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LETTER

Entrapping of iron(III) porphyrins in a polystyrene matrix and their photocatalytic activity in oxidation reactions by molecular oxygen

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Iron porphyrins can induce monooxygenation reactions on hydrocarbons, thus mimicking the catalytic cycle of Cytochrome P450. For this reason these complexes have been the object of many studies in order to gain more insight into the Cytochrome P450 mechanism and to build up catalytic systems that exhibit its reactivity in mild conditions [1, 2]. Heterogenization of homogeneous Cytochrome P450 models by using organic and inorganic matrices is receiving increasing attention because: (i) the isolation of the catalyst on the support should prevent intermolecular self reactions, (ii) it allows an easier recovery of the catalyst, (iii) it sometimes could improve its reactivity [3–5].

It has been recently reported that it is possible to entrap physically relatively large rhodium complexes inside a polystyrene complex utilizing solvent-dependent swelling, thus avoiding several synthetic steps needed for the chemical attachment [6]. Herein, we describe the preparation of new catalysts consisting of iron(III)–*meso*-tetraphenylporphyrin chloride (Fe(III)(tpp)(Cl)) and iron(III)–*meso*-tetra(2,6-dichlorophenyl)porphyrin chloride (Fe(III)(tdcpp)(Cl)) 'caged' into the voids of a polystyrene matrix. The catalytic activity of these systems is demonstrated using light as a 'reagent' in the oxidation of cyclohexene by molecular oxygen. The mechanism is discussed on the basis of the results reported by several authors on the photochemistry and photocatalysis of iron porphyrins in homogeneous solution [7–17].

Experimental

Material and methods

Fe(III)(tpp)(Cl) and Fe(III)(tdcpp)(Cl) were prepared and purified as previously reported [18]. The commercial polystyrene was from Fluka and it was washed with cyclohexane by reflux in a Soxhlet apparatus to remove any polymerization residue before use. UV–Vis spectra were recorded on a Perkin-Elmer model Lambda 6 spectrophotometer equipped with an integrating sphere. Gas chromatography analyses were carried out with a Dani 8521 gas chromatograph equipped with a flame ionization detector. Columns packed with Carbowax 20 M 5% on Chromosorb W-AW were used for analysis of the products.

Preparation of the iron porphyrin/polystyrene systems

Fe(III)(tpp)(Cl) and Fe(III)(tdcpp)(Cl) can be entrapped to different degrees inside 2% or 4% cross-linked polystyrene. A typical preparation involves the stirring for 12 h of a suspension of 1 g of resin in 10 ml of a solution of iron porphyrin (0.1 g dm^{-3}) in THF which is a solvent with high swelling properties towards polystyrene ($\delta = 9.9$ $(cal\ cm^{-3})^{1/2}$)**. After the evaporation of the solvent at reduced pressure, a contraction of the voids takes place leaving part of the porphyrin trapped inside the solid and part adsorbed on the surface. The adsorbed complex is washed away with different solvents with lower swelling properties than THF: methanol ($\delta = 14.5$ $(cal\ cm^{-3})^{1/2}$), cyclohexane ($\delta = 8.2$ $(cal\ cm^{-3})^{1/2}$), cyclohexene (not reported). This treatment removes part of the trapped complex too.

Filtration gives a brownish solid which presents the reflectance UV–Vis spectrum typical of the starting iron porphyrins Fe(III)(tpp)(Cl) or Fe(III)(tdcpp)(Cl). After washing with the above solvents, the amount of iron porphyrin entrapped by the resin was determined by spectrophotometric analyses after extracting the complex from polystyrene with CH_2Cl_2 which is a solvent with high swelling properties ($\delta = 9.7$ $(cal\ cm^{-3})^{1/2}$).

Photocatalytic activity of the Fe(III)(tdcpp)(Cl)/4% cross-linked polystyrene system (FePS)

A cyclohexene FePS suspension was irradiated with light of wavelength higher than 350 nm for 5 min in the presence of 760 torr of O_2. The formation of the products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one was then followed in the dark by gas chromatographic analysis.

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**According to the Hildebrand–Scatchard theory, if a polymer and a solvent have similar solubility parameters (δ), then solution will occur. The δ value of polystyrene is 9.2 $(cal\ cm^{-3})^{1/2}$ [19].

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TABLE 1. Amount of entrapped iron(III) porphyrin inside polystyrene

Iron porphyrin	Cross-linking (%)	Entrapped iron(III) porphyrin in different solvents[a,b] (%)		
		Methanol	Cyclohexane	Cyclohexene
Fe(III)(tpp)(Cl)	2	0.1		
Fe(III)(tpp)(Cl)	4	0.1	0.06	0.005
Fe(III)(tdcpp)(Cl)	2	0.013	0.006	
Fe(III)(tdcpp)(Cl)	4	0.06	0.06	0.06

[a] Percent by weight. [b] The error of the reported data is ±10%.

Results and discussion

The results reported in Table 1 show that the iron porphyrin complex is entrapped inside the polymer matrix to different degrees depending on several parameters: (i) the degree of cross-linking of the polymer that controls the swelling properties and the average size of the polymer voids; (ii) the swelling degree of the various solvents; (iii) the volume of the iron porphyrin complex.

The amount of iron porphyrin caged in the polystyrene matrix in different solvents follows the order: methanol > cyclohexane > cyclohexene* according to their increasing swelling properties. In CH_3OH suspensions the resin is found to enclose Fe(III)(tpp)(Cl) in higher amounts with respect to Fe(III)(tdcpp)(Cl). A possible explanation is that Fe(III)(tpp)(Cl) can diffuse toward more remote and smaller voids than the bigger octachloro derivative Fe(III)(tdcpp)(Cl), independently of the cross-linking degree. The amount of Fe(III)(tdcpp)(Cl) in the 4% cross-linked polystyrene is higher than the one in the 2% cross-linked sample, and the degree of trapping is constant in all the solvents investigated. This is indicative of a borderline case in which the size of the porphyrin and the dimension of the voids are comparable. Thus the catalyst, once trapped into the polymer, can be released only with a solvent with very high swelling properties (CH_2Cl_2).

In this work the ability of 'caged' iron porphyrins to work as catalysts is assessed by studying the oxidation of cyclohexene by molecular oxygen in the presence of the photoactivated FePS. The build up of the allylic oxidation products in time following 5 min irradiation is reported in Fig. 1. The photooxidation quantum yields, calculated as the ratio between the concentrations of the products at the end of the reaction and the moles of incident photons, were 1.5 for 2-cyclohexene-1-one and 0.7 for 2-cyclohexene-1-ol. Under identical conditions, both the resin in the absence of iron porphyrin and the non-irradiated FePS were found to be totally inactive.

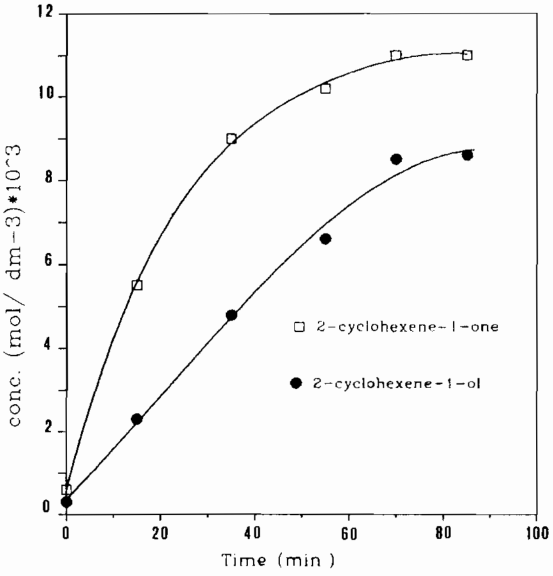

Fig. 1. Product formation in the photooxidation of cyclohexene by O_2 catalyzed by FePS, as followed after 5 min irradiation.

At the end of the oxidation process (*c.* 90 min), the amount of caged iron porphyrin was 40% lower than the initial one, although there was no evidence of leaching of the catalyst from the resin into cyclohexene as determined spectrophotometrically. This suggests that, during the photoreaction, the porphyrin ring undergoes partial degradation with the formation of small colourless fragments. The equivalents of 2-cyclohexene-1-one and 2-cyclohexene-1-ol per equivalent of consumed iron porphyrin were 2800 and 1200, respectively.

At this stage, we may assume that the primary photochemical act is the same as that reported by Hendrickson *et al.* [16] for Fe(III)(tpp)(Cl) in homogeneous solution. Irradiation in a ligand to metal charge transfer band causes the reduction of Fe(III) to Fe(II) and the oxidation of Cl^- to $Cl^{\bullet}$ (eqn. (1)). In the presence of O_2, photooxygenation of cyclohexene is then possible via peroxyl radical chain autooxidation.

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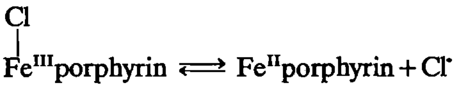
*Since the value of cyclohexene swelling properties is not reported, we checked the relative swelling empirically by measuring the increase in volume of a weighed amount of polystyrene in these solvents.



$$\overset{\mathrm{Cl}}{\overset{|}{\mathrm{Fe}}}{}^{\mathrm{III}}\mathrm{porphyrin} \rightleftharpoons \mathrm{Fe}^{\mathrm{II}}\mathrm{porphyrin} + \mathrm{Cl}^{\bullet} \qquad (1)$$

In conclusion, physically entrapped iron porphyrins inside a polystyrene matrix can be easily prepared when the swelling properties of the solvent and the cross-linking of the matrix make the polymeric voids small enough not to allow the complex to leach out. The FePS system catalyzes the photooxidation of cyclohexene by molecular oxygen with good quantum yields and turnover values, and it can be easily recovered by simple filtration at the end of the reaction. More detailed studies on the catalytic activity of the iron porphyrin/polystyrene systems towards alkenes and alkanes are underway in order to establish the role played by the polystyrene matrix in the catalytic processes, and to verify if the oxidation reactions are selective.

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