Factors which affect the catalytic activity of iron(III) meso tetrakis(2,6-dichlorophenyl) porphyrin chloride in homogeneous system

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Abstract

An optimization study of the reaction conditions of Fe(TDCPP)Cl when it is used as catalyst in the hydroxylation of cyclohexane by iodosylbenzene (PhIO) has been carried out. It was found that Fe(TDCPP)Cl follows the classical PhIO mechanism described for Fe(TPP)Cl, which involves the monomeric active species $Fe^{IV}(O)P^{+\cdot}$ (I). In the optimized condition ([Fe(TDCPP) = 3.0×10^{-4} mol l^{-1} in 1,2-dichloroethane (DCE); ultrasound stirring at 0°C; PhIO/FeP molar ratio = 100), this FeP led to a yield of cyclohexanol (C-ol) of 96% and a turnover number of 96. Therefore, Fe(TDCPP)Cl may be considered a good biomimetic model and a very stable, resistant and selective catalyst, which yields C-ol as the sole product. DCE showed to be a better solvent than dichloromethane (DCM), 1 DCE:1 MeOH mixture or acetonitrile (ACN). Since the $Fe^{IV}(O)P^{+\cdot}$ is capable of abstracting hydrogen atom from DCM, MeOH or ACN, the solvent competes with the substrate. Presence of O_2 lowers the yield of C-ol, as it can further oxidize this alcohol to carboxylic acid in the presence of radicals. Presence of H_2O also causes a decrease in the yield, since it converts the active species I into $Fe^{IV}(OH)P$, which cannot oxidize cyclohexane. Addition of excess imidazole or OH^- to the system results in a decrease in the yield of C-ol, due to the formation of the hexacoordinated complexes $Fe(TDCPP)Im_2^+$ (low-spin, $\beta_2 = 2.5 \times 10^8$ mol^{-2} l^2) and $Fe(TDCPP)(OH)_2^-$ (high-spin, $\beta_2 = 6.3 \times 10^7$ mol^{-2} l^2). The formation of both $Fe(TDCPP)Im_2^+$ and $Fe(TDCPP)(OH)_2^-$ complexes were confirmed by EPR studies. The catalytic activities of Fe(TDCPP)Cl and Fe(TFPP)Cl were compared. The unusually high yields of C-ol with Fe(TFPP)Cl obtained when ultrasound, DCM and O_2 atmosphere were used, suggest that a parallel mechanism involving the μ-oxo dimer form, O_2 and radicals may also be occurring with this FeP, besides the PhIO mechanism.

Keywords: Cyclohexane; Iron(III)porphyrin; Oxidation; Porphyrin; 2,6-Dichlorophenylporphyrin; Pentafluorophenylporphyrin; Homogeneous catalysis

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1. Introduction

Saturated hydrocarbons are among the main products of the petrochemical industry and are largely used as solvents and combustibles. However, its use as raw material is still a particularly difficult problem in fine and industrial chemistry, due to the inertness of C–H bonds [1], [2](a), [3]. In industry, there is a special interest in the oxidation of cyclohexane, since its product, cyclohexanol and cyclohexanone are used in the production of the textile fibres Nylon 6 and Nylon 6.6 [3]. Nevertheless, the industrial process used to make such products employs high pressures (≈ 15 bar) and temperatures ($\approx 150°C$) and Co^{II} salts as catalysts, leading to a yield of only 4% for the desired products and a selectivity of 80%. The remaining 20% consists of carboxylic acids originating from further oxidation of the cyclohexanol and cyclohexanone themselves. Therefore, the finding of catalysts capable of oxidizing organic compounds selectively and efficiently, under mild conditions, is desirable.

Ubiquitous cytochrome P-450 dependent monooxygenases catalyse the monooxygenation of a wide variety of organic substrates, using O_2 and NADPH in living organisms or single oxygen donors such as iodosylarenes in vitro [2]. Metalloporphyrins, which are analogous to the prosthetic group of these monooxygenases, have been extensively studied as chemical models of these enzymes over the past twenty years [1–10]. The first system described by Groves et al. [7](a,b), which was based on the very simple catalyst Fe(TPP)Cl (Fig. 1) and iodosylbenzene (PhIO) in the oxidation of cyclohexane, was able, qualitatively, to mimic all the reactions of the short catalytic cycle of P-450. However, this catalyst underwent fast oxidative degradation under the oxidizing conditions utilized. More stable and efficient catalysts were obtained with the introduction of electron-withdrawing substituents in the meso-aryl positions of the tetraphenylporphyrin. Examples of catalysts of this second generation of metalloporphyrins are
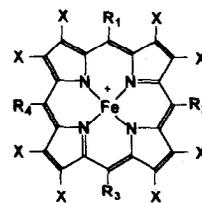
Ironporphyrin				
Fe(TPP)⁺	$R_1 = R_2 = R_3 = R_4 =$	Ph	X=	H
Fe(TDCPP)⁺		2,6 diClPh		H
Fe(TNPP)⁺		o-NO₂Ph		H
Fe(TFPP)⁺		C₆F₅		H
Fe(TFPPBr₈P)⁺		C₆F₅		Br
Fe(TDCPCl₈P)⁺		2,6 diCl Ph		Cl
Fe(MNPP)⁺	$R_1 = o$-NO₂Ph	$R_2 = R_3 = R_4 = Ph$		H

Fig. 1. Structure of ironporphyrins.

Fe(TDCPP)Cl and Fe(TFPP)Cl (Fig. 1) [9](a), [10]. More recently, even more robust polyhalogenated metalloporphyrins involving electron-withdrawing substituents on the β-pyrrole positions have been described in the literature [9](b), constituting the third generation of metalloporphyrins. This is the case of Fe(TDCPCl$_8$P)Cl (Fig. 1) [2](e).

Iron(III) meso tetrakis(2,6-dichlorophenyl)porphyrin chloride (Fe(TDCPP)Cl) was first synthesized by Traylor et al. [9](a) and it efficiently and selectively hydroxylated cyclohexane (C-ol = 73%) with pentafluoroiodosylbenzene as the oxidant. Since then, this FeP has been frequently employed as a cytochrome P-450 model and many studies to elucidate the reaction intermediates and its structure have been carried out [9](c,d), [11–16]. There are also several reports on its catalytic activity in the epoxidation of cyclohexene [9](a–c), cyclooctene [17](a), cis-stilbene [12], norbornene [9](a,c,f), styrene [18] and adamantylideneadamantane [9](c), oxidation of androgens [19], hydroxylation of cyclohexane [9](a), adamantane [1](c), heptane [2]e and norbornane [9](g), photooxidation of alkanes and cycloalkanes [2](a,f,g). There are also articles on the catalytic activity of Fe(TDCPP)Cl supported on (1-imidazolyl)methylated polystyrene,

poly-4-vinylpyridine, imidazole propyl gel (IPG) and silica modified with pyridine groups [4,17](a,b). Our group has already reported works on the catalytic activity of Fe(TDCPP)Cl both in solution or supported on IPG, in the hydroxylation of cyclohexane by PhIO [20](a). In its reaction with iodosylbenzene, the active intermediate species iron-oxo(IV) porphyrin π-cation radical $Fe^{IV}(O)P^{+\cdot}$ (I) has been established [15](b). This species is analogous to compound I of the horseradish peroxidase [6]. However, despite all these works, no systematic study of this FeP as catalyst in homogeneous system has been reported. In fact, few studies on the optimization of conditions of reactions catalyzed by FeP appear in the literature. The best-known one is a report by Nappa and Tolman [8], which describes a systematic study of the catalytic activity of Fe(TPP)Cl in the oxidation of hydrocarbons by PhIO. This work has been of great importance since it presents a postulated mechanism for the hydroxylation reactions catalysed by FeP in the presence of PhIO (Fig. 2), which has served as a guide in the catalytic studies of various FeP.

Using Fe(TDCPP)Cl, which has been recognized as a typical and adequate biomimetic system in these hydroxylation reactions, we present in this paper a systematic study of how factors such as solvent type, catalyst concentration, stirring method, temperature, presence of dioxygen, presence of H_2O, reaction time, PhIO/FeP molar ratio and addition of imidazole or OH^- to the reaction mixture affect the catalytic activity of this FeP in the oxidation of

$$PhIO + Fe(III)P \xrightarrow{1} PhI + Fe(IV)(O)P^+$$

$$Fe(IV)(O)P^+ + \text{⟨⟩} \xrightarrow{2} Fe(III)P + \text{⟨⟩–OH}$$

$$Fe(IV)(O)P^+ + PhIO \xrightarrow{3} Fe(III)P + PhIO_2$$

$$Fe(IV)(O)P^+ + Fe(III)P \xrightarrow{4} \text{degraded catalyst}$$

where: Fe(III)P = iron (III)porphyrin, Fe(IV)(O)P⁺ = catalytic species I,
PhIO₂ = iodoxibenzene, PhIO =iodosylbenzene, PhI =iodobenzene

Fig. 2. Mechanism for the hydroxylation of cyclohexane by PhIO and iron(III)porphyrin and possible competitive reactions [8].

cyclohexane by PhIO. We will also draw a parallel discussion comparing the catalytic activities of Fe(TDCPP)Cl and Fe(TFPP)Cl in order to show that, whereas with the former the evidences are that it only follows the classical PhIO mechanism described by Nappa and Tolman [8], the unusual high yields of cyclohexanol attained with the latter have led us to propose that besides the PhIO mechanism, a parallel process involving dioxygen and $Fe^{II}(TFPP)$ species may be also occurring. We have chosen cyclohexane as substrate because the great inertness of its C–H bonds provides information about the nature, reactivity and stability of the active species I $Fe^{IV}(O)(TDCPP)^{+\cdot}$ and about the factors that affect the formation of this species such as the presence of axial ligands like imidazole and OH^-. Moreover, the inertness of the cyclohexane C–H bonds led us to realize that competitive reactions for the active species I take place between the solvent and cyclohexane in these systems, which are difficult to notice with other more reactive substrates like olefins or with less stable catalysts like Fe(TPP)Cl.

2. Experimental

2.1. Materials

Dichloromethane (DCM) and dichloroethane (DCE) were distilled and stored on 4A molecular sieves. Acetonitrile (ACN) and methanol (MeOH) were stored on 3A molecular sieves. N,N-dimethylformamide (DMF) was stirred over KOH at room temperature overnight, decanted and then distilled at reduced pressure. Cyclohexane purity was determined by gas chromatographic analysis.

2.1.1. Iodosylbenzene (PhIO)

Iodosylbenzene was obtained through the hydrolysis of iodosylbenzene diacetate [21]. Samples were stored in a freezer and the purity was checked every six months by iodometric assay.
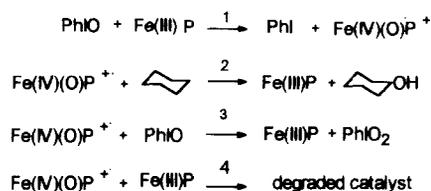
2.1.2. Iron(III) meso tetrakis(2,6-dichlorophenylporphyrin) chloride (Fe(TDCPP)Cl)

TDCPPH$_2$ was purchased from Midcentury. Iron insertion into the free base was carried out adapting the method described by Adler et al. [22]. DMF was removed by rotary evaporator and the obtained Fe(TDCPP)Br (λ_{max} (DMF) 392, 418, 508, 570, 642 nm) was washed with water, which converted it to Fe(TDCPP)OH (λ_{max} (DCM) 334, 414, 576 nm). The attained FePOH was purified by silica column chromatography, using a mixture of 5% MeOH in DCM as eluent. The DCM solution of Fe(TDCPP)OH was bubbled through with hydrogen chloride gas, which converted it to Fe(TDCPP)Cl (λ_{max} (DCM) 342, 416, 506, 578, 644 nm). The UV–Vis spectra were recorded on a Hewlett Packard 8452 Diode Array UV–Vis spectrophotometer.

2.2. Oxidation reactions

The reactions were carried out in a 2 ml vial with an open top screw cap containing a silicone teflon coated septum. In a standard reaction, 200 μl of FeP solution in the desired solvent and 200 μl of cyclohexane were added to the vial containing iodosylbenzene (≈ 0.50–2.50 mg) under argon atmosphere and the flask was adapted in a dark chamber. The mixture was stirred either by magnetic stirring or ultrasound (ultrasound laboratory cleaner Minison–Thornton, 40 W, 50–60 Hz), at room temperature or at 0°C (with the aid of an ice bath). The reaction was quenched after the desired time by adding 25 μl of saturated sodium bisulfite solution in ACN and 25 μl of saturated borax solution in MeOH to prevent further oxidation.

To study the effect of the addition of imidazole, 3.4; 6.8 or 34 μl of an imidazole solution in DCE (5.98×10^{-2} mol l^{-1}) were also added to the vial to obtain Im/FeP molar ratios of 1:1, 2:1 or 10:1, respectively. To study the effect of the addition of OH$^-$ ions, 4.5; 9.0 or 50 μl of a tetrabutylammonium hydroxyde (TBAOH) solution in ACN (2.75×10^{-2} mol l^{-1}) (obtained

adapting the method described by Cundiff et al. [23] and reported by us elsewhere [20](b)) in order to obtain OH$^-$/FeP molar ratios of 1:1, 2:1 or 11:1, respectively.

2.2.1. Product analysis

The product was analyzed by gas chromatography using n-octanol as the internal standard. The yields were based on iodosylbenzene. Gas chromatographic analysis were performed on either a CG 37-002 gas chromatograph, or a CG 500 gas chromatograph coupled to a CG 300 integrator or a Varian CX 300 gas chromatograph coupled to a workstation operating software. Nitrogen was used as the carrier gas with an hydrogen flame ionization detector. The stainless steel column (length, 1.8 m; internal diameter, 3 mm) was packed with 10% Carbowax 20 M on Chromosorb WHP. The attained products were analyzed by comparison of their retention times with authentic samples. The control reaction was carried out under the same conditions, in the absence of FeP.

2.3. EPR spectra

The EPR spectra were recorded in a Varian E-109 century line spectrometer operating in the X-band. The g values were found by taking the frequency indicated by 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 Cr^{3+} reference signals. The Helitran (Oxford Systems) low temperature accessory was employed to obtain the spectra in the specified temperature range.

3. Results and discussion

3.1. Oxidation reactions

3.1.1. Effect of solvent

A good solvent for these hydroxylation reactions should be oxidatively stable and should at

Table 1
Effect of solvent on the yield of cyclohexanol (%) [a] in the oxidation of cyclohexane with PhIO using Fe(TDCPP)Cl as catalyst

Solvent	C-ol (%)
DCE	72
DCE/ACN	28
ACN	15
DCE/MeOH	46
DCM	45

Conditions: argon atmosphere, magnetic stirring at 25°C for 1 h, PhIO/FeP molar ratio of 10–17:1, [Fe(TDCPP)Cl] = 3.0×10^{-4} mol l^{-1}.
[a] Based on starting PhIO, error average = 10%.

least partly dissolve PhIO [17](b). The solvents or solvent mixtures used in this present study and the catalytic results are presented in Table 1.

The very low catalytic activity observed when ACN was used as solvent (Table 1, C-ol = 15%), is due to its immiscibility with cyclohexane and to the possibility of its acting as substrate and being converted to HCN and formaldehyde in the presence of PhIO [24]. As Fe(TDCPP)$^+$ is dissolved in ACN, the active catalytic species **I** Fe^{IV}(O)P$^{+\cdot}$ responsible for the oxidation of the substrate also tends to remain dissolved in this solvent. As a result, the contact between this species **I** and cyclohexane is minimized. Therefore, it is more probable that the active species **I** should transfer the oxygen atom to the solvent where it is dissolved and which may undergo oxidation. Consequently competition for species **I** takes place between cyclohexane (Fig. 2, reaction 2) and ACN, leading to low yields of cyclohexanol.

To promote the miscibility of ACN and cyclohexane, and to minimize the competitive process of ACN oxidation, we decided to use a DCE/ACN 1:1 mixture. However, despite obtaining a homogeneous solution, the yield of cyclohexanol was still low (Table 1, C-ol = 28%), probably due to solvent oxidation.

Knowing that DCE assures the miscibility of polar solvents and cyclohexane and that MeOH is a good solvent for PhIO, we decided to utilize

a DCE/MeOH 1:1 mixture as solvent. However, the yield of cyclohexanol was still not satisfactory (Table 3, C-ol = 46%). Here, MeOH may also be acting as substrate, as has been described by Lindsay-Smith et al. [17], who reported competition with cyclohexane for species **I**:

$$Fe^{III}P \xrightarrow{PhIO} Fe^{IV}(O)P^{+\cdot} \xrightarrow{MeOH} Fe^{III}P + CH_2O$$
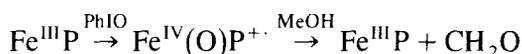
Since Fe(TDCPP)$^+$ bears electron-withdrawing substituents in its meso-aryl positions, the metal ion has an electrophilic character. Consequently, the catalytic species Fe^{IV}(O)(TDCPP)$^{+\cdot}$ is very reactive, being able to abstract hydrogen from MeOH, converting it to formaldehyde.

Finally, we have tested DCM and DCE as solvent in these reactions. DCM led to a cyclohexanol yield of 45%, whereas with DCE we attained 72% (Table 1). In the case of DCM, its oxidation may also be occurring, as in the cases of MeOH and ACN. This fact has already been observed with Fe(MNPP)Cl (Fig. 1) during the study of its active species in DCM, where production of HCl and CO$_2$ has been observed [20](c). In this way, DCM competes with cyclohexane for species **I**:

$$CH_2Cl_2 + Fe^{IV}(O)P^{+\cdot} \to HCl + CO_2 + Fe^{III}P$$
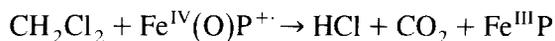
With DCE, hydrogen abstraction is more difficult. Therefore, the solvent does not compete with cyclohexane for species **I** and the complete mixing between DCE and substrate leads to better catalytic results.

3.1.2. Effect of catalyst concentration

Varying the concentration of Fe(TDCPP)Cl has no effect on the yield of cyclohexanol. Whereas Nappa and Tolman [8] have observed that for Fe(TPP)Cl the yields of cyclohexanol were lower at low or very high catalyst concentrations, with Fe(TDCPP)Cl they were constant and around 72% in the concentration range of 1.3×10^{-4}–1.2×10^{-3} mol l^{-1}. In the case of Fe(TPP)Cl, the lower yields were explained in terms of the competitive reactions described in Fig. 2.

Table 2

Effect of stirring method and temperature on the yield of cyclohexanol (%) [a] in the oxidation of cyclohexane with PhIO using Fe(TDCPP)Cl as catalyst

Stirring method	T (°C)	C-ol(%)			
		Fe(TDCPP)		Fe(TFPP)	
		DCM	DCE	DCM	DCE
magnetic	25	45	72	111 [20](d)	100 [20](d)
magnetic	0	–	72	–	–
ultrasound	25	–	45	–	–
ultrasound	0	72	96	140 [20]d	–

Conditions: argon atmosphere, reaction time = 1 h, PhIO/FeP molar ratio of 17:1, solvent: DCE [FeP] = 2.0–3.0 × 10^{-4} mol l^{-1}.

[a] Based on starting PhIO, error average = 10%.

At low Fe(TPP)Cl concentrations, the yield of cyclohexanol is low because PhIO is not completely consumed by the catalyst in reaction 1 before reaction 3 starts (Fig. 2). With Fe(TDCPP)Cl this is not a problem because the electron-withdrawing substituents increase the electrophilicity of the metal-oxo active species I, enhancing its reactivity towards cyclohexane. At high Fe(TPP)Cl concentrations, the yield of cyclohexanol is low because the catalyst itself competes with cyclohexane for the active species I (Fig. 2, reaction 4) and is degraded. With Fe(TDCPP)Cl, the catalytic activity does not decrease under this condition for two reasons: (1) the electron-withdrawing substituents remove electron density from the porphyrin ring, making it less susceptible to electrophilic attacks from another Fe(TDCPP)Cl molecule; (2) the auto-oxidative attack is sterically hindered by the bulky Cl-substituents, increasing the catalyst lifetime. Evidence for the latter comes

from measuring the extent of porphyrin recovery at the end of the reaction by UV–Vis spectroscopy, which was 100%.

3.1.3. Effect of stirring method, temperature, presence of water and presence of dioxygen. Comparison with the catalytic activity of Fe(TFPP)Cl under the same conditions

3.1.3.1. Stirring method and temperature. The effect of temperature and stirring method in the catalytic activity of Fe(TDCPP)Cl either in DCM or in DCE are shown in Table 2. Data for the catalytic activity of Fe(TFPP)Cl under the same conditions are also presented [20](d) and will be discussed further on.

For Fe(TDCPP)Cl in DCE solution, the use of ultrasound stirring at 25°C results in lower yields (Table 2, C-ol = 45%) than magnetic stirring (Table 2, C-ol = 72%). This happens because ultrasound promotes local heating, causing a decrease in the catalytic activity of Fe(TDCPP)Cl. With ultrasound stirring at 0°C, though, the yield of cyclohexanol rises to 96% (Table 2), due to: (i) at lower temperatures, local heating is prevented; (ii) the catalytic active species I is more stable at low temperatures; (iii) ultrasound stirring is more effective to mix and homogenize the reactants, promoting rate enhancements in reactions which form radical species and favoring the process of hydrogen atom abstraction, subsequent to cavitation [25]. The presence of solid particles of PhIO may act as cavitation nucleus.

With Fe(TDCPP)Cl in DCM solution, ultra-

Table 3

Effect of dioxygen and H$_2$O on the yield of cyclohexanol (%) [a] in the oxidation of cyclohexane with PhIO using Fe(TDCPP)Cl as catalyst

Stirring method	T (°C)	Solvent	C-ol (%)					
			Fe(TDCPP)			Fe(TFPP)		
			Argon	O$_2$	H$_2$O	Argon	O$_2$	H$_2$O
magnetic	25	DCE	72	60	–	100 [20](d)	100	–
magnetic	25	DCM	45	45	–	111 [20](d)	–	–
ultrasound	0	DCM	72	60	60 [20](d)	140 [20](d)	173 [20](d)	205 [20](d)

Conditions: reaction time = 1 h, PhIO/FeP molar ratio of 17:1, [FeP] = 2.0–3.0 × 10^{-4} mol l^{-1}.

[a] Based on starting PhIO, error average = 10%.

sound at 0°C also led to a higher yield than magnetic stirring (Table 2, C-ol = 72 and 45%, respectively), for the same reasons mentioned above. However, the yield was lower than that obtained in DCE because ultrasound stirring facilitates the formation of radical species from DCM. As a result, it competes with cyclohexane for species **I**, being oxidized to HCl and CO_2, as described in item Section 3.1.1. This leads to the lower yield of cyclohexanol observed in this case.

3.1.3.2. Presence of dioxygen.

The catalytic activity of Fe(TDCPP)Cl in DCE solution with magnetic stirring and at room temperature was decreased from 72% of cyclohexanol yield in the presence of argon to 60% in the presence of dioxygen (Table 3). It seems that dioxygen participates by oxidizing the cyclohexanol produced when it is present in high amount. So, there a further reaction may be occurring between cyclohexanol and the active species **I** in this condition, producing cyclohexyloxy radicals in equilibrium with open chain aldehyde radicals, which are easily oxidized by dioxygen to carboxylic acids [3,26,27].

However, when DCM is used with magnetic stirring at room temperature, it may act as substrate, competing with cyclohexane and lowering the yield of cyclohexanol (Table 3, C-ol = 45%). In this condition, the presence of dioxygen does not affect the catalytic activity of Fe(TDCPP)Cl due to the relative low amount of cyclohexanol produced. However, when reactions using DCM were carried out with ultrasound stirring at 0°C under argon atmosphere, the active species **I** was stabilized and the reaction mixture was better homogenized, favoring the formation of cyclohexanol in high amounts (Table 3, C-ol = 72%). In this condition, the presence of dioxygen again causes cyclohexanol to be oxidized to carboxylic acids, decreasing its yield (Table 3, C-ol = 60%).

3.1.3.3. Presence of H_2O [20](d).

Presence of H_2O and ultrasound stirring led to a decrease in the cyclohexanol yield (Table 3, C-ol = 60%) [20](d). This happens because the following process may occur:

$$Fe^{IV}(O)P^{+\cdot} + Fe^{III}P + H_2O$$

$$\rightarrow 2Fe^{IV}(OH)P \quad [17](d)$$
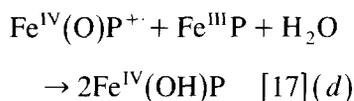
leading to the formation of $Fe^{IV}(OH)P$. This species cannot abstract hydrogen atom from cyclohexane, and consequently does not oxidize it.

3.1.3.4. Comparison between the catalytic activities of Fe(TDCPP)Cl and Fe(TFPP)Cl.

It is thought that Fe(TDCPP)Cl follows the classical mechanism described by Nappa and Tolman (Fig. 2) [8] for the hydroxylation of cyclohexane by PhIO, which involves the monomer $Fe^{IV}(O)P^{+\cdot}$ as the active species. When one takes into consideration the catalytic activity of Fe(TFPP)Cl, which also bears electron-withdrawing substituents, and compares it with that of Fe(TDCPP)Cl, an interesting discussion arises and confirms that Fe(TDCPP)Cl follows the classical route.

Fe(TFPP)Cl has been reported as being a very efficient catalyst for hydroxylations and epoxidations, because its pentafluorophenyl substituents protect it against oxidative self-destruction. In a recent work [20](d), our group has reported unusual high yields of cyclohexanol when this FeP is used as catalyst in the hydroxylation of cyclohexane by PhIO (Tables 2 and 3). These yields were explained in terms of a parallel mechanism containing reactions which have already been described in the literature and which we think occurs simultaneously with the classical mechanism described by Nappa and Tolman [8].

To start with, Ellis and Lyons [28](a) have proposed a mechanism which is dependent on the μ-oxo diiron(III) species of Fe(TFPP)$^+$. The formation of the dimer in this case is possible because the pentafluorophenyl substituents do not hinder its formation. According to Ellis and Lyons [28](a), this dimer may disproportionate

into $Fe^{II}P$ and $Fe^{IV}(O)P$, according to the following equilibrium:

$$(Fe^{III}P)_2O \rightleftharpoons Fe^{IV}(O)P + Fe^{II}P \qquad (1)$$
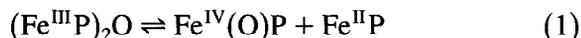
$Fe^{II}P$ formed in Eq. 1 is readily stabilized due to the high Fe^{III}/Fe^{II} potential and intervenes in Eq. 4, which will be described below [28].

More recently, Gray et al. [29] have proposed a catalytic cycle for the hydroxylation of alkanes by $Fe(TFPPBr_8)$ and O_2, where radicals are generated by oxidation and reduction of alkyl-hydroperoxides, with the participation of the monomers $Fe^{III}(TFPPBr_8)$ and $Fe^{II}(TFPPBr_8)$. We then proposed a similar catalytic mechanism for $Fe(TFPP)$, which involves the $Fe^{II}P$ species and O_2 [20](d).

If radicals, probably originating from the solvent (RH), are present in the reaction medium, O_2 may react with them according to Eq. 2:

$$O_2 + R^{\cdot} \rightarrow ROO^{\cdot} \qquad (2)$$

These ROO · radicals may abstract hydrogen from another solvent molecule, giving rise to a 'hydroperoxide-like' molecule:

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \qquad (3)$$
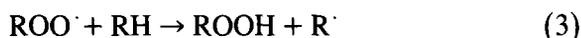
$Fe^{II}P$ then intervenes in the reductive cleavage of ROOH:

$$Fe^{II}P + ROOH \rightarrow Fe^{III}P + RO^{\cdot} \qquad (4)$$

the RO · radicals may react with cyclohexane to give cyclohexanol:

$$RO\cdot + \underset{}{\text{⬡}} \longrightarrow R\cdot + \underset{}{\text{⬡}OH} \qquad (5)$$
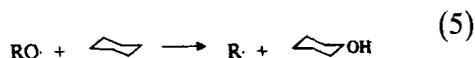
The hydroxylation reactions carried out in the presence of $Fe(TDCPP)Cl$ or $Fe(TFPP)Cl$ as catalyst (Tables 2 and 3) confirm that the O_2 parallel mechanism described in Eqs. 1–5 occurs with the latter, but not with the former. When DCE, magnetic stirring and argon atmosphere were used, the yields of cyclohexanol were 100 and 72% for $Fe(TFPP)Cl$ and $Fe(TDCPP)Cl$, respectively (Table 2). Changing the solvent to DCM, the yield obtained with $Fe(TDCPP)Cl$ decreases to 45%, whereas with

$Fe(TFPP)Cl$ it rises to 111% (Table 2). As for $Fe(TFPP)$, we have interpreted that the O_2 parallel mechanism may be taking place because the three species responsible for its triggering are present in the reaction medium: (i) $Fe(TFPP)$ in the μ-oxo dimer form gives rise to $Fe^{II}P$ species (Eq. 1); (ii) O_2 may be present in catalytic amounts in the reaction media, since the argon bubbling does not assure its total removal from the system; (iii) radicals R · from DCM are formed, which together with O_2 and $Fe^{II}P$, triggers the parallel mechanism (Eqs. 2–5).

When magnetic stirring is replaced by ultrasound in the latter reaction (Table 2), the yield of cyclohexanol goes up to 140%, since this stirring method favors radical formation from DCM even more. With DCE, the parallel mechanism does not occur because it is difficult to generate radicals from this solvent and the yield remains around 100% (Table 2). This shows that the presence of R · radicals generated from the solvent is essential for the O_2 parallel mechanism.

As for $Fe(TDCPP)Cl$, in spite of the presence of radicals from DCM and O_2, the parallel mechanism does not take place. This happens because the formation of the $Fe(TDCPP)$ μ-oxo dimer does not occur due to the bulky ortho-chloro-substituents and so the parallel mechanism is not triggered. As a result, radicals formed from DCM may be only taking part in the competition with cyclohexane for species I, leading to the formation of HCl and CO_2 and causing a decrease in the yield of cyclohexanol.

The fact that the presence of the FeP μ-oxo dimer species is essential to trigger the O_2 parallel mechanism was evidenced by the observation that, in the presence of O_2 and R ·, it does not occur with $Fe(TDCPP)Cl$. Carrying out reactions of $Fe(TFPP)Cl$ in the presence of water/ultrasound/DCM (Table 3) or imidazole/magnetic stirring/DCE (Table 4) provided more evidence of the importance of such a dimer. When water is present, it induces the formation of the dimeric species which,

together with ultrasound, DCM and O_2 in catalytic amount, triggers the parallel mechanism, increasing the yield to 205% (Table 3). On the other hand, in the presence of imidazole, the yield was 100% (Table 4) because this ligand inhibits the formation of dimer. This factor associated with the use of magnetic stirring and DCE prevents the parallel mechanism and therefore, only the PhIO mechanism [8] takes place. With Fe(TDCPP)Cl, H_2O probably leads to the formation of the catalytically inactive $Fe^{IV}(OH)(TDCPP)^+$ [17](d) species, causing a decrease in the yield of cyclohexanol from 72 to 60% (Table 3).

Evidence for the fact that the parallel mechanism involves O_2 was obtained by carrying out reactions in DCM or DCE, under O_2 atmosphere and with ultrasound stirring (Table 3). With Fe(TFPP) under O_2 atmosphere and in DCM solution, the yield increased from 111% (catalytic amount of O_2, Table 3) to 173% (O_2 atmosphere, Table 3). Therefore, in this medium, R' radicals generated from DCM reacted with O_2 and led to the parallel mechanism (Eq. 3) in the presence of $(FeTFPP)_2O$. When DCE and magnetic stirring were used, O_2 had no effect on the catalytic activity of Fe(TFPP) because the formation of radicals from this solvent is not favored and only the PhIO mechanism [8] occurred. With the non-dimer-forming Fe(TDCPP)Cl, O_2 almost always leads to a decrease in the cyclohexanol yields, as was

Table 4
Effect of imidazole as axial ligand on the yield of cyclohexanol (%) [a] in the oxidation of cyclohexane with PhIO using Fe(TDCPP)Cl as catalyst

Im/FeP molar ratio	C-ol (%)	
	Fe(TDCPP)	Fe(TFPP)
0	75	100 [20](d)
1:1	60	100 [20](d)
2:1	60	–
10:1	20	–

Conditions: magnetic stirring at 25°C for 1 h, solvent: DCE, PhIO/FeP molar ratio of 17:1, [Fe(TDCPP)$^+$] = 5.0×10^{-4} mol l^{-1}.
[a] Based on starting PhIO, error average = 10%.
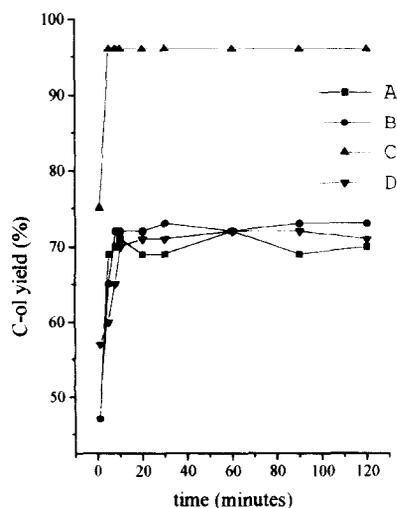
Fig. 3. Change of yield of cyclohexanol with time in the oxidation of cyclohexane by PhIO and Fe(TDCPP)Cl (A) [Fe(TDCPP)Cl] = 2.0×10^{-4} mol l^{-1}, magnetic stirring at 25°C; (B) [Fe(TDCPP)Cl] = 3.0×10^{-4} mol l^{-1}, magnetic stirring at 25°C; (C) [Fe(TDCPP)Cl] = 3.0×10^{-4} mol l^{-1}, ultrasound stirring at 0°C; (D) [Fe(TDCPP)Cl] = 1.2×10^{-4} mol l^{-1}, magnetic stirring at 25°C.

emphasized before. In the absence of dimer species to trigger the O_2 parallel mechanism, the only effect of O_2 is to further oxidize cyclohexanol to carboxylic acid.

3.1.4. Effect of reaction time

The change in the yields of cyclohexanol during the course of the oxidation of cyclohexane shows that the maximum rate of alcohol formation is at the beginning of the reaction. For FeP concentrations of 2.0×10^{-4}, 3.0×10^{-4} or 1.2×10^{-4} mol l^{-1} and using magnetic stirring at 25°C, C-ol$_{max}$ = 72% after 8 min reaction (Fig. 3). However, when ultrasound stirring is used as the stirring method at 0°C, there is an increase in the rate of production of cyclohexanol. In this way, after 5 min reaction, the maximum yield (C-ol$_{max}$ = 96%) has already been reached.

3.1.5. Effect of PhIO / FeP molar ratio

With unhindered FeP such as Fe(TPP)Cl and Fe(MNPP)Cl, the yield of cyclohexanol decreases as the PhIO/FeP ratio increases [8],

[20](c). This happens because the PhIO in excess competes with cyclohexane for the active species **I** (Fig. 2, reaction 3). When Fe(TDCPP)Cl is employed as catalyst, the yield of cyclohexanol does not decrease in the face of excess PhIO, but remains constant with PhIO/FeP molar ratios ranging from 10 to 100 by using both magnetic stirring at 25°C (C-ol = 72%) and ultrasound stirring at 0°C (C-ol = 96%). The competitive reaction 3 is not favored in this case because the Cl-substituents remove electron density from the ring, activating the ferryl active species **I** towards cyclohexane. So one can use higher PhIO/FeP ratios and obtain high turnover numbers for Fe(TDCPP)Cl with the same amount of catalyst.

3.1.6. Effect of axial ligand

When imidazole is added to the reaction media, there is a decrease in the yield of cyclohexanol from 75% to 60% for Im/FeP molar ratios of 1:1 or 2:1 (Table 4). With an Im/FeP molar ratio of 10, the decrease is even more pronounced (Table 4, C-ol = 20%). It is known that Fe(TDCPP)$^+$ has a marked tendency to form bis-imidazole complexes in DCE ($\beta_2 = 2.5 \times 10^8$ mol^{-2} l^2). The low-spin hexacoordinated Fe(TDCPP)Im$_2^+$ complex obtained in this case makes the formation of the catalytic active species **I** more difficult, accounting for the low yields. It is known that the coordination of imidazole to Fe(TDCPP)$^+$ is a thermodynamically favorable process, since the Cl-substituents make the central Fe^{III} ion more electrophilic, increasing its affinity for nitrogenous bases that donate electrons through a resonance effect [11]. However, the mechanism for bis-imidazole coordination to the FeP occurs by the following process: first, imidazole coordinates to the Fe(TDCPP)Cl complex, giving Fe(TDCPP)ImCl:

$$\text{Fe(TDCPP)Cl} + \text{Im} \rightleftharpoons \text{Fe(TDCPP)ImCl}$$
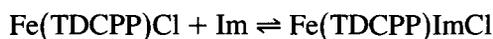
Then, the coordination of a second imidazole occurs in two steps, where the determining one involves the exchange of the Cl$^-$ ligand for imidazole through a dissociative process [30](a,b):

$$\text{Fe(TDCPP)ImCl} \rightleftharpoons \text{Fe(TDCPP)Im}^+ + \text{Cl}^-$$

$$\text{Fe(TDCPP)Im}^+ + \text{Im} \rightleftharpoons \text{Fe(TDCPP)Im}_2^+$$

As the electron-withdrawing substituents lower the electron density of both the pyrrolic nitrogen atoms and Fe^{III} ion of Fe(TDCPP)$^+$, the liberation of Cl$^-$ is more difficult, making the bis-coordination of imidazole kinetically slower [30](c). This explains the differences in the results obtained with the various Im/Fe(TDCPP)$^+$ molar ratios. When the ratio is 1:1 or 2:1, the FeP may not be totally bis-coordinated to imidazole and the amount of high spin Fe^{III} that remains in the system is enough to maintain the yield around 60%. In the presence of excess imidazole, the exchange of the Cl$^-$ ligand for imidazole is favored by the displacement of the equilibriums involved in the last two steps towards the Fe(TDCPP)Im$_2^+$ complex. Consequently, a large amount of Fe(TDCPP)Im$_2^+$ is formed and this complex is less efficient in the oxidation of cyclohexane.

The addition of OH$^-$ ions to the system also leads to a decrease in the yield of cyclohexanol to 50% (Table 5) for OH$^-$/FeP molar ratios of 1:1, 2:1 and 11:1. Through UV–Vis spectrophotometric titration of a Fe(TDCPP)Cl solution in DCE with a TBAOH solution in acetonitrile, we have found that Fe(TDCPP)$^+$ forms thermodynamically stable high-spin bis-hydroxy complexes ($\beta_2 = 6.3 \times 10^7$ mol^{-2} l^2). The hexaco-

Table 5
Effect of OH$^-$ as axial ligand on the yield of cyclohexanol (%) [a] in the oxidation of cyclohexane with PhIO using Fe(TDCPP)Cl as catalyst

OH$^-$/FeP	C-ol (%)
0	72
1:1	50
2:1	48
10:1	58

Conditions: magnetic stirring at 25°C for 1 h, PhIO/FeP molar ratio of 17:1, solvent: DCE, [Fe(TDCPP)$^+$] = 3.0 × 10^{-4} mol l^{-1}.

[a] Based on starting PhIO, error average = 10%.
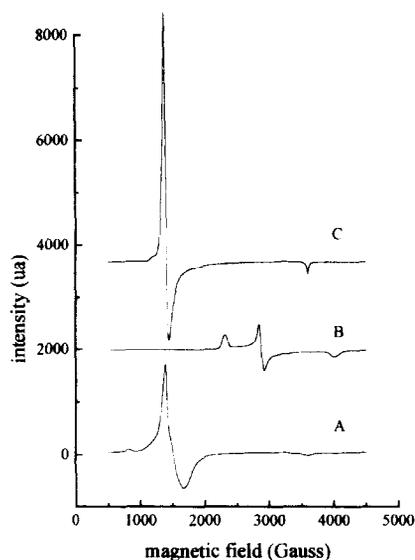
Fig. 4. EPR spectra of (A) Fe(TDCPP)Cl solution in DCE (100 μl, 8.1×10^{-4} mol l^{-1}); (B) A after addition of imidazole solution in DCE (50 ml, 3.7×10^{-2} mol l^{-1}); (C) A after addition of TBAOH solution in ACN (70 ml, 3.1×10^{-2} mol l^{-1}).

ordination in this case makes the formation of the catalytic species $\mathbf{I}$ difficult. But as OH$^-$ is a weak field ligand, the interaction between its orbitals with those of the FeP is not as significant as the one with imidazole. Consequently, OH$^-$ and Fe^{III} are not so tightly bonded, allowing the separation of the OH$^-$ ion in favor of the formation of the active species $\mathbf{I}$, even in the presence of excess OH$^-$.

3.2. EPR spectra

Evidence for the formation of low-spin Fe(TDCPP)Im$_2^+$ upon addition of imidazole in excess came from the EPR studies (Fig. 4). After the addition of an imidazole solution in DCE to a Fe(TDCPP)Cl solution also in DCE, one can observe the disappearance of the high-spin Fe^{III} signal at $g = 5.8$ and the appearance of the respective low-spin signals at $g_z = 2.54$; $g_y = 2.15$ and $g_x = 1.90$ (Fig. 4B). Upon addition of a TBAOH solution in ACN to a Fe(TDCPP)Cl solution in DCE, the high-spin Fe(TDCPP)(OH)$_2^-$ complex was obtained. The corresponding EPR spectrum shows that the

high-spin Fe^{III} signal at $g = 5.8$ present in the spectrum of Fe(TDCPP)Cl decreases in the presence of low amounts of OH$^-$ but, when an excess of OH$^-$ is added to the system, the signal again increases and becomes highly symmetric, giving an indication that the high-spin Fe(TDCPP)(OH)$_2^-$ complex was formed (Fig. 4C). The number of coordinated ligands and the thermodynamic stability constant β_2 had been determined for both Fe(TDCPP)Im$_2^+$ and Fe(TDCPP)(OH)$_2^-$ through UV–Vis spectrophotometric titrations. The procedure for the titrations and the calculations are described by us elsewhere [20](b).

4. Conclusions

This optimization study of the reaction conditions for Fe(TDCPP)Cl led us to obtain a yield of cyclohexanol of 96% and a turnover number of 96 (Table 3, ultrasound stirring at 0°C, PhIO/FeP molar ratio = 100, [Fe(TDCPP)] = 3.0×10^{-4} mol l^{-1}). This result was far better than that reported in the literature using the same FeP (C-ol = 73%, turnover number = 45, [Fe(TDCPP)] = 8.0×10^{-4} mol l^{-1}) [9](a).

The most important goal of this study was that the reactions carried out in this work provided insight into the mechanism followed by Fe(TDCPP)Cl in the hydroxylation of cyclohexane by PhIO. The evidence is that it goes through the same PhIO classical mechanism already described for Fe(TPP)Cl [7](a,b), [8], which involves the monomeric active species $\mathbf{I}$ Fe^{IV}(O)P$^{+\cdot}$. Unlike Fe(TFPP)Cl, Fe(TDCPP)Cl does not follow the parallel mechanism involving O$_2$ and radicals. Therefore it does not lead to unusually high yields of cyclohexanol, thanks to its bulky chloro-substituents, which hinder the formation of its respective μ-oxo dimer, thus avoiding the alternative route. Because Fe(TDCPP)Cl only follows the PhIO mechanism, it may be considered a good biomimetic model even under conditions such as the use of

ultrasound stirring, high PhIO/FeP molar ratio and low amount of catalyst. The Cl-substituents make Fe(TDCPP)Cl a very resistant and selective catalyst for the hydroxylation of cyclohexane, yielding cyclohexanol as the sole product.

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