH₃CN (1:10) and added to reaction in regular intervals of 15 min, in aliquots corresponding to a half-substrate amount. The reactions were followed by GC-FID and by GC-MS. For all the substrates, the resulting sulfones were isolated by preparative TLC using CH₂Cl₂ as eluent and characterized by ¹H NMR (please see the Supplementary information for the analytical data of compounds 8-14). The GC-FID analyses were performed on a Varian 3900 chromatograph using helium as the carrier gas (30 cm/s). The GC-MS analyses were performed on a Finnigan Trace GC/MS (Thermo Quest CE instruments) using helium as the carrier gas (35 cm/s). In both cases fused silica capillary DB-5 type columns (30 m, 0.25 mm i.d., 0.25 µm film thickness) were used. The ¹H NMR spectra were recorded on a Bruker Avance 300 at 300.13 MHz, using CDCl₃ as solvent and TMS as the internal reference.



Fig. 3. Typical GC–MS chromatograms illustrating the model fuel oxidation reaction profile with H_2O_2 in the presence of catalyst (I) for a sub/cat molar ratio of 150. (A) Initial reaction mixture before the addition of H_2O_2 ; (B) after 60 min of reaction; (C) after 120 min of reaction and (D) after 180 min of reaction. The model fuel is a solution of 3 (R_t = 5.73), **4** (R_t = 7.23), **a**d **7** (R_t = 12.41) in hexane (with 0.03 mmol each).

4. Conclusions

In this work we demonstrate that [Mn(TDCPP)Cl] (catalyst I) and [Mn(TPFPP)Cl] (catalyst II) are able to efficiently oxidize several organosulfur compounds, namely sulfides and refractory S-containing aromatic compounds, such as benzothiophenes and dibenzothiophene, under very mild conditions (at room temperature, using diluted aqueous hydrogen peroxide and acetonitrile as solvent). For both catalysts, and for all the substrates tested, the corresponding sulfones are obtained in good to excellent yields at the end of the oxidation reactions. Nevertheless [Mn(TDCPP)Cl] give rise to the best results, affording higher conversions in lower reaction times. In fact, the conversion of benzothiophene (3) reaches 99.9% in 90 min, whereas the conversion of dibenzothiophene (7) attains 99.9% after 120 min of reaction, both for catalyst (I)/substrate molar ratio of 150. The substituted benzothiophenes (4-6) give rise to similar results, conversions being always higher for a catalyst (I)/substrate molar ratio of 150 instead of 300. As expected, less hindered sulfides (1-2) are very efficiently transformed into the corresponding sulfones. In the case of thioanisole (1), the conversion reaches 99.9% even for a catalyst (I)/substrate molar ratio of 600, after 90 min of reaction.

The oxidation of a model fuel (a solution of benzothiophene, 3-methylbenzothiophene, 2-methylbenzothiophene, and dibenzothiophene in hexane) was performed using hydrogen peroxide and [Mn(TDCPP)CI] as catalyst, attaining total conversion into the corresponding sulfones. This is a very promising evidence of the potential application of these manganese complexes for the removal of refractory S-containing organic compounds from fuels.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata. 2012.06.044.

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