

Catalytic Activity of Halogenated Iron Porphyrins in Alkene and Alkane Oxidations by Iodosylbenzene and Hydrogen Peroxide

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Uma ferro porfirina poli-clorada, $\text{Fe}(\text{P}(\text{Cl}_2)_2)\text{Cl}$, foi sintetizada e usada como catalisador em reações de oxidação de hidrocarbonetos por iodosilbenzeno e peróxido de hidrogênio, em solução e ancorado covalentemente na aminopropilsilica. Embora a $\text{Fe}(\text{P}(\text{Cl}_2)_2)\text{Cl}$ tenha mostrado a mesma eficiência da ferro porfirina precursora, $\text{Fe}(\text{P})\text{Cl}$, na epoxidação de alcenos, foi um catalisador mais eficiente na hidroxilação de alcanos por iodosilbenzeno, com preferência por carbonos secundários na oxidação do adamantano e primário na oxidação do pentano. Essa seletividade reflete o impedimento estérico da espécie ferro-oxo ou, alternativamente, a grande reatividade do oxidante ativo gerado da $\text{Fe}(\text{P}(\text{Cl}_2)_2)\text{Cl}$. A $\text{Fe}(\text{P}(\text{Cl}_2)_2)\text{Cl}$ ancorada mostrou baixa atividade catalítica quando comparada com o catalisador homogêneo e com a $\text{Fe}(\text{P})\text{Cl}$ ancorada. Peróxido de hidrogênio foi um oxidante pobre para este sistema. A excessiva substituição dos hidrogênios por grupos sacadores de elétrons na periferia do anel porfirínico dificulta a formação do intermediário ativo na reação de oxidação. O mecanismo alternativo de oxidação envolve a participação de radicais.

A poly-halogenated iron porphyrin, $\text{Fe}(\text{P}(\text{Cl}_2)_2)\text{Cl}$, has been synthesised and used as a catalyst in hydrocarbon oxidations by iodosylbenzene and hydrogen peroxide both in solution and covalently bound to aminopropylated silica. The poly-chlorinated iron porphyrin shows the same efficiency of the related $\text{Fe}(\text{P})\text{Cl}$, in the epoxidation of alkenes but higher efficiency in the hydroxylation of alkanes by iodosylbenzene, with increased preference for the oxidation of secondary carbon in adamantane and primary carbon in the oxidation of pentane. These selectivities may reflect the steric constraints around the oxo-iron species or, alternatively, it may arise from the greater reactivity of the active oxidant from $\text{Fe}(\text{P}(\text{Cl}_2)_2)\text{Cl}$. The supported iron(III) porphyrin showed lower activity as compared with the homogeneous analogue and the related supported $\text{Fe}(\text{P})\text{Cl}$. The poly-chlorinated iron porphyrin is a poor catalyst with hydrogen peroxide. Excessive substitution by electron withdrawing groups on the porphyrin periphery eventually prohibits the formation of the key intermediate in catalytic oxidations. The alternative oxidation mechanism could involve radical participation.

Keywords: poly-halogenated iron porphyrins, catalysis, supported catalysts, hydrocarbon oxidation

Introduction

About 25 years have passed since an iron(III) porphyrin, [iron(III) tetraphenylporphyrin] with iodosylbenzene was first used as a functional model for cytochrome P-450 for hydrocarbon oxidation.¹ The success of this pioneering work led to the synthesis of other metallo tetraarylporphyrins

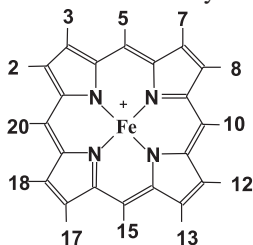
and the development of three generations of catalysts, which differ depending on the degree of substitution on the porphyrin ring.² Although the syntheses of the second and third generation porphyrins involve more expensive starting materials and are more time consuming, their improved robustness towards oxidative degradation and greater catalytic efficiency has led to detailed studies on oxidations catalyzed by these complexes.²⁻⁵ A further approach to

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improve these systems has involved anchoring the complexes onto solid supports with the aim of allowing catalyst recovery and reuse. In this way, immobilization of the catalyst might provide a way to reduce the overall cost of using these compounds in synthesis.^{6,7}

One aspect of our studies has been to develop robust metallo porphyrins for use with the clean oxidant hydrogen peroxide and, in particular, to use porphyrin ligands that can be readily attached to solid supports. This has led us to synthesize metallo tetraarylporphyrins containing one pentafluorophenyl group. The latter group is susceptible to nucleophilic substitution in the *para*-position, enabling immobilization by covalent binding to an amino-functionalized support.⁸

In this paper we report the catalytic results obtained with iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octachloroporphyrin, $\text{Fe}(\text{PCL}_8)\text{Cl}$ (Figure 1), in alkene and alkane oxidation by iodosylbenzene and hydrogen peroxide, both in homogeneous solution and when anchored onto aminopropylsilica and compare these results with those obtained with the analogue iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin, $\text{Fe}(\text{P})\text{Cl}$ (Figure 1). The $\text{Fe}(\text{PCL}_8)\text{Cl}$ catalyst has been synthesized by the method reported for the manganese analogue,⁸ and characterized by UV/Vis and electron paramagnetic resonance (EPR) spectroscopy. The interactions of $\text{Fe}(\text{PCL}_8)\text{Cl}$ and the related $\text{Fe}(\text{P})\text{Cl}$ (Figure 1), with imidazole have also been investigated to help understand the effect of the extra chlorine atoms on β -pyrrole carbons on the reactivity of the former catalyst.



$\text{Fe}(\text{P})\text{Cl}$	Iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin
$\text{Fe}(\text{PCL}_8)\text{Cl}$	Iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octachloroporphyrin

Figure 1. Iron(III) porphyrin catalysts.

Experimental

Instrumental methods

GC analyses were performed with two systems using nitrogen as the carrier gas: (i) a Varian Star 3400CX

chromatograph with a flame ionization detector using a DB-wax (1 mm film thickness) megabore column (30 m, i.d. 0.54 mm) and the results were analyzed on a Varian Workstation and (ii) a Hewlett Packard HP 6890 Series GC System, coupled to a flame ionization detector, using a capillary column [HP-INNOWAX, cross-linked poly(ethylene glycol), 30 m; i.d. 0.25 mm, film thickness 0.25 μm]. FAB⁺ mass spectra were obtained on a V. G. Analytical Autospec spectrometer using 4-nitrobenzyl alcohol as the matrix. UV-Vis spectra were obtained with a Hewlett-Packard 8452A diode array spectrometer. In the case of supported catalysts the spectra were recorded in a 2 mm path length quartz cell, using a mixture of the supported iron porphyrin and the support in a suspension in CCl_4 . EPR spectra were recorded with a Varian E-109 spectrometer, operating in the X band frequency (9 GHz) with a gain of 10^3 and 20 mW of microwave power and amplitude modulation of 4 gauss at liquid helium temperature.

Materials

Unless otherwise specified all compounds used were purchased from Aldrich, Merck or Reagen and were analytical grade. Methanol was refluxed over a magnesium and iodine mixture and after distillation stored over 4 Å molecular sieves. Iodosylbenzene was prepared in two steps from iodobenzene following the method described by Saltzmann and Sharefkin⁹ and the purity was shown to be 97%, determined by iodometric titration. The alkene (*Z*-cyclooctene) was purified by passing it through a short activated alumina column (Merck) immediately before use. Aminopropyl modified silica with 9% functionalization was purchased from Aldrich and used without further treatment. Silica gel used for column chromatography was Kiesegel 60 Merck (230-400 mesh). TLC used aluminium backed silica gel 60 F_{254} plates (Merck). The $\text{H}_2(\text{P})$, $\text{Zn}(\text{P})$ and $\text{Fe}(\text{P})\text{Cl}$ used in this study were synthesized previously.⁸

Synthesis of iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octachloroporphyrin, $\text{Fe}(\text{PCL}_8)\text{Cl}$

The free base 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octachloroporphyrin, $\text{H}_2(\text{PCL}_8)$, was prepared by chlorination of zinc 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin, $\text{Zn}(\text{P})$ (42.5 mg), with *N*-chlorosuccinimide (58.5 mg) followed by demetallation with trifluoroacetic acid, as described previously.⁸ $\text{H}_2(\text{PCL}_8)$ was

purified by chromatography on a silica column with hexane:dichloromethane (3:1) as eluent to give 40.3 mg (3.4×10^{-5} mol, 78% yield) of $H_2(PCI_8)$. UV-Visible (CH_2Cl_2): λ_{nm} ($\epsilon = \times 10^2$ L mol $^{-1}$ cm $^{-1}$): 444(210), 542(22), 628(4), 692(1). m/z (FAB $^+$): 1186.654 (100% - relative abundance), corresponding to $C_{44}H_{11}N_4F_5^{35}Cl_{11}^{37}Cl_3$.

Iron porphyrin, $Fe(PCI_8)Cl$, was obtained by metallation of the free ligand $H_2(PCI_8)$ 40.3 mg (3.4×10^{-5} mol) with iron(II) chloride dihydrate (55.3 mg 3.4×10^{-4} mol) in acetonitrile (25 mL) following the method described by Kadish *et al.*¹⁰ At the end of the reaction the solvent was removed under vacuum and the resulting iron porphyrin was purified by chromatography on a silica column. Elution with dichloromethane gave a small amount of free base porphyrin and methanol:dichloromethane (1:1) mixture gave the desired compound. Hydrogen chloride was bubbled through the solution to ensure that chloride was the axial ligand. TLC analysis on silica using methanol:dichloromethane as eluent confirmed the presence of $Fe(PCI_8)Cl$ as the only product. The solution was evaporated to dryness and 39.7 mg (3.2×10^{-5} mol) of $Fe(PCI_8)Cl$ were obtained (94% yield). UV-Visible (CH_2Cl_2), $Fe(PCI_8)Cl$: λ_{nm} ($\epsilon = \times 10^2$ L mol $^{-1}$ cm $^{-1}$): 394 (854); 440 (933). m/z (FAB $^+$): 1239.566 (100% - relative abundance) corresponding to $FeC_{44}H_9N_4F_5^{35}Cl_{11}^{37}Cl_3$.

Synthesis of supported catalyst

The supported catalyst was prepared through reaction of $Fe(PCI_8)Cl$ (0.184 mmol) with aminopropylated-silica (500 mg) in diglyme at 140 °C under argon for 6 h, following the method described of Mansuy *et al.*^{4,11} The resulting solid was filtered and extracted with CH_2Cl_2 (24 h) and then CH_3OH (24 h) by a Soxhlet procedure. The solid was then dried at 80 °C for 24 h. The iron porphyrin loading was obtained by elemental analysis (CNH) as 0.348 μ mol per g of silica. Soret band at 420 nm.

Alkene and alkane oxidations

Iodosylbenzene. Reactions were performed in air at room temperature in small conical vessels (3 mL) with magnetic stirring. The iron porphyrin or supported iron porphyrin (0.25 μ mol) was stirred with the desired substrate (500 μ mol) in dichloromethane (1.5 mL) before the oxidant (25 μ mol) was added. For reactions in the presence of co-catalyst (imidazole) the heterocyclic base was added as a solution in dichloromethane (see Table 7 for concentrations). The formation of reaction products was monitored by removing aliquots (0.5 μ L) for GC analysis. For some reactions the molar ratio of porphyrin (0.25

μ mol):oxidant:substrate was 1:25:6000. In order to evaluate the catalyst stability it was reused with five new charges (80 μ mol each) of PhIO added at 2 h intervals. The yields following each of the five consecutive additions were calculated from the total amount of oxidant used. For the supported catalyst, recycling was carried out after the fourth cycle of repeated iodosylbenzene addition by recovering the solid by filtration, washed with methanol, dried and reused it in a new reaction.

Hydrogen peroxide. The reactions were performed in a similar way to those described above. Iron porphyrin and co-catalyst were stirred in a dichloromethane : acetonitrile (1:1) solvent mixture. The substrate was then added and followed, a few minutes later, by hydrogen peroxide (30% m/v) using a micro syringe. The reaction was monitored by GC analysis. In the best conditions, the hydrogen peroxide was added in small portions (50 μ L) from a stock solution [0.125 mol L $^{-1}$ in dichloromethane:acetonitrile (1:1)] at 20 min intervals until the total amount of oxidant used reached 25 μ mol.

The H_2O_2 content after reactions was analysed by titration with a standard solution of potassium permanganate 3.75×10^{-2} mol L $^{-1}$.

Titration of $Fe(PCI_8)Cl$ and $Fe(P)Cl$ with imidazole

Titration of $Fe(PCI_8)Cl$ and $Fe(P)Cl$ with imidazole were carried out with iron porphyrin solutions in 0.2 mm path length cells at 24 °C. The reaction was monitored by following visible spectral changes of ~ 22.5 μ mol L $^{-1}$ solutions (CH_2Cl_2) of iron porphyrin upon addition of aliquots of ligand stock solution (0.17 mol L $^{-1}$) up to constant absorbance at 560 nm or 550 nm for $Fe(PCI_8)Cl$ and $Fe(P)Cl$, respectively. The equilibrium constant (β_n) and the axial ligand number (n) were calculated from the equation of Fleisher and Fine,¹² using absorbance data from $\lambda = 560$ or 550 nm:

$$\log [(A-A_0)/(A_{oo}-A)] = n \log [L]_{ad} + \log \beta_n$$

where A_0 is the absorbance of the initial iron porphyrin solution, A is the absorbance of the solution containing some concentration of the ligand and A_{oo} the absorbance of the solution containing iron porphyrin totally coordinated to the ligand.

This equation can be used under conditions where $\beta_n \leq 10^5$, since little ligand reacts with the iron porphyrin, and the amount of ligand added ($[L]_{ad}$) effectively equals the concentrations of the ligand in the equilibrium ($[L]$).¹³⁻¹⁶ By plotting $\log [(A - A_0) / (A_{oo} - A)]$ versus $\log [L]_{ad}$ the n and β_n values are obtained. In the case of $\beta_n \geq 10^5$, there is

a large iron porphyrin-ligand interaction and thus almost all the ligand added to the system reacts with the iron porphyrin. Therefore $[L]$ differs considerably from $[L_{ad}]$, and the plot $\log [(A - A_o) / (A_{oo} - A)]$ versus $\log [L_{ad}]$, has to be replaced by the plot of $\log [(A - A_o) / (A_{oo} - A)]$ versus $\log [L]$. $[L]$ can be calculated by following equation:^{16,17}

$$[L] = [L_{ad}] - [FeP] [(A - A_o) / (A_{oo} - A)]$$

Results and Discussion

Synthesis and characterization of homogeneous, $Fe(PCl_8)Cl$, and heterogeneous, $Si-Fe(PCl_8)Cl$, catalysts

The iron porphyrin $Fe(PCl_8)Cl$ was synthesized following the method reported previously for the manganese analogue⁸ and UV/Vis spectroscopy shows a Soret band at 440 nm. This is, as expected, red shifted when compared to the value for $Fe(P)Cl$ (416 nm) due to the eight electronegative chlorine atoms on the β -pyrrole carbons.^{18,19}

The iron porphyrin was immobilized onto aminopropylated silica to give a catalyst loading of 0.348 mmol g^{-1} of support. Normally, the iron porphyrins bearing pentafluorophenyl substituents are grafted by nucleophilic aromatic substitution of a *para*-fluorine.^{4,11} However, in this case one or more chlorine atoms on the β -pyrrole carbon could also be substituted leading to a catalyst immobilized through the pyrrole of the porphyrin ring, resulting in a strained macrocycle on the support. This could explain the blue shifted Soret band (420 nm) of $Si-Fe(PCl_8)Cl$ compared to the iron(III) porphyrin in dichloromethane (444 nm). Also the EPR spectrum of the solid catalyst indicates a distorted porphyrin macrocycle around the iron centre (Figure 2b). The EPR spectra confirm the presence of the iron(III) in both homogeneous and supported systems, through the characteristic signals of this species (Figure 2a and 2b). However, the g values and the morphology of the spectrum of homogeneous $Fe(PCl_8)Cl$ differ from those of the supported metallo porphyrin, reflecting the different symmetries of these two iron centers. In solution the iron is a high spin 5/2 system, with a g_x value of 5.635 and $g_{||}$ of 2.000 (Figure 2a). When the iron porphyrin is attached to the support, the EPR spectrum shows a more intense and asymmetric signal at $g=4.3$ attributed to a rhombic iron porphyrin structure (Figure 2b). This signal and a rhombic symmetry of the iron d orbitals has been found for other distorted species having an oxo or nitrene metal-pyrrole nitrogen bond, (P)Fe-X-N (X is O or N) reported by Mansuy *et al.*²⁰⁻²² and Groves and Watanabe.²³ The catalytic results also

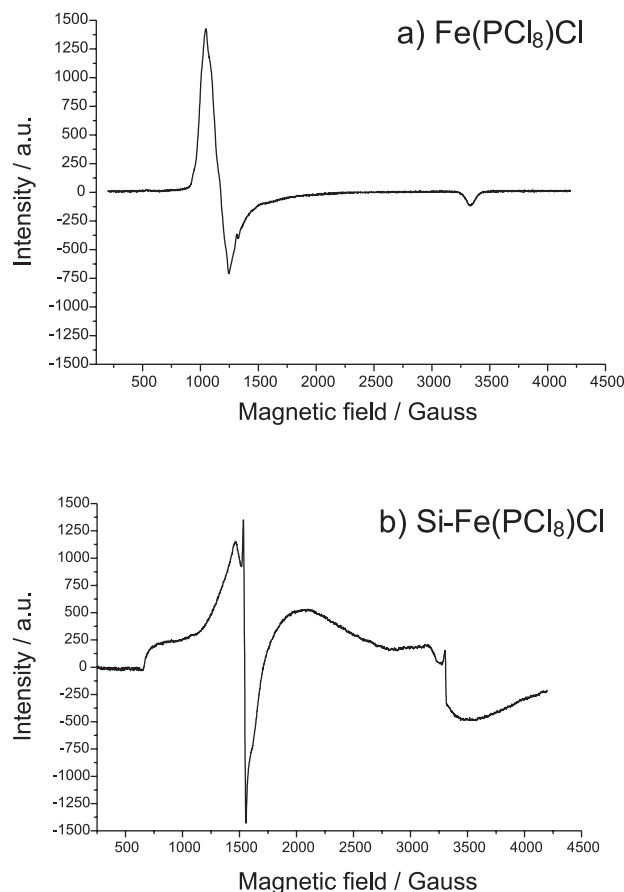


Figure 2. EPR spectra of $Fe^{III}(PCl_8)Cl$ in dichloromethane solution (a) and supported on aminopropylated silica (b). Both spectra were recorded at 4 K and gain 10^3 , 20 mW microwave power at 9.12 GHz and 10 G modulation.

reflect the high constraint around the iron center of anchored $Fe(PCl_8)Cl$.

With the aim of understanding the accessibility of the iron centre, the coordination of $Fe^{III}(PCl_8)Cl$ with axial ligands was investigated through spectrophotometric titration with imidazole. The parent iron porphyrin, $Fe(P)Cl$, was also studied for comparison to help evaluate the steric and electronic effects of β -chlorine substituents on the axial ligand coordination.

The Figures 3 and 4 show the changes in UV/Vis spectra during titration of both iron porphyrins and Table 1 shows the number of ligands (n) and the equilibrium

Table 1. Values for the number of coordinated Im ligand (n) and stability constants (β_n) for $Fe(P)Im$ complexes

Iron porphyrin	n	β_n (mol ⁻² L ²)	Reference
$Fe(TPPCl)Im_2$	2	4.8×10^5	27
$Fe(TDCPP)Im_2$	2	8.1×10^8	28
$Fe(P)Im_2$	2	2.74×10^6	this work
$Fe(PCl_8)Im$	1	$1.72 \times 10^{3*}$	this work

* Units mol⁻¹ L.

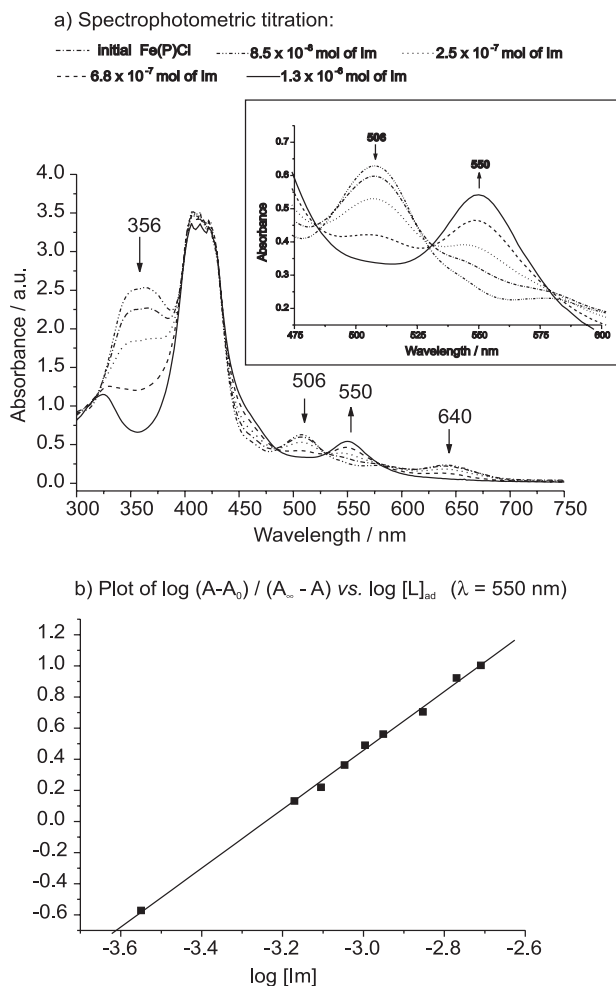


Figure 3. (a) Spectrophotometric titration of Fe(P)Cl in CH_2Cl_2 (700 mL, 3.57×10^{-4} mol L^{-1} , 2.5×10^{-7} mol) with imidazole (0.17 mol L^{-1} , CH_2Cl_2); (b) Plot of $\log(A-A_0)/A_\infty-A$ vs. $\log[L]$ ($\lambda = 550$ nm) used to calculate the number of coordinated Im (n) and stability constant (β_n) for Fe(P)(Im) $_n$ complexes.

constants (β_n) for both iron porphyrins. It can be observed that the addition of imidazole to a solution of Fe(P)Cl results in a decrease in the absorption at 506 and 640 nm and a simultaneous increase in the absorption at 550 nm (Figure 3a), due to the chlorine/imidazole ligands exchange with isosbestic points at 495, 525 and 590 nm (Figure 3). The overall equilibrium constant was determined as described in the experimental using the equation for $\beta_n \geq 10^5$. It is observed in Table 1 that Fe(P)Cl is able to coordinate with two imidazole ligands with overall equilibrium constant of 2.74×10^6 mol $^{-2}$ L 2 which is higher than Fe(TPP)Cl (TPP = 5,10,15,20-tetraphenylporphyrin) in the same solvent,^{23,25} but lower than Fe(TDCPP)Cl (TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin) in dichloroethane, as determined by Serra *et al.*²⁶

The addition of imidazole to a solution of Fe(PCl $_8$)Cl results in different spectral changes as shown in Figure 4a.

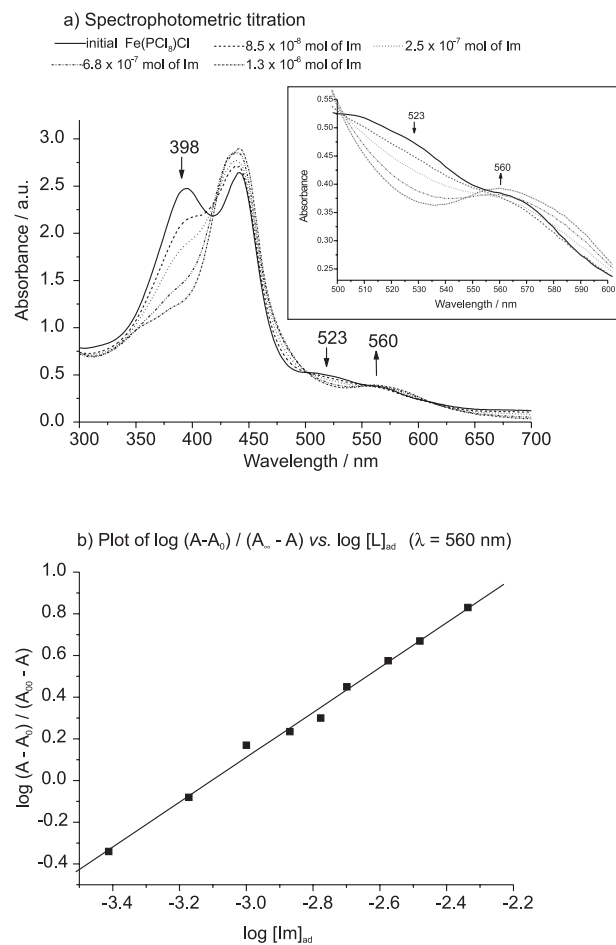


Figure 4. (a) Spectrophotometric titration of Fe(PCl $_8$)Cl in CH_2Cl_2 (700 mL, 3.57×10^{-4} mol L^{-1} , 2.5×10^{-7} mol) with imidazole (0.17 mol L^{-1} , CH_2Cl_2); (b) Plot of $\log(A-A_0)/A_\infty-A$ vs. $\log[L]_{\text{ad}}$ ($\lambda = 560$ nm) used to calculate the number of coordinated Im (n) and stability constants (β_n) for Fe(PCl $_8$)(Im) $_n$ complexes.

There is a decrease in the absorption at 523 nm and a simultaneous increase in the absorption at 560 nm with isosbestic points at 502, 555 and 618 nm. Only one imidazole ligand binds to the metal centre in Fe(PCl $_8$) $^+$ as estimated from the plot of Figure 4b and the equilibrium constant (β_1) was estimated as 1.72×10^3 mol $^{-1}$ L (Table 1).

It was expected that, if steric effects are absent, the more electron deficient porphyrin ring might give the metal a higher affinity for axial ligands as observed by Serra *et al.*²⁶ and Hatano *et al.*²⁷ However, in the case of Fe(PCl $_8$)Cl the extra steric hindrance and the distortion of the porphyrin ring provoked by the β -chlorine atoms dominates the electron-withdrawing effect of these substituents and prevents the binding of the second ligand to the metal, in the same way as observed by Balch *et al* for Fe(TMP) (TMP = 5,10,15,20-tetramesitylporphyrin) which coordinates with only one OH $^-$ ion.²⁸

Alkene and alkane oxidations by iodosylbenzene catalysed by Fe(PCl₈)Cl in homogeneous solution and anchored to aminopropylated silica

The catalytic activity of Fe(PCl₈)Cl for hydrocarbon oxidation in homogeneous solution was examined with cyclooctene, cyclohexane, adamantane and pentane (Tables 2 and 3) to evaluate the selectivity and accessibility of the iron centre in this robust catalyst compared to the related second generation iron porphyrin, Fe(P)Cl.

The reactions were carried out under two conditions: (i) FeP : PhIO : substrate ratio of 1 : 100 : 2000 which are defined as the standard conditions in our laboratory and allows comparison with many other iron porphyrin systems and (ii) FeP : PhIO : substrate ratio of 1 : 25 : 6000, which are optimized conditions since the lower oxidant and higher substrate relative concentrations favors substrate oxidation over unwanted competitive reactions.

For cyclooctene and cyclohexane oxidations, the results from Table 2, do not show an improvement over Fe(P)Cl (entries 1, 2 and 4, 5) despite the increased electrophilicity of the macrocycle due to the presence of the additional electron-withdrawing Cl groups. A similar result was also obtained for the analogous manganese porphyrin system.⁸ These results are probably related to the structure of the reactive intermediate to which the

porphyrin has to be oxidized during catalysis. Excessive substitution by electron-withdrawing groups on the porphyrin periphery may prohibit the formation of the key oxoiron(IV) porphyrin π -cation radical, O=Fe^{IV}P⁺, as reported by Gross and Simkhovich for similar second and third iron porphyrins.⁵ Mansuy *et al.*³¹ observed that with very electron-deficient porphyrins, O=Fe^{IV}P⁺ is not favoured as the π -cation radical cannot be stabilised by the porphyrin ring and the active oxidant behaves more as a radical species, \cdot O-Fe^{IV}P.

The best catalytic results were obtained in optimised conditions (Table 2, entries 3 and 6) since the lower oxidant and higher substrate relative concentrations favour substrate oxidation over unwanted competitive reactions.

In contrast to cyclooctene and cyclohexane, for adamantane, the catalytic activity of Fe(PCl₈)Cl was higher than that for Fe(P)Cl (Table 3 - entries 1 and 2). In the adamantane oxidation, the robust iron porphyrin Fe(PCl₈)Cl shows a higher preference for 2-position (C^{sec}) over 1-position (C^{tert}) compared to Fe(P)Cl, with statistically corrected selectivity C^{tert}/C^{sec} of 4 and 14 respectively for both iron porphyrins. This difference in selectivity may reflect the difference in steric constraints around the oxo-iron species. Alternatively it may arise from the greater reactivity of the active oxidant from Fe(PCl₈)Cl which results in an earlier transition state in the oxidation step.

Table 2. Cyclooctene and cyclohexane oxidations by PhIO catalysed by Fe(PCl₈)Cl and Fe(P)Cl

Entry	Catalyst	Substrate	Product yields (%) ^a			Total
			Epoxide	ol	one ^b	
1	Fe(PCl ₈)Cl	Cyclooctene	85	—	—	85
2	Fe(P)Cl ^c	Cyclooctene	82	—	—	82
3	Fe(PCl ₈)Cl ^d	Cyclooctene	100	—	—	100
4	Fe(PCl ₈)Cl	Cyclohexane	—	45	—	45
5	Fe(P)Cl ^c	Cyclohexane	—	42	3	48
6	Fe(PCl ₈)Cl ^d	Cyclohexane	—	76	9	94

Fe(PCl₈P)Cl and Fe(P)Cl (0.25 μ mol) at 25 °C; FeP : PhIO : substrate ratio of 1 : 100 : 2000; solvent : 1.5 mL of dichloroethane; ol = cyclohexanol; one = cyclohexanone; epoxide = cyclooctenoxide; ^a yields related to PhIO; ^b PhIO conversion, ketone yields assume the consumption of two PhIO; ^c from ref. 29; ^d Fe(PCl₈P)Cl (0.25 μ mol) : PhIO : substrate (1:25: 6000).

Table 3. Adamantane and pentane oxidations by PhIO catalysed by Fe(PCl₈)Cl and Fe(P)Cl

Entry	Catalyst	Substrate	Product Yields (%) ^a				Total ^c
			1-ol	2-ol	3-ol	one ^b	
1	Fe(PCl ₈)Cl	Adamantane	54	38	—	3	98
2	Fe(P)Cl ^d	Adamantane	69	15	—	<1	84
3	Fe(PCl ₈)Cl	Pentane	4	22	11	5	47
4	Fe(PCl ₈)Cl ^e	Pentane	13	36	15	9	82
5	Fe(P)Cl	Pentane	<1	20	12	<1	32
6	Fe(P)Cl ^e	Pentane	2	28	15	4	53

Fe(PCl₈)Cl and Fe(P)Cl (0.25 μ mol) at 25 °C; FeP : PhIO : substrate ratio of 1 : 100 : 2000; solvent : 1.5 mL of dichloroethane; 1-ol, 2-ol, 3-ol = 1-,2-,3-alcohol; ^a yields related to PhIO; ^b overall ketones; ^c PhIO conversion, ketone yields assume the consumption of two PhIO; ^d from ref. 29; ^e Fe(PCl₈P)Cl or Fe(P)Cl (0.25 μ mol) : PhIO : substrate (1:25: 6000) .

Homogeneous $\text{Fe}(\text{PCl}_8)\text{Cl}$ is also very effective at hydroxylating aliphatic C-H bonds in linear alkanes such as pentane, and is better than $\text{Fe}(\text{P})\text{Cl}$ (Table 3 entries 3 and 4 vs. 5 and 6). The regioselectivity of pentane oxidation also reflects the steric hindrance around the catalytic centre, favouring the more accessible but less reactive position 1. The 2-ol/3-ol ratio is 2 in this case which is lower than that observed for $\text{Fe}(\text{TDCPP})\text{Cl}$, a second generation catalyst (2-ol/3-ol of 3.7) and similar to that observed for the analogue $\text{Fe}(\text{TDCCl}_8\text{PP})\text{Cl}$ [$\text{TDCCl}_8\text{PP} = 5,10,15,20$ -tetrakis(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octachloroporphyrin] (2-ol/3-ol of 2.1) reported by Mansuy *et al.*³⁰

These authors explained the selectivity of the oxidation in terms of the active oxidant having a more radical structure as is $\cdot\text{O-Fe}^{\text{IV}}\text{P}$.³¹

No degradation of the catalyst was observed through UV/Vis spectroscopy, even when $\text{Fe}(\text{PCl}_8)\text{Cl}$ was used in homogeneous reactions after five additions of the oxidant (each with catalyst:oxidant, 1: ~320, added at 2 h intervals,

Table 4. Epoxidation of cyclooctene with repeated addition of PhIO catalysed by $\text{Fe}(\text{PCl}_8)\text{Cl}$ and $\text{Si-Fe}(\text{PCl}_8)\text{Cl}$, in dichloromethane

Addition of PhIO	Epoxide yield (%) ^a	
	(homogeneous solution)	($\text{Si-Fe}(\text{PCl}_8)\text{Cl}$)
1	85	30
2	90	28
3	82	31
4	78	27
5	79	27 ^b

$\text{Fe}(\text{PCl}_8)\text{Cl}$ (0.25 μmol); PhIO (80 μmol per addition); cyclooctene (500 μmol); CH_2Cl_2 1.5 mL; ^a based on PhIO; ^b the supported catalyst isolated from reaction 4 was washed with methanol and dried at low pressure before this reaction.

Table 5. Product yields from the oxidation of hydrocarbons by PhIO catalysed by iron(III) porphyrins anchored to aminopropylated silica

Entry	Substrate	Catalyst	Products Yield (%) ^a			Total ^b
			Epoxide	ol	one	
1	Cyclooctene	$\text{Si-Fe}(\text{PCl}_8)$	30	—	—	30
2	Cyclooctene	$\text{Si-Fe}(\text{P})\text{Cl}$ ^c	82	—	—	82
3	Cyclohexane	$\text{Si-Fe}(\text{PCl}_8)$	—	2	2	6
4	Cyclohexane	$\text{Si-Fe}(\text{P})\text{Cl}$ ^c	—	9	12	33

$\text{Si-Fe}(\text{PCl}_8\text{P})\text{Cl}$ and $\text{Si-Fe}(\text{P})\text{Cl}$ (0.25 μmol) at 25 °C; ol = cyclohexanol; one = cyclohexanone; 1.5 mL of dichloroethane; ^a yields related to PhIO; ^b PhIO conversion, ketone yields assume the consumption of two PhIO; ^c from ref 29.

Table 6. Product yields from the oxidation of adamantane by PhIO catalysed by iron(III) porphyrins anchored to aminopropylated silica

Entry	Substrate	Catalyst	Product yields ^a (%)			Total ^b
			1 - ol	2 - ol	2 - one	
1	Adamantane	$\text{Si-Fe}(\text{PCl}_8)$	29	12	5	51
2	Adamantane	$\text{Si-Fe}(\text{P})\text{Cl}$ ^c	52	19	4	79

$\text{Si-Fe}(\text{PCl}_8\text{P})\text{Cl}$ and $\text{Si-Fe}(\text{P})\text{Cl}$ (0.25 μmol) at 25 °C; 1-ol (1 - adamantanol); 2-ol (2 - adamantanol); (2-one) 2-adamantanone; 1.5 mL of dichloroethane; ^a yields related to PhIO; ^b PhIO conversion, ketone yields assume the consumption of two PhIO; ^c from ref 29.

Table 4), giving a total of 1323 catalytic turnovers. This result confirmed the stability of $\text{Fe}(\text{PCl}_8)\text{Cl}$.

The supported poly-halogenated iron porphyrin was less efficient as a catalyst than the homogeneous analogue and supported $\text{Fe}(\text{P})\text{Cl}$ (Table 5 and 6). This is probably related to the increase in steric hindrance of the catalytic site on the support that restricts the access of the oxidant and substrate to the iron center, which is already disfavoured due to the high polarity of the solid surface. The high distortion of the iron(III) porphyrin symmetry brought about by the solid support and confirmed by the EPR spectrum of this material (Figure 2b), indicates that the solid behave as another very bulky group which reduces the activity of the catalyst.

Although immobilised catalyst have lower activity compared to solution, they can be recycled giving a reproducible yield of cyclooctene epoxide (Table 4, entry 5), and a total turnover number of 458. Furthermore, in future development the supported catalyst were to be used in synthesis it can be remove by filtration at the end of the reaction, thus aiding purification of products.

Alkene and alkane oxidations by hydrogen peroxide catalysed by $\text{Fe}(\text{PCl}_8)\text{Cl}$ in homogeneous solution and anchored to aminopropylated silica

The biologically important oxidant hydrogen peroxide can also be used as a source of oxygen in catalytic oxidations of hydrocarbons catalysed by synthetic metallo porphyrins. This is an attractive process because hydrogen peroxide is cheap and considered to be an environmentally clean oxidant producing water and oxygen as the only by-products.^{33,34} Manganese porphyrins have been reported as

Table 7. Oxidation of cyclooctene and cyclohexane by hydrogen peroxide catalysed by Fe(PCl₈)Cl

Entry	Substrate	conditions	Products yields (%) ^a			
			ol	one	epoxide	Total
1	cyclooctene	One aliquot of H ₂ O ₂	—	—	< 1	< 1
2	cyclooctene	Slow addition of 4 aliquots of H ₂ O ₂	—	—	24	24
3 ^b	cyclooctene	Slow addition of 4 aliquots of H ₂ O ₂ ; Im	—	—	11	11
4	cyclohexane	One aliquot of H ₂ O ₂	< 1	< 1	—	< 1
5	cyclohexane	Slow addition of 4 aliquots of H ₂ O ₂	< 1	< 1	—	< 1
6 ^b	cyclohexane	Slow additions in 4 aliquots of H ₂ O ₂ ; Im	9	11	—	20

Fe(PCl₈P)Cl (0.25 μmol) at 25 °C; 1.5 mL of CH₂Cl₂:CH₃CN (1:1); ol = cyclohexanol; one = cyclohexanone; epoxide = cyclooctenoxide; ^a yields related to H₂O₂; ^b ratio of catalyst : H₂O₂ : Im (imidazole) : substrate (1 : 100 : 100 : 2000).

better catalysts than iron porphyrins for these oxidations with H₂O₂,² due to the high catalase activity of the iron porphyrins which leads to loss of hydrogen peroxide to give water and dioxygen.⁶ However, Nam *et al.*^{35, 36} have shown that electron-deficient iron porphyrins with hydrogen peroxide are capable of efficient transfer of oxygen to alkenes and alkanes to give oxygenated products. The precise nature of the active species in these systems which appears to be depended on the substituents and axial ligand of the iron porphyrin may be an oxoiron(IV) porphyrin π -cation radical or an iron-peroxo species.^{37,38}

The efficiency of Fe(PCl₈)Cl to catalyse alkene and alkane oxidation with hydrogen peroxide was investigated in solution using cyclooctene and cyclohexane as substrates, in standard reaction conditions as defined for iodosylbenzene, which are similar of those used by Nam *et al.*³⁶ In order to favour the heterolytic over the homolytic cleavage of O—O bond to give the high valent oxoiron(IV) porphyrin π -cation radical the reactions were also carried out in the presence of imidazole and by the slow addition of the oxidant in small aliquots as suggested by Nam *et al.*³⁶, and others.³⁹⁻⁴² The results show that Fe(PCl₈)Cl is an ineffective catalyst for the oxidation of cyclooctene and cyclohexane if the oxidant is added in one aliquot at the start of the reaction (Table 7, entries 1 and 4). UV/Vis analysis of the solution after reaction showed that under these conditions the catalyst was partially or completely destroyed. This suggests that the hydrogen peroxide is homolytically cleaved to generate the potent oxidizing radical, HO·, in a Fenton-type reaction and these attacks and destroys the porphyrin ring. When the reactions were repeated with the same amount of oxidant, added slowly in 4 aliquots, cyclooctene gave 24 % of epoxide (Table 7, entry 2) but no oxidation products were detected from cyclohexane (Table 7, entry 5). Monitoring the hydrogen peroxide concentration after reaction showed that more than 50 % of unreacted oxidant was still present at the end of cyclooctene oxidation indicating that catalyst

destruction (as confirmed by UV/Vis spectrum) may in part be responsible for the low epoxide yields. The presence of imidazole as co-catalyst led to a decrease in the epoxide yield (Table 7, entry 3). Only one imidazole binds to metal centre in Fe(PCl₈), as noted from the titration data with this ligand, and the oxidant interaction with the iron centre would occur at the second axial position of the iron centre. However, this interaction is probably prevented by the greater steric hindrance around this axial site. This results in a competition between imidazole and hydrogen peroxide to bind to the iron porphyrin. For the cyclohexane, the presence of imidazole led to an increasing in product yields (Table 7 - entry 6). However, the low selectivity for hydroxylation indicates radical participation in this case.

A more detailed study of the intermediate species in these systems using UV/Vis and EPR spectroscopy is under investigation in our laboratory in order to better understand these mechanism oxidations.

Conclusions

The synthesis and use of the new third generation iron porphyrin Fe(PCl₈)Cl, iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octachloroporphyrin as a catalyst in hydrocarbon oxidation is described and compared with its second generation analogue Fe(P)Cl, iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)-porphyrin.

Although Fe(PCl₈)Cl, is no more efficient for alkane epoxidation than analogues, Fe(P)Cl, it is a superior catalyst for alkane hydroxylation. In alkane oxidation Fe(PCl₈)Cl shows a greater selectivity than Fe(P)Cl for less reacting / less hindered C—H bonds arising from a more reactive / less hindered active oxidant.

When covalently bound to aminopropylated silica, Fe(PCl₈)Cl is less efficient as a catalyst than in solution, although it can readily be recovered and reused.

When hydrogen peroxide is used, in place of PhIO, fast

addition of the oxidant favours radical destruction of the catalyst. With more controlled addition of hydrogen peroxide, moderate yields of hydrocarbon oxidation are obtained.

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