



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 (thioanisole, 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)Cl] and [Mn(TPFP)Cl], 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)Cl] 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 catalyst 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

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[5,10,15,20-tetrakis(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(TPFP)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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