

Supported iron(III)porphyrins pentafluorophenyl-derivatives as catalysts in epoxidation reactions by H₂O₂: the role of the silica-support and sulfonatophenyl residues in the activation of the peroxidic bond

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Abstract

Ionic Fe(III)porphyrins pentafluorophenyl-derivatives: 5,10,15-tris(pentafluorophenyl)-20-(4-*N*-methylpyridyl)porphyrin iron(III) ([Fe{M(4-*N*-MePy)TPFP}]²⁺), 5,10,15-tris(4-*N*-methylpyridyl)-20-(pentafluorophenyl)porphyrin iron(III) ([Fe{T(4-*N*-MePy)MPFP}]⁴⁺) and 5,10,15-tris(pentafluorophenyl)-20-(3-sulfonatophenyl)porphyrin iron(III) ([Fe{M(3-SO₃P)TPFP}]) immobilised on silica gel (SiO₂) and modified silica with sulfonatophenyl (SiSO₃⁻), propylimidazole (IPG), sulfonatophenyl plus propylimidazole (SiSO₃⁻(IPG)), propyltrimethylammonium (SiN⁺) and propyltrimethylammonium plus propylimidazole (SiN⁺(IPG)) were studied in the epoxidation of (*Z*)-cyclooctene by H₂O₂. The better yields of product, *cis*-epoxycyclooctane, were achieved with the catalytic systems, [Fe{M(4-*N*-MePy)TPFP}]-SiSO₃(IPG), [Fe{M(3-SO₃P)TPFP}]-IPG and [Fe{M(3-SO₃P)TPFP}]-SiO₂, where is more probable to have available sulfonatophenyl groups. That is, where there is no ionic binding Fe(III)porphyrin-support via sulfonatophenyl. A charge effect supplied by the available sulfonatophenyl residues and a more polar microenvironment provided by the silica-support promote the heterolytic cleavage of the O–O bond, which is essential to obtain high yields of products in oxidation reactions. Effects of general acid–base catalysis, as occurs in enzymes, and higher reduction potential provided by electron-withdrawing groups, present on porphyrin ring or axial ligand, as recently reported by Nam and coworkers for homogeneous Fe(III)porphyrins, to promote the heterolysis of the O–O bond are ruled out.

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1. Introduction

Reactions of Fe(III)porphyrins with several simple oxidants such iodobenzene, hypochlorite, *m*-chloro-

perbenzoic acid and hydrogen peroxide have been extensively studied in oxygenation of organic compounds catalysed by metal complexes, with the aim of developing efficient biomimetic catalysts for oxygenation reactions and understanding the mechanisms of transference of an oxygen atom [1]. In particular, H₂O₂ is a biologically important and clean oxidant, since it gives only water as by-product,

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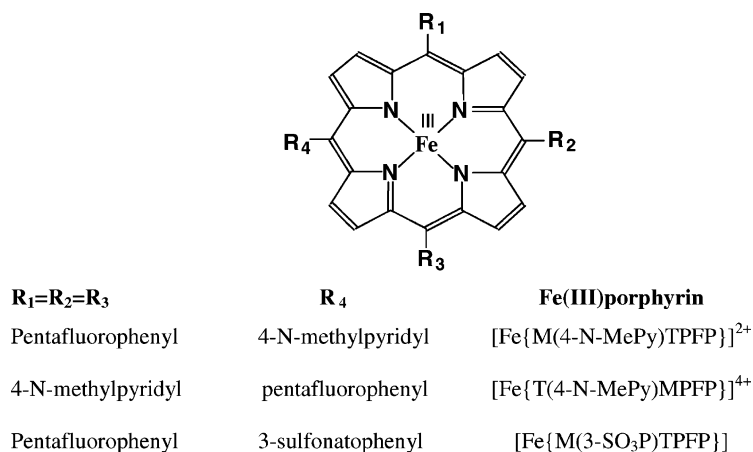


Fig. 1. Fe(III)porphyrins pentafluorophenyl-derivatives.

being, therefore, target of various reports in oxidation chemistry [2].

Initially emerged a dichotomy between heterolytic, yielding an intermediate $[\text{Fe}^{\text{IV}}\text{porp}^{\bullet+}(\text{O})]$ [3], or homolytic, yielding a intermediate $[\text{Fe}^{\text{IV}}\text{porp}(\text{O})]$, [4,5] cleavage of the O–O bond in homogeneous $[\text{porpFe}(\text{III})\text{--OOH}]$ complexes, which was recently elucidated by Nam et al. [6,7]. In the report, the authors verify that the O–O bond of hydroperoxides can be cleaved both heterolytically and homolytically by Fe(III)porphyrins in aqueous and organic solvents and that the predominant pathway is affected by the electronic nature of the iron porphyrin, substituents of the hydroperoxide and axial ligand. It was suggested that the heterolytic O–O bond cleavage, able to oxidise several organic compounds such as epoxidation of olefins and hydroxylation of alkanes, is facilitated when less electron density resides on the O–O bond of the $[\text{porpFe}(\text{III})\text{--OOH}]$ intermediate.

In addition to the environmental importance of the H_2O_2 in oxidation chemistry, another important aspect in the developing of efficient biomimetic catalysts for oxidation of organic compounds is the use of catalysts that can be recovered and reused. In this sense, an approach has been to immobilising a metalloporphyrin on a solid matrix (silica gel [8,9], zeolite [10] or ion exchange resin [11]), that also allows controlling the reactivity of the system through the microenvironment created by the support [12].

This paper describes the epoxidation of a cycloalkene, the (*Z*)-cyclooctene, by H_2O_2 catalysed by asymmetric Fe(III)porphyrins pentafluorophenyl-derivatives $[\text{Fe}\{\text{M}(4\text{-N-MePy})\text{TPFP}\}]^{2+}$, $[\text{Fe}\{\text{T}(4\text{-N-MePy})\text{MPFP}\}]^{4+}$ and $[\text{Fe}\{\text{M}(3\text{-SO}_3\text{P})\text{TPFP}\}]$ (Fig. 1), bound to two bis-functionalised silica: (i) with propylimidazole and sulfonatophenyl groups, SiSO_3^- (IPG) and (ii) with propylimidazole and propyltrimethylammonium groups, SiN^+ (IPG) (Fig. 2). Systems

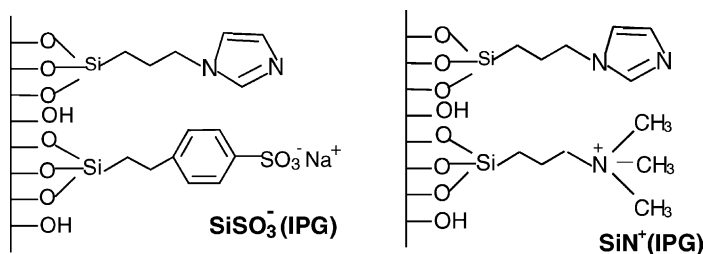


Fig. 2. Bis-functionalised supports.

containing only one functional group each one: sulfonatophenyl, SiSO_3^- , propyltrimethylammonium, SiN^+ , and propylimidazole, IPG, and no modified silica, SiO_2 , also were used as supports. Ionic Fe(III) porphyrins are attached to the support by electrostatic interactions between the charge of the *meso*-position on the iron porphyrin (4-*N*-methylpyridyl or sulfonatophenyl) and the counter-charge present on the support (sulfonatophenyl or propyltrimethylammonium). Moreover, the propylimidazole of the support is coordinated to the central iron, analogous to proximal ligands of enzymes [13] and in the case of the no modified silica, the silanol groups coordinate to the iron(III). The role of the functional groups, present on the Fe(III)porphyrin and/or modified support and of the silica-support in the activation of H_2O_2 are discussed.

2. Experimental

2.1. Materials

All solvents and reagents were of commercial grade unless otherwise stated and were purchased from Merck, Fluka and Aldrich. Dichloromethane (DCM), dichloroethane (DCE), methanol (MeOH), *N,N*-dimethylformamide (DMF) and acetonitrile (ACN) HPLC grade were used as received. (*Z*)-cyclooctene was purified by column chromatography on basic alumina prior to use and their purities were checked by gas chromatographic analysis. Hydrogen peroxide (H_2O_2 30% in H_2O , Fluka) was stored at 5 °C and checked by titration every 3 months [14].

2.1.1. Iron(III)porphyrins

2.1.1.1. $[\text{Fe}\{M(4-N\text{-MePy})\text{TPFP}\}]^{2+}$. $[\text{Fe}\{M(4-N\text{-MePy})\text{TPFP}\}]^{2+}$ was obtained and characterised as already reported [8].

2.1.1.2. $[\text{Fe}\{T(4-N\text{-MePy})\text{MPFP}\}]^{4+}$. The synthesis of the T(4-*N*-Py)MPFP H_2 , precursor ligand, was carried out by the method described by Adler et al. [15]. The compound was isolated by column chromatography on silica gel using DCM/acetone 1:1 as eluent. T(4-*N*-Py)MPFP H_2 obtained was charac-

terised by thin layer chromatography (TLC) on silica gel ($R_f = 0.17$ in DCM/acetone 1:1), UV–VIS spectroscopy (DCM) λ_{max} , nm (ϵ , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$), 418 (1.7×10^5), 512, 544 (sh), 586, 642 (w). FAB MS (m/z 708, calculated average m/z 708) and ^1H NMR (β -pyrrole: $\delta = 8.87$ s (4H), $\delta = 8.93$ d (2H), chemical shift undetermined d (2H), pyridyl: $\delta = 8.17$ d (6H), $\delta = 9.07$ d (2H), N–H pyrrole: $\delta = -2.91$ s (2H)), which confirmed the structure and the purity of the porphyrin; yield: 6.4%. Iron insertion into T(4-*N*-Py)MPFP H_2 was achieved by heating the free-base porphyrin and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at reflux in ACN for 26 h. At the end of the reaction, the solvent was removed under vacuum. The Fe(III)porphyrin was dissolved in water and NaClO_4 was added to the solution, producing a precipitate. The mixture was cooled overnight and the solid Fe(III)porphyrin was isolated by filtration.

The compound was methylated by reaction with large excess (360 equivalents) of CH_3I in DMF at room temperature under argon [16]. The unreacted CH_3I and DMF were removed under vacuum. The iodide anion was exchanged by chloride using an ion exchange resin Dowex 1 \times 2-200 1-chloride (Aldrich). The product gave one spot by TLC on silica using 15% (v/v) MeOH in DCM as eluent ($R_f = 0$); UV–VIS: (MeOH) λ_{max} , nm (ϵ , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$) 350, 418 (1.4×10^4), 580; yield: 95%.

2.1.1.3. $[\text{Fe}\{M(3\text{-SO}_3\text{P})\text{TPFP}\}]$. The synthesis of the precursor M(P)TPFP H_2 was carried out according Lindsey's method [17]. The compound was isolated by column chromatography on silica gel using DCM/cyclohexane 1:3 as eluent and characterised by thin layer chromatography (TLC) on silica gel ($R_f = 0.51$ in DCM/cyclohexane 1:3), UV–VIS spectroscopy (DCM) λ_{max} , nm (ϵ , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$), 412 (3.0×10^5), 506, 582. FAB MS (m/z 885, calculated average m/z 884) and ^1H NMR (β -pyrrole: $\delta = 8.96$ d (2H), $\delta = 8.81$ d (2H), $\delta = 8.89$ q (4H); phenyl: $\delta = 8.19$ – 8.21 m (2H), $\delta = 7.76$ – 7.84 m (3H), N–H pyrrole: $\delta = -2.83$ s (2H); yield: 45%.

M(P)TPFP H_2 was sulfonated according to the method of Meunier et al. [19] by refluxing chlorosulfonic acid, previously added to porphyrin at 0 °C, in DCM. The sulfonated porphyrin obtained was isolated by column chromatography on silica gel using

MeOH as eluent. Iron insertion into M(3-SO₃P)TPF-PH₂ was carried out by reacting the free-base porphyrin and FeCl₂·4H₂O at reflux in ACN for 4 h. [Fe{M(3-SO₃P)TPFP}] was isolated by column chromatography on silica gel using MeOH as eluent. The H⁺ cation was exchanged by Na⁺ using an ion exchange resin Dowex 50 W × 8–100 50 W hydrogen acid (Aldrich). The product gave one spot by TLC on silica using 15% (v/v) MeOH in DCM as eluent (*R*_f = 0.17), UV–VIS spectroscopy (DCM) λ_{max}, nm (ε, mol⁻¹ dm³ cm⁻¹), 413 (6.7 × 10⁴), 505; yield: 54%.

2.1.2. Solid supports

IPG, SiSO₃⁻ and SiSO₃⁻(IPG) were obtained and characterised as recently reported [13]. SiN⁺ was prepared heating a suspension of silica gel with trimethoxy-3-(trimethylammonium)propylsilane in toluene at reflux according to the method of Leal et al. [18] and the resulting material was dried under vacuum at 100 °C for 8 h. Elemental analysis: C = 3.71%, H = 1.79% and N = 0.74%, which corresponds to 5.28 × 10⁻⁴ mol of propyltrimethylammonium/g of SiN⁺. SiN⁺(IPG) was prepared by reacting a suspension of SiN⁺ with 3-chloropropyltrimethoxysilane and imidazole in toluene at reflux according to the method described by Leal et al. [18]. The solid obtained was dried under vacuum at 100 °C. Elemental analysis: C = 6.83%, H = 1.92% and N = 1.41%, which corresponds to 2.35 × 10⁻⁴ mol of imidazole/g of SiN⁺(IPG).

2.1.3. Preparation of immobilised Fe(III)porphyrins

Fe(III)porphyrins bond to the solid supports were achieved by stirring the respective solution of Fe(III)porphyrin, [Fe{M(4-*N*-MePy)TPFP}]²⁺ and [Fe{T(4-*N*-MePy)MPFP}]⁴⁺ in DCE/ACN 1:1 and [Fe{M(3-SO₃P)TPFP}] in DCM, with a suspension of support for about 20 min. The amount of complex bound to the solid matrix was 7.5 × 10⁻⁶ mol of Fe(III)porphyrin/g of support. The resulting catalysts [Fe{M(4-*N*-MePy)TPFP}]-support and [Fe{T(4-*N*-MePy)MPFP}]-support were washed with DCE/ACN and [Fe{M(3-SO₃P)TPFP}]-support washed with DCM in a Soxhlet extractor overnight to remove unbound and weakly bound Fe(III)porphyrin. The solids were dried for 3 h at 100 °C.

2.2. UV–VIS spectra

The UV–VIS spectra were recorded on a Hewlett-Packard 8453 Diode Array UV–VIS spectrophotometer. In the case of supported Fe(III)porphyrins, spectra were recorded in a 2 mm path length quartz cell, with the supported catalyst in a suspension in CCl₄. The “blank” was recorded previously and consisted of a support/CCl₄ suspension.

2.3. EPR spectra

The EPR spectra were recorded on a Varian E-109 century line spectrometer operating at the X-band, at a temperature of about 4 K. The *g* values were calculated by taking the frequency indicated in a HP 5340. A frequency meter and the field measured at the spectral features, which were recorded with increased gain and expanded field. Routine calibrations of the field setting and scan were made with DPPH and Cr³⁺ reference signals. The Helitran (Oxford Systems) low temperature accessory was employed to obtain the spectra in the specified temperature range.

2.3.1. EPR spectra of immobilised Fe(III)porphyrins

The EPR spectra of supported iron porphyrins were recorded at a temperature of ca. 4 K after addition of the immobilised catalyst to an EPR tube containing 200 μl DCE.

2.4. Product analysis by gas chromatography

Gas chromatographic analyses were performed on a Hewlett-Packard HP 6890 Series GC System, coupled to a flame ionisation detector, using a capillary column (HP-INNOWAX, cross-linked poly(ethylene glycol), length 30 m; i.d. 0.25 mm, film thickness 0.25 μm) and nitrogen as carrier gas.

2.5. Procedure for catalytic oxidations

All substrates were checked prior to use, by gas chromatography, to ensure that they were free from oxidation products. Reactions were performed in a 2 cm³ vial sealed with a Teflon-coated silicone septum and stirred at room temperature. Catalyst, imidazole or 1-methylimidazole (in some cases), substrate and internal standard (cyclohexanone) were

mixed in DCM/ACN and then the oxidant was added. Yields based on the oxidant added were determined by removing aliquots of the reaction mixture and analysing them by gas chromatography. No reaction occurred in control reactions in the absence of the Fe(III)porphyrin.

3. Results and discussion

3.1. Characterisation of supported Fe(III)porphyrins by UV–VIS spectroscopy

The electronic spectra of the supported catalysts confirmed the presence of Fe(III)porphyrins on the supports, being a qualitative method of characterisation. It was not possible to obtain information in molecular level using this technique because there are not effective spectral differences between the several systems Fe(III)porphyrin-support [13,20]. A typical spectrum is shown in Fig. 3. The loadings were quantified by measuring the amount of unloaded Fe(III)porphyrin, in the solvent washings, by UV–VIS spectroscopy (Table 1).

As already mentioned [13], systems in which ionic binding is favoured, as for [Fe{T(4-*N*-MePy)MPFP}

MPFP}]⁴⁺ bound to the anionic supports SiSO₃⁻ and SiSO₃⁻(IPG), have the highest loadings, and a difficult leaching of the Fe(III)porphyrin from the support during the reaction. On the other hand, the complex [Fe{M(3-SO₃P)TPFP}] bound to the solid supports present a high amount of loading, comparable to the highly charged [Fe{T(4-*N*-MePy)MPFP}]⁴⁺. This behaviour is due to the fact of the solvent used in the Soxhlet extraction for the systems [Fe{M(3-SO₃P)TPFP}]-support to have been the DCM, which is a non-polar and non-coordinating solvent, unlikely of Soxhlet extraction using ACN, which is a polar solvent and favours the leach off, lowering the quantity of loading, as observed for [Fe{M(4-*N*-MePy)TPFP}]²⁺. Actually the systems [Fe{M(3-SO₃P)TPFP}]-support are the unique washed with DCM (Table 1) due to the fact of the [Fe{M(3-SO₃P)TPFP}] undergoes high amount of leaching (about 60%) from the IPG and SiO₂ when washed with DCE/ACN in a Soxhlet extraction.

3.2. Characterisation of supported Fe(III)porphyrins by EPR spectroscopy

Analysis by EPR spectroscopy of Fe(III)porphyrins immobilised on solid supports was performed. This study provided information on the spin and oxidation

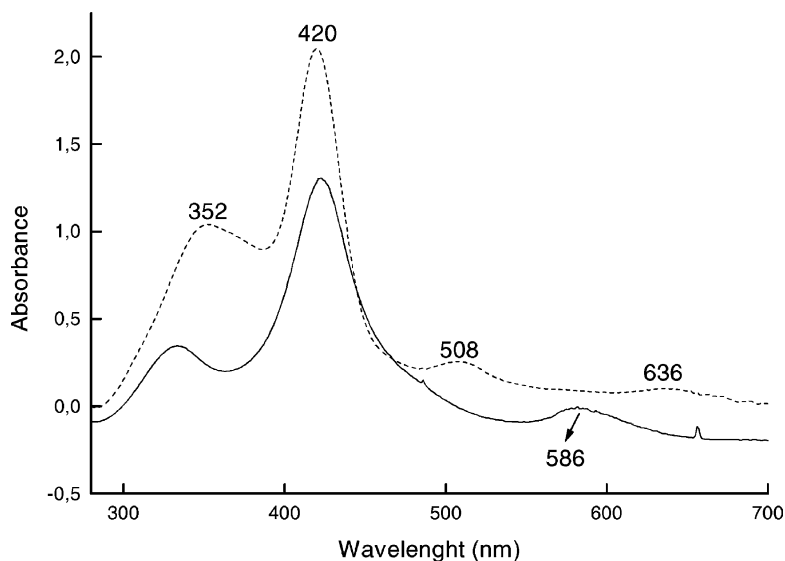


Fig. 3. UV–VIS spectra of dashed line: solution of [Fe{T(4-*N*-MePy)MPFP}](PF₆)₄ in DCE/ACN (1:1) and solid line: [Fe{T(4-*N*-MePy)MPFP}]-IPG in CCl₄.

Table 1
Amounts of Fe(III)porphyrin bound to the solid supports

Support	Fe(III)porphyrins	Solvent used in Soxhlet extractor	Loading (%)
IPG	[Fe{M(4- <i>N</i> -MePy)TPFP}] ²⁺	DCE/ACN	86
IPG	[Fe{T(4- <i>N</i> -MePy)MPFP}] ⁴⁺	DCE/ACN	92
IPG	[Fe{M(3-SO ₃ P)TPFP}]	DCM	99
SiSO ₃ ⁻	[Fe{M(4- <i>N</i> -MePy)TPFP}] ²⁺	DCE/ACN	90
SiSO ₃ ⁻	[Fe{T(4- <i>N</i> -MePy)MPFP}] ⁴⁺	DCE/ACN	98
SiSO ₃ ⁻ (IPG)	[Fe{M(4- <i>N</i> -MePy)TPFP}] ²⁺	DCE/ACN	91
SiSO ₃ ⁻ (IPG)	[Fe{T(4- <i>N</i> -MePy)MPFP}] ⁴⁺	DCE/ACN	99
SiN ⁺	[Fe{M(3-SO ₃ P)TPFP}]	DCM	99
SiN ⁺ (IPG)	[Fe{M(3-SO ₃ P)TPFP}]	DCM	99
SiO ₂	[Fe{M(3-SO ₃ P)TPFP}]	DCM	99
SiO ₂	[Fe{M(4- <i>N</i> -MePy)TPFP}] ²⁺	DCE/ACN	70
SiO ₂	[Fe{T(4- <i>N</i> -MePy)MPFP}] ⁴⁺	DCE/ACN	95

state of the central atom present on supported iron porphyrin, indicating that the samples contain high-spin iron(III) (signals in $g_{\perp} \sim 6$ and $g_{\parallel} \sim 2$), which suggests that in all cases the complexes are mono-coordinated, as previously observed for [Fe{M(4-*N*-MePy)TPFP}]-IPG [8]. A typical spectrum of the supported-Fe(III)porphyrin studied is shown in Fig. 4. The unique different spectrum observed was obtained for [Fe{M(4-*N*-MePy)TPFP}]-SiSO₃ (IPG), presenting signal in $g = 4.3$, which is consistent with a distorted structure of the Fe(III)porphyrin (Fig. 5). It was believed initially

that the distortion of the Fe(III)porphyrin would be the factor responsible by the high yield of epoxide obtained with this catalyst (Table 3). However, a new attachment of the [Fe{M(4-*N*-MePy)TPFP}]²⁺ and a posterior Soxhlet extraction for 48 h resulted in an EPR spectrum no distorted (Fig. 5) of the [Fe{M(4-*N*-MePy)TPFP}]-SiSO₃ (IPG), but in a new reaction the yield of *cis*-epoxycyclooctane with this no distorted catalyst was maintained, indicating that the distortion of the Fe(III)porphyrin is not responsible by the high yields of product epoxide.

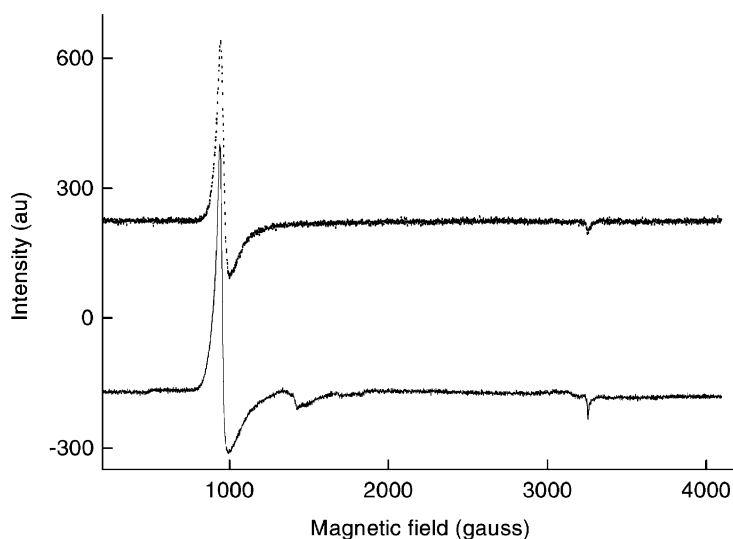


Fig. 4. EPR spectra of dash line: solution of [Fe{T(4-*N*-MePy)MPFP}](PF₆)₄ in DCE/ACN (1:1) and solid line: suspension of [Fe{T(4-*N*-MePy)MPFP}]-SiSO₃ in DCE.

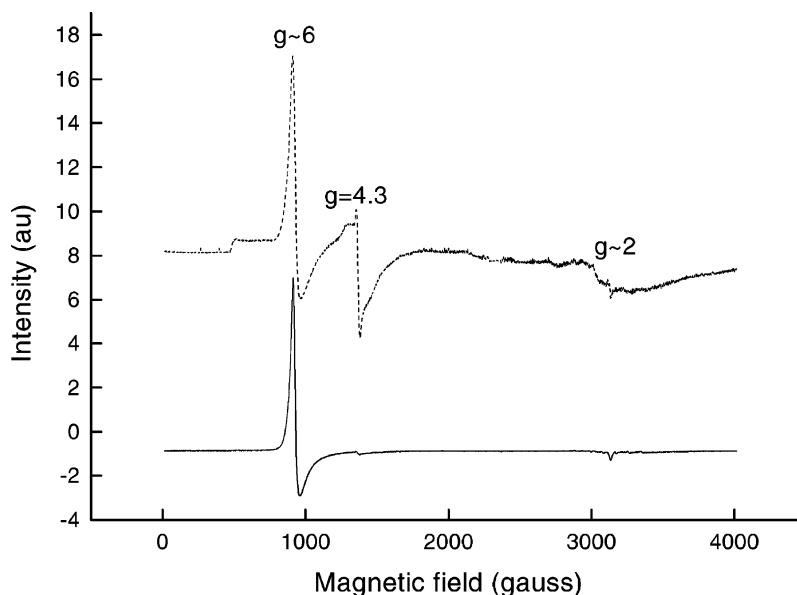


Fig. 5. EPR spectra of dash: $[\text{Fe}\{\text{M}(4\text{-}N\text{-MePy})\text{TPFP}\}]\text{-SiO}_3$ (IPG) distorted (washed in Soxhlet for 8 h) and solid: $[\text{Fe}\{\text{M}(4\text{-}N\text{-MePy})\text{TPFP}\}]\text{-SiO}_3$ (IPG) no distorted (washed in Soxhlet for 48 h).

For the systems immobilised on supports containing propylimidazole groups (IPG, $\text{SiSO}_3^-(\text{IPG})$ and $\text{SiN}^+(\text{IPG})$), it is believed that the imidazole is coordinated to the iron(III). At this point is necessary to stand out that studies in homogeneous media of the $[\text{Fe}\{\text{M}(4\text{-}N\text{-MePy})\text{TPFP}\}]^{2+}$ with imidazole and OH^- , as ligand-models for propylimidazole and for silanol of the silica, respectively, showed that this Fe(III)porphyrin has a higher affinity by the OH^- compared with imidazole (stability constant $\text{Fe(III)porphyrin-OH} = 5.0 \times 10^7$ and $\text{Fe(III)porphyrin-imidazole} = 1.3 \times 10^7$) [8]. However, for supports containing propylimidazole groups, this coordinates rather to the iron(III), since the face-approximation of the Fe(III)porphyrin and silanol groups are hindered by the alkyl chain from propylimidazole. In flexible supports, as polymers, would be possible the coordination of the oxygen from the surface to the iron(III) competing with imidazole [21].

For the support-systems without imidazole (SiSO_3^- and SiN^+), it is thought that there is predominance of ionic binding with the periphery of the ionic Fe(III)porphyrins. Thus, the fifth site of coordination of the iron can be fulfilled by an atom from the support, by a molecule of solvent or by the counter ion

of the Fe(III)porphyrin before immobilisation, such as the Cl^- anion.

Studies concerning to identification of intermediates formed during the oxidation reaction by EPR were carried out by mixing a solution of Fe(III)porphyrin with H_2O_2 , in a molar ratio catalyst/oxidant 1:10 at ca. 4 and 15 K, but no intermediates species were detected. In this step, it was observed only a decreasing of the signals characteristic of high-spin iron(III).

3.3. Epoxidation of (Z)-cyclooctene by H_2O_2

3.3.1. Homogeneous system

The epoxidation of (Z)-cyclooctene with H_2O_2 catalysed by the Fe(III)porphyrins pentafluorophenyl-derivatives was initially studied since only one product *cis*-epoxycyclooctane is formed and, moreover, there is various reports in the literature using this substrate, allowing to compare efficiency and reactivity conferred by the catalytic systems presented here with that previously studied. The results obtained with the homogeneous catalysts are showed in Table 2 and were performed to help understanding the studies carried out with supported Fe(III)porphyrins, presented in Table 3.

Table 2

Epoxidation of (*Z*)-cyclooctene by H₂O₂ catalysed by homogeneous Fe(III)porphyrins

Catalyst	<i>cis</i> -Epoxyoctane (%) ^a
[Fe{M(4- <i>N</i> -MePy)TPFP}]Cl ₂	32
[Fe{M(4- <i>N</i> -MePy)TPFP}]Cl ₂ + imidazole	30
[Fe{M(4- <i>N</i> -MePy)TPFP}]Cl ₂ + 1-methylimidazole	34
[Fe{T(4- <i>N</i> -MePy)MPFP}](PF ₆) ₄	38
[Fe{M(3-SO ₃ P)TPFP}] ^b	12

^a Yields based on starting H₂O₂ after 24 h in DCM/ACN (1:1), magnetic stirring and room temperature. Amounts: Fe(III)porphyrin, 2.3 × 10⁻⁷ mol; alkene, 200 μl; H₂O₂, 1 μl (9.7 × 10⁻⁶ mol); imidazole or 1-methylimidazole, 2.3 × 10⁻⁷ mol; DCM/ACN (1:1), 800 μl.

^b E_{red}^0 Fe(III)/Fe(II) = -1.41 V vs. SCE [25]; +0.07 V for [Fe(TPFP)]Cl vs. SCE [24], both in DCM.

Table 3

Epoxidation of (*Z*)-cyclooctene by H₂O₂ catalysed by immobilised Fe(III)porphyrins

Catalyst	<i>cis</i> -Epoxyoctane (%) ^a
[Fe{M(4- <i>N</i> -MePy)TPFP}]-SiSO ₃	22
[Fe{M(4- <i>N</i> -MePy)TPFP}]-SiSO ₃ + imidazole	26
[Fe{M(4- <i>N</i> -MePy)TPFP}]-SiSO ₃ + 1-methylimidazole	24
[Fe{M(4- <i>N</i> -MePy)TPFP}]-IPG	11
[Fe{M(4- <i>N</i> -MePy)TPFP}]-SiSO ₃ (IPG)	52
[Fe{M(4- <i>N</i> -MePy)TPFP}]-SiO ₂	4
[Fe{T(4- <i>N</i> -MePy)MPFP}]-SiSO ₃	22
[Fe{T(4- <i>N</i> -MePy)MPFP}]-IPG	12
[Fe{T(4- <i>N</i> -MePy)MPFP}]-SiSO ₃ (IPG)	23
[Fe{T(4- <i>N</i> -MePy)MPFP}]-SiO ₂	3
[Fe{M(3-SO ₃ P)TPFP}]-SiN	13
[Fe{M(3-SO ₃ P)TPFP}]-IPG ^b	50
[Fe{M(3-SO ₃ P)TPFP}]-SiN (IPG)	11
[Fe{M(3-SO ₃ P)TPFP}]-SiO ₂ ^b	44

^a Yields based on starting H₂O₂ after 24 h in DCM/ACN (1:1), magnetic stirring and room temperature. An amount of 30 mg of supported catalyst (equivalent to 2.3 × 10⁻⁷ mol); alkene, 200 μl; H₂O₂, 1 μl (9.7 × 10⁻⁶ mol); imidazole or 1-methylimidazole, 2.3 × 10⁻⁷ mol; DCM/ACN (1:1), 800 μl.

^b Experiments filtering the solid catalysts before the end of the reaction and adding fresh oxidant, show catalytic activity only with [Fe{M(3-SO₃P)TPFP}]-IPG and [Fe{M(3-SO₃P)TPFP}]-SiO₂. Analyses by UV-VIS spectra indicated about 8% of leaching.

The results reveal that the yields of *cis*-epoxycyclooctane obtained with the homogeneous catalysts are lower than the reported for some synthetic Fe(III)porphyrins in aprotic solvent (DCM/ACN), which reached 65% of the epoxide with the system [Fe(TMP)]Cl/5-chloro-1-methylimidazole [22] and 62% of the same product with the catalyst [Fe(TPFP)]Cl [23]. In several and conclusive studies with homogeneous Fe(III)porphyrins as catalysts for epoxidation of alkenes by H₂O₂, Nam et al. [6,7,22] attribute the high yields of epoxide obtained from heterolytic cleavage of the O–O bond, favoured by the presence of electron-withdrawing substituents, on the metalloporphyrin, oxidant or axial ligand, which render more electron-deficient catalytic systems.

It has been reported that one of the most efficient homogeneous catalysts for epoxidation reactions by H₂O₂ is the [Fe(TPFP)]Cl [6,23], but the homogeneous pentafluorophenyl-derivatives here studied did not achieve the same efficiency, probably due to the presence of a different *meso*-substituent, 4-*N*-methylpyridyl or 3-sulfonatophenyl in comparison with the [Fe(TPFP)]Cl. It is described [6,24] that the pentafluorophenyl groups on the porphyrin ring shift the reduction potential to more positive values, increasing the electron-deficiency of the Fe(III)porphyrin, becoming the catalyst more efficient for heterolytic cleavage of H₂O₂. It was observed that the substitution of one pentafluorophenyl group of the [Fe(TPFP)]⁺ by one sulfonatophenyl to render the [Fe{M(3-SO₃P)TPFP}] shift dramatically the reduction potential to more negative values [25] ($E_{[\text{Fe}(\text{TPFP})]^+}^0 = +0.07$ V and $E_{[\text{Fe}\{\text{M}(3\text{-SO}_3\text{P})\text{TPFP}\}]^0} = -1.41$ V), decreasing the electron-deficiency, favouring the homolytic cleavage, which is responsible by low yields of epoxide.

3.3.2. Heterogeneous system

In order to study the effect of the solid support and its functional groups in the activation of H₂O₂ by Fe(III)porphyrins, the iron complexes immobilised on the various supports were used as catalysts in the epoxidation of (*Z*)-cyclooctene (Table 3).

The results presented in Table 3 show that three catalytic systems give good yields of *cis*-epoxycyclooctane in aprotic solvent: [Fe{M(3-SO₃P)TPFP}]-IPG, [Fe{M(3-SO₃P)TPFP}]-SiO₂ and [Fe{M(4-*N*-MePy)TPFP}]-SiSO₃ (IPG).

In the system $[\text{Fe}\{\text{M}(4\text{-}N\text{-MePy})\text{TPFP}\}]\text{-SiSO}_3$ (IPG) (52% of *cis*-epoxycyclooctane, Table 3) where the Fe(III)porphyrin contains only one perypheric positive charge, there is, probably, a higher amount of available sulfonatophenyl groups, that is, there is not predominance of ionic binding Fe(III)porphyrin-support via sulfonatophenyl, since is expected that the majority of Fe(III)porphyrin molecules are coordinated to the imidazol groups present on the support (Fig. 6A). On the other hand, in the system $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MPFP}\}]\text{-SiSO}_3$ (IPG) (23% of *cis*-epoxycyclooctane, Table 3) there is, probably, a lower quantity of available sulfonatophenyl groups, since the $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MPFP}\}]^{4+}$ has three perypheric positive charges favouring the ionic binding between the positive charges from Fe(III)porphyrin and the sulfonatophenyl groups

present on the support (Fig. 6B) and therefore, minimising the coordination of the imidazole groups present on the support to the Fe(III)porphyrin. In the system $[\text{Fe}\{\text{M}(4\text{-}N\text{-MePy})\text{TPFP}\}]\text{-IPG}$ (Fig. 6C), there is not the presence of sulfonatophenyl groups and the yield of epoxide is low (11% of *cis*-epoxycyclooctane, Table 3).

Studies using the catalytic systems based in the $[\text{Fe}\{\text{M}(3\text{-SO}_3\text{P})\text{TPFP}\}]$ are in agreement with the tendency observed above. Good yields of product, in the epoxidation by H_2O_2 , were obtained with $[\text{Fe}\{\text{M}(3\text{-SO}_3\text{P})\text{TPFP}\}]\text{-IPG}$ (50% of *cis*-epoxycyclooctane, Table 3) and $[\text{Fe}\{\text{M}(3\text{-SO}_3\text{P})\text{TPFP}\}]\text{-SiO}_2$ (44% of *cis*-epoxycyclooctane, Table 3), which are the systems where there are available sulfonatophenyl groups (Fig. 6D and E, respectively), due to the absence of positive charge on the support, necessary

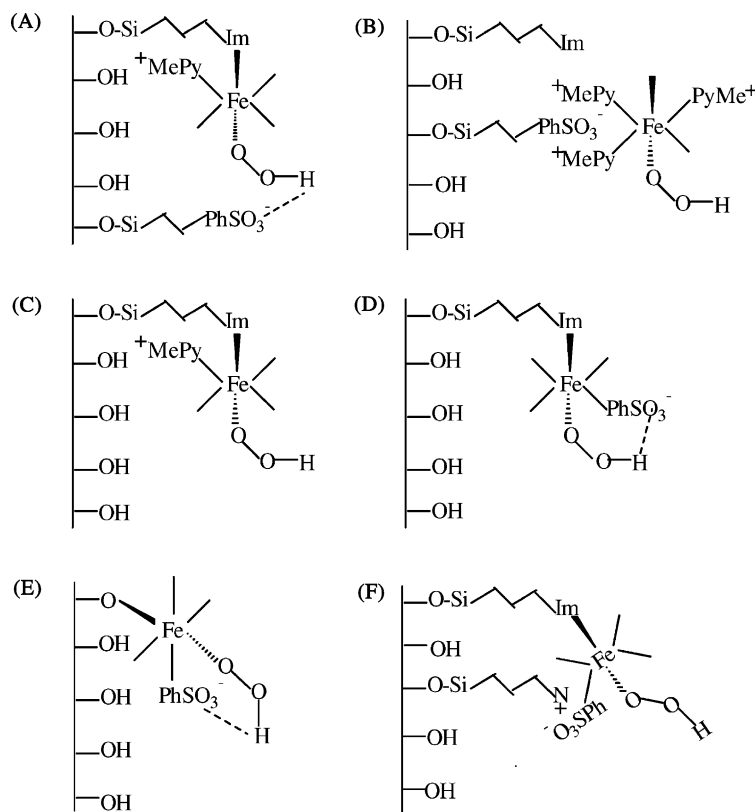


Fig. 6. Schematic representation of the interaction between Fe(III)porphyrin-hydroperoxo intermediate and solid supports showing the role of the available sulfonatophenyl groups and the polar environment supplied by the support: (A) $[\text{Fe}\{\text{M}(4\text{-}N\text{-MePy})\text{TPFP}\}]\text{-SiSO}_3$ (IPG); (B) $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MPFP}\}]\text{-SiSO}_3$ (IPG); (C) $[\text{Fe}\{\text{M}(4\text{-}N\text{-MePy})\text{TPFP}\}]\text{-IPG}$; (D) $[\text{Fe}\{\text{M}(3\text{-SO}_3\text{P})\text{TPFP}\}]\text{-IPG}$; (E) $[\text{Fe}\{\text{M}(3\text{-SO}_3\text{P})\text{TPFP}\}]\text{-SiO}_2$; (F) $[\text{Fe}\{\text{M}(3\text{-SO}_3\text{P})\text{TPFP}\}]\text{-SiN}$ (IPG).

to form ionic binding Fe(III)porphyrin-support via sulfonatophenyl, which occurs in the system [Fe{M(3-SO₃P)TPFP}]-SiN (IPG) (11% of *cis*-epoxycyclooctane, Table 3; Fig. 6F). However, the homogeneous catalyst [Fe{M(3-SO₃P)TPFP}] gives low yield of product (12% of *cis*-epoxycyclooctane, Table 2) although contains available sulfonatophenyl groups, due to the absence of linkage Fe(III)porphyrin-support. This result suggests that the more polar microenvironment provided by the silica-support is also essential to reach high yields of epoxide.

Then, it can be concluded that the polarity supplied by the support in association to available anionic sulfonatophenyl groups, without effective ionic binding Fe(III)porphyrin-support through these sulfonatophenyl residues, are the factors responsible by the raised yields of product in epoxidation reactions with H₂O₂.

In studies with peroxidases, it is reported [26] that the introduction of a charged residue promotes the polarisation of the O–O bond, facilitating the heterolysis and the consequent formation of the active oxidant [Fe^{IV}porp^{•+}(O)], which is the intermediate responsible by the oxidation. In this sense, the anionic sulfonatophenyl groups would be exerting this charge-effect through hydrogen bond with the terminal hydrogen of the Fe(III)porphyrin-hydroperoxo (Fig. 6A, D and E). Moreover, the polar microenvironment supplied by the silica-support helps in this polarisation of the O–O bond, which is necessary for the heterolysis.

The possibility of the sulfonatophenyl groups act as effective general acid–base catalyst, in analogy to “pull effect” in heme-peroxidases was excluded due to:

- (i) To act as a general base by abstracting a proton from the H₂O₂ and therefore facilitating the binding of H₂O₂ to the iron(III), the sulfonatophenyl groups (pK_a of the benzenesulfonic acid = 0.70) would need to have a pK_a value near to the H₂O₂ (pK_a = 11.6). As the pK_a of H₂O₂ is much higher than of the sulfonatophenyl, the latter is unable to act as a general base in this case.
- (ii) Moreover, in a previous paper studying the activation of H₂O₂ with Mn(III)porphyrins, our group concluded [13], by addition of imidazole ligand to the reaction, that functional groups (imidazole

ligand) when fixed on the support or on the metalloporphyrin are not capable to act as general acid–base catalyst, which is reported as essential condition for the heterolytic activation of H₂O₂ by Mn(III)porphyrins [27], in contrast to the reported for Fe(III)porphyrins. At this point, is right to assert that the factors that dominate the mechanisms of activation of the H₂O₂ by synthetic Fe(III) and Mn(III)porphyrins are certainly different. For Mn(III)porphyrins general acid–base catalysis is essential [27], as occurs in heme-peroxidases, but for Fe(III)porphyrins, it seems that redox potential effects in the catalytic systems are the key factor [6,7].

Recently, Nam et al. [6] elucidated the factors (presence of electron-withdrawing substituents able to shift the reduction potentials for more positive values) that manage the heterolysis of H₂O₂ in homogeneous catalysis using Fe(III)porphyrins. In this paper, we presented others efficient catalytic systems for epoxidation of alkenes by H₂O₂, in which the microenvironment, more polar and containing available sulfonatophenyl residues, provided by the system Fe(III)porphyrin-solid support, achieve the heterolytic activation of H₂O₂, resulting the active oxidant, [Fe^{IV}porp^{•+}(O)], for oxidation of organic compounds.

4. Conclusions

The activation of H₂O₂ by homogeneous Fe(III)porphyrins was recently elucidated by Nam et al. after a long-standing dichotomy, evidencing that the presence of electron-withdrawing substituents on the porphyrin ring or axial ligand promotes the heterolysis, leading to the formation of [Fe^{IV}porp^{•+}(O)], which is the active oxidant, in contrast to the classical “push–pull effect” which occurs in some heme-enzymes.

The present paper discusses the factors responsible by the heterolysis of H₂O₂ catalysed by grafted Fe(III)porphyrins on chemically modified silica gel suggesting that the presence of available sulfonatophenyl groups, when there is not ionic binding Fe(III)porphyrin-support via sulfonatophenyl, associated to a more polar microenvironment supplied by the silica-support, favour the heterolysis, leading to high

yields of the epoxide *cis*-epoxycyclooctane, through an effect of charge, able to polarise the O–O bond. Others effects in the activation of H₂O₂ as: a general acid–base, as happens with Mn(III)porphyrins, and more positive redox potentials, as occurs for homogeneous Fe(III)porphyrins, are not operating here.

These studies open the possibility to use the systems Fe(III)porphyrin-support containing free sulfonatophenyl residues and H₂O₂ in others oxidation reactions more specific, as degradation of pollutants or oxidation of drugs, since the H₂O₂ is a clear and cheap oxidant and Fe(III)porphyrin-support is a efficient, robust and recyclable catalyst.

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