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# Manganese(III) porphyrins: catalytic activity and intermediate studies in homogeneous systems

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**Abstract**

We studied how solvent, stirring method, PhIO/MnP molar ratio, presence of water and axial ligand affect the catalytic activities of Mn(TPP)Cl, Mn(MNPP)Cl, Mn(TDCPP)Cl and Mn(TFPP)Cl in the oxidation of cyclohexane by PhIO. A study of the catalytic intermediates in the reaction between Mn(TPP)Cl or Mn(TDCPP)Cl and PhIO was also carried out by UV–Vis and EPR spectroscopies. The reaction of Mn(TPP)Cl with PhIO showed the formation of a mixture of species $Mn^{IV}(O)P^{\cdot+}$ and $Mn^{V}(O)P$ as intermediates, which were confirmed by the deconvolution of the UV–Vis spectra. Addition of imidazole as cocatalyst favoured the formation of the intermediate species $Mn^{V}(O)P$, evidenced by the UV–Vis band at 408 nm. The corresponding EPR spectra gave evidence that in the presence of imidazole, $Mn^{IV}(O)P^{\cdot+}$ species are formed only in very low amounts. For Mn(TDCPP)Cl the dominating intermediate species is $Mn^{IV}(O)P^{\cdot+}$. Addition of imidazole to halogen-substituted MnP systems does not result in increase of the C-ol yields because very stable bis-imidazole-MnP complexes are formed. Anchoring of such MnP on imidazole propyl gel (IPG) results in better catalytic activity because in this case, the catalyst is mono-coordinated to the support and imidazole favours the formation of the intermediate species $Mn^{V}(O)P$.

*Keywords:* Porphyrins; Manganeseporphyrins; Catalysis; Intermediates; Oxidation

## 1. Introduction

Porphyrins are important for all organisms [1]. They are indispensable of their function as complexing ligands for catalytically active metal. This relates not only to metabolism, but also to the provision of energy in living creatures and photosynthesis in the plant kingdom [1]. Tetraarylporphyrins, specially iron and manganese complexes with chloro or fluoro substituents (Fig. 1) can catalyze very similar oxidations to those brought about by cytochrome P-450 and for this reason they have received much attention in recent years [2,3]. These porphyrins share several of the unusual properties related to catalytic resistance to degradation due to the introduction of electron-withdrawing sub-

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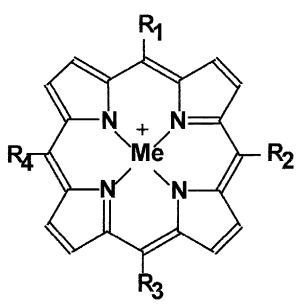
stituents in the *meso*-aryl position of the tetraphenylporphyrin [2,3].

A logical approach to the design of models for heme proteins might be the attachment of the metalloporphyrin to the support through coordination to ligands on the surface of the silica. The coordinative bond then serves the dual role of anchor and moderator of the metal ion activity [4]. Silica, for example, has been an attractive support for metalloporphyrins, since it is inert even under drastic conditions and has been used as coordinative support by converting its surface silanol groups into silypropyl derivatives, which act as ligands [2,4]. The large majority of the studies have employed bound imidazole (Fig. 2) or pyridine [4]. The great advantage of these supported systems is that they consist of hemin in isolated sites, in the same way that the active site of P-450 consists of a protohemin in a hydrophobic pocket [5]. The site-isolation on a solid support prevents porphyrin oxidative degradation by bimolecular interaction and/or self-oxidation. The combination of electron-withdrawing substituents in the metalloporphyrins with immobilization on the inorganic supports results in very efficient, selective and easy-to-recover catalysts.

Some different features about biomimetic oxidation catalytic behaviour can be discussed comparing iron and manganese porphyrins [6].




**Metalloporphyrin**

| | | |
|---|---|---|
| 1 | Mn(TPP)Cl | $R_1 = R_2 = R_3 = R_4 =$ $C_6H_5$ |
| 2 | Mn(MNPP)Cl | $R_1 = R_2 = R_3 =$ $C_6H_5$ $R_4 =$ *o*-$NO_2$Ph |
| 3 | Mn(TDCPP)Cl | $R_1 = R_2 = R_3 = R_4 =$ 2,6 diClPh |
| 4 | Mn(TFPP)Cl | $R_1 = R_2 = R_3 = R_4 =$ $C_6F_5$ |

Fig. 1. Manganeseporphyrins.

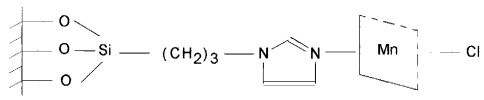



Fig. 2. Manganeseporphyrin–IPG.

The catalytic epoxidation of *cis*-stilbene by Mn(TDCPP)Cl with iodozylbenzene (PhIO) provides both *cis*- and *trans*-stilbene oxides. The rearrangement from *cis*-stilbene to *trans*-stilbene oxides has led to the suggestion of a radical oxidation mechanism, which does not occur with ironporphyrins [7]. The presence of nitrogen base acting as an axial ligand using manganeseporphyrins (MnP) remarkably improves alkene epoxidation stereoselectively and stereospecifically [2,8]. This has been shown to be due to the stabilization of the manganese(V)–oxo porphyrin, ($Mn^{V}$(O)P), with prevention of formation of the manganese(IV)–oxo porphyrin ($Mn^{IV}$(O)P) [6,9–11] which is less active.

Despite a great deal of work with these biomimetical systems, there are relatively few systematic studies about the factors that affect their catalytic efficiency. A classical study about the hydroxylation of cyclohexane using FeP as catalysts and PhIO as the oxygen donor was reported by Nappa and Tollman in 1985 [12]. We have done studies on the optimization of reaction conditions in this kind of systems using substituted ironporphyrins as catalyst [13–15]. We observed that the yields of oxidized products were critically dependent on factors such as solvent, stirring method, axial ligand and presence of water. However these kind of studies have not been extensively done for MnP in the hydroxylation of alkanes. In this work we have investigated how these factors affect the catalytic activities of MnP **1** to **4** (Fig. 1) in the hydroxylation of cyclohexane using PhIO as oxygen donor. The catalytic intermediates for Mn(TPP)Cl **1** and Mn(TDCPP)Cl **3** in their reaction with PhIO were studied by UV–Vis

spectroscopy. The reaction for **1** was also monitored by EPR spectroscopy. The detected intermediates were related to the catalytic activities obtained.

## 2. Experimental

### 2.1. Materials

Dichloromethane (DCM) and 1,2-dichloroethane (DCE) were distilled and stored on 4 Å molecular sieves. Acetonitrile (ACN) and methanol were stored on 3 Å molecular sieves. *N,N*-dimethylformamide (DMF) was stirred over KOH at room temperature overnight, decanted, then distilled. Cyclohexane purity was determined by gas chromatographic analysis.

### 2.2. Porphyrins and manganeseporphyrins

Mn(TPP)Cl was purchased from Aldrich, and $TDCPPH_2$ and $TFPPH_2$ were purchased from Midcentury. The synthesis and purification of $MNPPH_2$ has been described previously [16]. Manganese insertion into the free base porphyrins was done by adapting the method described by Adler et al. [17]. DMF was removed in the flash evaporator and the manganeseporphyrins were washed with water. The manganeseporphyrins were purified by silica column chromatography, using a cyclohexane–dichloromethane 1:2 mixture as eluent.

### 2.3. Iodosylbenzene (PhIO)

It was obtained through the hydrolysis of iodosylbenzenediacetate [18]. Samples were stored in freezer and the purity was checked every six months by iodometric assay.

### 2.4. Solid supports

Imidazole propyl gel (IPG) was prepared according to the method described by Basolo et al. [19]. Elemental analysis: C = 5.34%; H = 1.20%; N = 0.65%, which corresponds to $2.2 \times 10^{-4}$ mol of imidazole per gram of IPG.

### 2.5. Preparation of supported manganeseporphyrins (MeP–IPG)

The metalloporphyrin ligation to IPG was achieved by stirring a DCM solution of a known amount of metalloporphyrin with a suspension of the support for 10–20 min. The resulting supported catalyst was washed with DCM to remove unbound catalyst and weakly bound porphyrin and dried for 3 h at 60°C. The loadings were quantified by measuring the amount of unloaded metalloporphyrin in the combined reaction solvent and washings by UV–Vis spectroscopy.

### 2.6. 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, the solvent (100 $\mu$L) and cyclohexane (100 $\mu$L) were added to the vial containing the MnP ($\sim$ 0.30 mg) and iodosylbenzene ($\sim$ 0.50 mg) under argon atmosphere, and the flask was adapted in a dark chamber. When the mixture was stirred with ultrasound (ultrasound laboratory cleaner Minison–Thornton, 40 W, 50–60 Hz) the temperature was 0°C, and when magnetic stirring was used, the temperature was 25°C. The reaction mixture was stirred for 1 h, and a saturated sodium bisulfite aqueous solution (25 $\mu$L) was added to the reaction mixture in order to quench further oxidation.

#### 2.6.1. Product analysis

The product was analyzed by gas-chromatography using *n*-octanol as the internal standard. Yields were based on iodosylbenzene. Gas chromatographic analyses were performed on a CG 37-002 or CG 500 gas chromatograph coupled to a CG 300 integrator. Nitrogen was used as the carrier gas with a hydrogen flame ionization detector. The inox column (length, 1.8 m;

internal diameter, 3 mm) was packed with 10% Carbowax 20 M on chromosorb WHP. The products were analyzed by a comparison of their retention times with those of authentic samples. Control of all reactions was carried out under the same experimental conditions, but in the absence of MnP. All the reactions were carried out in duplicate or triplicate.

### *2.7. Catalytic intermediates studies through UV–Vis spectra*

UV–Vis spectra were obtained on a Hewlett Packard Diode Array model 8452 spectrophotometer. 150 $\mu$L of PhIO solution ($1.2 \times 10^{-2}$ mol $\cdot$ L$^{-1}$) were added to a 0.2 cm path length cell (Hellma) containing 150 $\mu$L of MnP solution in DCM ($2.0 \times 10^{-4}$ mol L$^{-1}$) and the mixture was stirred either by ultrasound or manually. Consecutive spectra were recorded. In measurements at low temperature, the cell was transferred to an optical dewar (Kontes) containing methanol previously cooled to $-55$°C.

### *2.8. Catalytic intermediates studies through EPR spectra*

The EPR spectra were recorded on a Varian E-109 century line spectrometer operating at the X band at 4–5 K. The $g$ values were found by taking the frequency indicated in a HP 5340A 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 temperature range specified. 100 $\mu$L of PhIO solution ($1.86 \times 10^{-2}$ mol L$^{-1}$) and 100 $\mu$L of cyclohexane were added to a EPR tube containing 150 $\mu$L of MnP solution in DCM ($3.0 \times 10^{-4}$ mol L$^{-1}$) and the mixture was stirred either by ultrasound or manually. Consecutive spectra were recorded.

## 3. Results and discussion

### *3.1. Solvent effect*

The solvent must dissolve both the MnP and PhIO and be oxidatively stable, not being oxidized by the catalyst. For the PhIO–MnP (**1**, **2**, **3** and **4**) systems, the choice of solvent is extremely important, since it may or not favour the reaction with radicalar mechanism [10,11]. It is generally observed that these systems are more efficient in DCM, in which the catalyst is more soluble (see Table 1). Contrary to what has already been observed by our group in the case of FeP, the competitive oxidation reactions between DCM and cyclohexane for the catalyst are not so evident with MnP [15,20].

We observed a significant decrease in the catalytic activity of Mn(TFPP)Cl **(4)** and Mn(MNPPCl) **(2)** when ACN was used as solvent, if compared to the same systems in DCM or DCE. ACN may be competing with cyclohexane for the catalytic active center, being oxidized to HCN and formaldehyde [21]. This effect is even more pronounced with **2** and **4**, due to the presence of the nitro and fluorosubstituents, respectively. The use of a more polar solvent such as ACN may favour the formation of the radicalar catalytic intermediate $Mn^{IV}(O)P^{\cdot+}$, responsible for the low selectivity observed in these cases [6,10,11].

Table 1
Yields of cyclohexanol (%) [a] in the hydroxylation of cyclohexane with PhIO using MnP as catalyst. Effect of solvent

| MnP | DCM | | DCE | | ACN | |
|---|---|---|---|---|---|---|
| | C-ol | C-one | C-ol | C-one | C-ol | C-one |
| Mn(TPP)Cl | 43 | 23 | 30 | 12 | 38 | 25 |
| Mn(MNPP)Cl | 49 | 9 | 51 | 17 | 11 | 12 |
| Mn(TDCPP)Cl | 27 | 4 | 17 | 4 | 31 | 6 |
| Mn(TFPP)Cl | 83 | 13 | 77 | 16 | 39 | 21 |

Conditions: [MnP] = $5 \times 10^{-4}$ mol L$^{-1}$, PhIO/MnP molar ratio of 10:1, magnetic stirring at 25°C, reaction time: 1 h, argon atmosphere.

[a] Error average of 3%, based on the starting PhIO. C-ol = cyclohexanol. C-one = cyclohexanone.

The catalytic activity of Mn(TDCPP)Cl **3** is unexpectedly low in all solvents, when compared to the other MnP. A similar result was obtained before in the oxidation of alkanes using PhIO or $H_2O_2$ as oxygen donor [22]. With this catalyst, the nature of the porphyrin ligand dominates over the solvent effect, in some way. As it will be seen below in the study of catalytic intermediates, there is no evidence of the presence of the active species $Mn^{V}(O)P$ in significant amount for Mn(TDCPP)Cl. $Mn^{IV}(O)P^{\cdot+}$ species predominate, leading to lower yields of cyclohexanol.

### 3.2. Effect of ultrasound stirring

The reactions using ultrasound stirring were carried out at 0°C in order to enable a better control of temperature in the reaction media, since this stirring method provokes super-heating in the cavitation nucleus. On the other hand when magnetic stirring at 0°C was used with MnP–PhIO systems, PhIO was poorly solubilized, leading to a decrease in the yields of oxidized products. For that reason, we used higher temperatures (25°C) with magnetic stirring in the systems studied.

It has been observed that ultrasound (us) is responsible for a great increase in the C-ol yields, without loss of selectivity, when FeP bearing electron-withdrawing substituents in the *ortho-meso*-phenyl positions of the porphyrin ring are used as catalysts [14,15]. This increase was attributed to the fact that this stirring method mixes and homogenizes the reactants more efficiently than magnetic stirring. These results led us to investigate the effect of ultrasound stirring in the MnP-catalyzed reactions. The results in Table 2 show that with both DCM and DCE, the use of ultrasound is not favorable.

Magnetic stirring led to better yields and selectivity than ultrasound stirring, in both DCM and DCE (Table 2). Ultrasound may be inhibiting the catalytic activity of the MnP favoring radicalar processes which result in the formation of $Mn^{IV}$ species and free organic radicals responsible for the poor selectivity obtained with MnP **2** and **4**. UV–Vis spectra recorded show that a great amount of $Mn^{IV}(OH)P$ is formed when ultrasound stirring is used (data not shown). The high stability of such species makes catalyst recovery difficult, leading to a decrease in the turnover number.

Table 2
Yields of cyclohexanol (%) [a] in the hydroxylation of cyclohexane with PhIO using MnP as catalyst. Effect of stirring method and effect of water in the reaction media

| MnP | Absence of water | | | | Presence of water [b] | | | |
|---|---|---|---|---|---|---|---|---|
| | magnetic [c] | | ultrasound [d] | | magnetic [c] | | ultrasound [d] | |
| | C-ol | C-one | C-ol | C-one | C-ol | C-one | C-ol | C-one |
| Mn(TPP)Cl | 43 | 23 | 25 | 7 | 29 | 15 | 16 | 10 |
| Mn(MNPP)Cl | 49 | 9 | 24 | 12 | 53 | 5 | 62 | 22 |
| Mn(TDCPP)Cl | 27 | 4 | 16 | 2 | 23 | 3 | 21 | 3 |
| Mn(TFPP)Cl | 84 | 13 | 35 | 15 | 66 | 15 | 58 | 13 |

Conditions: $[MnP] = 5 \times 10^{-4}$ mol $L^{-1}$, PhIO/MnP molar ratio of 10:1, solvent: DCM, argon atmosphere, reaction time: 1 h.
[a] Based on the starting PhIO.
[b] Reactions carried out under water saturated argon stream.
[c] At 25°C. [d] At 0°C. C-ol = cyclohexanol. C-one = cyclohexanone.

### 3.3. Effect of water

We have observed that the presence of water in the reaction media may enhance the catalytic activity of Fe(TPP)Cl and Fe(MNPP)Cl [15], as water may favor the formation of the active dimeric species PFe–O–FeP. This species leads to good catalytic yields, since it is more resistant to oxidative destruction than the analog monomeric species [15]. In order to better understand the effect of water in the catalytic sites of MnP, we have carried out studies of hydroxylation reactions under argon atmosphere saturated with water. The results are shown in Table 2.

It can be observed that there is a decrease in the yield of cyclohexanol in the presence of water, when magnetic stirring is used. It is known that MnP has a water molecule and a $Cl^-$ ion as axial ligands [23]. Therefore, a water saturation in these systems may lead to a substi-

tution of the $Cl^-$ for water molecule in the 6th coordination. The aqua ligand, in turn, may undergo conversion to a hydroxo ligand during the catalytic cycle [10,11]. Anionic ligands may stabilize the formation of $Mn^{IV}(OH)P$ species [24], which is less efficient from the catalytic point of view [4] accounting for the lower yields obtained with these MnP when water was present in the system.

With the electron-withdrawing substituted MnP ultrasound stirring and presence of water favor their catalytic activity. It is known that ultrasound is responsible for the formation of free radicals in organic media [25]. This effect is even greater when $H_2O$ is present, since $OH^{\cdot}$ radicals and radicals subsequent to $OH^{\cdot}$ formation are generated. These $OH^{\cdot}$ radicals may enhance the formation of the active oxo-manganese intermediate responsible for oxygen atom transfer to cyclohexane.

Ultrasound may cause the destruction of Mn(TPP)Cl **1**. Since MnTPP does not bear electron-withdrawing substituents in the *meso*-aryl positions of the porphyrin ring, it may be easily destroyed in these conditions.

### *3.4. Effect of axial ligand*

#### *3.4.1. Imidazole*

The results obtained in the catalytic oxidation of cyclohexane by PhIO using MnP either in solution, in solution containing imidazole or supported on IPG are presented in Table 3. The influence of the rigid support and imidazole as axial ligand in the mechanism of the MnP-catalyzed reactions can be observed.

The MnP–IPG systems are better catalysts than the corresponding homogeneous systems (Table 3). The difference between these systems is due to the presence of imidazole in the matrix, which acts as cocatalyst. In this case, the formation of the intermediate species L–$Mn^V(O)P$ is favored by the coordination of imidazole (from IPG) in the 5th position and PhIO in the 6th position (L is the imidazole group from IPG coordinated to Mn) [26].

Mn(TPP)Cl **1** and Mn(MNPP)Cl **2** in solution containing imidazole as ligand show the pronounced effect of the cocatalyst. The latter favors the formation of the intermediate species $Mn^V(O)P$, making the MnP more efficient and selective. It is interesting to see that the increase in the yields of C-ol when Mn(TDCPP)Cl **3** and Mn(TFPP)Cl **4** are used is not so expressive as in the cases of **1** and **2**. This different behaviour of the tetra-substituted porphyrin is due to the presence of the electron-withdrawing substituents, which increase the affinity of the MnP for imidazole. The equilibrium constant for the formation of the complex $Mn(TDCPP)(Im)_2$ ($\beta_2 = 2.5 \times 10^6$) is much higher than the same constant for $Mn(TPP)(Im)_2$ ($\beta_2 = 9.2 \times 10^3$).

Table 3
Yields of cyclohexanol (%) [a] in the hydroxylation of cyclohexane with PhIO using MnP as catalyst. Effect of axial ligand

| MnP | Solution | | Trifluorosulphonate acid [b] | | Imidazole [c] | | IPG [d] | |
|---|---|---|---|---|---|---|---|---|
| | C-ol | C-one | C-ol | C-one | C-ol | C-one | C-ol | C-one |
| Mn(TPP)Cl | 19 | 7 | — | — | 72 | 5 | 41 [e] | 0 |
| Mn(MNPP)Cl | 49 | 4 | — | — | 75 | 8 | 67 | 0 |
| Mn(TDCPP)Cl | 17 [e] | 5 | 72 | 20 | 24 | 5 | 67 [e] | 0 |
| Mn(TFPP)Cl | 56 | 8 | 82 | 8 | 55 | 6 | 70 | 4 |

Conditions: $[MnP] = 5 \times 10^{-4}$ mol $L^{-1}$, PhIO/MnP molar ratio of 20:1, solvent: DCE, magnetic stirring, at 25°C, reaction time: 1 h, argon atmosphere.

[a] Error average of 3%, based on the starting PhIO. C-ol = cyclohexanol. C-one = cyclohexanone.

[b] Trifluorosulphonate acid/MnP molar ratio of 4:1.

[c] Imidazole/MnP molar ratio of 1:1.

[d] $1.1 \times 10^{-6}$ mol of MnP per gram of IPG, $2.2 \times 10^{-4}$ mol of imidazole per gram of IPG.

[e] Ref. [22].

In that way, Mn(TDCPP)Cl **3** and Mn(TFPP)Cl **4** form bis-imidazole complexes, which hinders the formation of the intermediate active species.

### 3.4.2. Trifluorosulphonate acid

In the presence of excess trifluorosulphonate acid, Mn(TDCPP)Cl **3** and Mn(TFPP)Cl **4** give rise to higher yields of cyclohexanol, but the selectivity of the reaction is altered. In this case, trifluorosulphonate acid is acting as cocatalyst. Since it is present in excess in the reaction media, it axially coordinates to the MnP, favoring the formation of the intermediate species $Mn^{V}(O)P$. Therefore, trifluorosulphonate plays an important role as a weak electron-donating ligand in the intermediate geometry [10]. Mansuy et al. [11] also observed and improved MnP catalyst systems using $CH_3COONH_4$ as cocatalyst.

Contrary to what was observed with imidazole, trifluorosulfonate acid leads to better catalytic results in the case of MnP bearing halogenated substituents (Table 3). This is due to the tendency that the MnP have to form bis-coordinated complexes with imidazole, which contrary to trifluorosulfonate, is not easily displaced during the catalytic cycle.

## 3.5. Intermediates studies

The differences between the positions of the UV–Vis band observed for $Mn^{III}P$ compounds ($\lambda = 478$ nm in DCM) and $Mn^{IV}(O)P$ ($\lambda = 420$ nm) or $Mn^{V}(O)P$ ($\lambda = 408$ nm) [27] allowed us to follow the transfer of the oxygen atom from PhIO to the MnP complex, which leads to the formation of a manganese–oxo porphyrin two electrons oxidized above de $Mn^{III}$ state. In the case of $Mn^{IV}(O)P^{\cdot+}$ species, the first one-electron oxidation occurs in the manganese atom center and the second one-electron oxidation can occur on the porphyrin ligand [27]. To form the $Mn^{V}(O)P$ species, the second one-electron oxidation should occur in the mixed manganese and porphyrin $e_g$ orbitals. These mixed orbitals are more easily formed when the MnP contains an axial ligand, such as imidazole [10,11].

### 3.5.1. Mn(TPP)Cl

When the reaction between PhIO and Mn(TPP)Cl **1** in DCM is monitored by UV–Vis spectroscopy we observe the disappearance of the band at 478 nm, which means that the $Mn^{III}P$ is being consumed (Fig. 3). At 34 s of reaction (Fig. 3C), we can see a large band at 420 nm. This band has been assigned to a mixture of $Mn^{IV}(O)P^{\cdot+}$ and $Mn^{V}(O)P$ species [27]. The deconvolution of this spectrum [28] (Fig. 3, insert) can show the $Mn^{V}(O)P$ component of the spectrum at 408 nm and the $Mn^{IV}(OH)P$ at 430 nm. After 30 min of reaction, the band in 420 nm shifts to a sharper band in 430 nm, indicating the disappearance of $Mn^{V}(O)P$ species (Fig. 3D). In the absence of substrate, $Mn^{IV}(O)P^{\cdot+}$ species is converted to $Mn^{IV}(OH)P$, probably involving one-electron oxidation of the solvent. The $Mn^{IV}(OH)P$ species persists several hours and disappears slowly, and after 24 h, a 47% recovery of $Mn^{III}P$ is observed. It has been known that $Mn^{IV}(OH)P$ is relatively stable when compared with $Mn^{V}(O)P$ [6]. We observed the same spectral behaviour when the reaction was carried out at $-55$°C (Fig. 3) and at 25°C (data not shown).

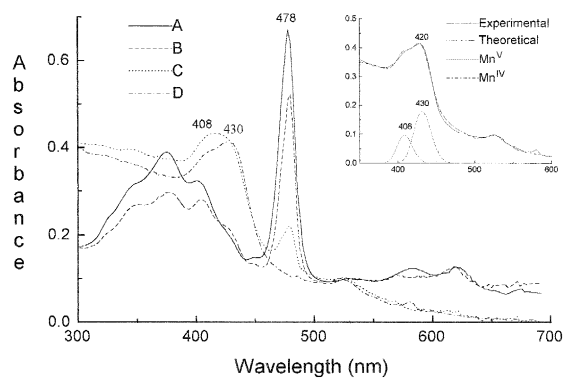



Fig. 3. UV–Vis spectra at $-55$°C of: (A) Mn(TPP)Cl (300 $\mu$L of $1.0\times10^{-4}$ mol $L^{-1}$) in DCM; (B) after addition of PhIO (150 $\mu$L of solution $1.2\times10^{-2}$ mol $L^{-1}$) in DCM to a solution of Mn(TPP)Cl (150 $\mu$L of solution $2.0\times10^{-4}$ mol $L^{-1}$); (C) B after 34 s of reaction; (D) B after 30 min of reaction. Insertion: Deconvolution of experimental spectrum D on Simulac [26] in the $Mn^{V}$ and $Mn^{IV}$ bands.

When the reaction occurs in the presence of imidazole we can see the fast formation of $Mn^{V}(O)P$ and a small amount of $Mn^{IV}(O)P^{\cdot+}$ (Fig. 4B), evidenced by a large band at 408 nm. In Fig. 4C, we can observe a decrease in the amount of $Mn^{V}(O)P$ species through the decrease in the intensity of the band at 408 nm, and the intensity of the absorption at 430 nm was unchanged, which corresponds to the $Mn^{IV}(O)P$ species initially present. The band at 478 nm disappears completely. In the presence of imidazole we can observe good percentage of recovery of the catalyst in its initial form $Mn^{III}P$ (80%), calculated after 24 h, based on the absorbance at 478 nm. It proves that the intermediate species $Mn^{V}(O)P$ predominates in the presence of imidazole. These results explain the higher yields and selectivity towards C-ol obtained with Mn(TPP)Cl **1** in the presence of imidazole if compared to the result attained in the absence of imidazole under the same conditions (Table 3).

It was observed in a report elsewhere [29] that in the reaction of Mn(TPP)IPG with PhIO, the $Mn^{V}(O)P$ and $Mn^{IV}(O)P^{\cdot+}$ species are formed promptly and simultaneously. However, the $Mn^{V}(O)P$ is converted to $Mn^{IV}(OH)P$ which is more stable. This factor explains why the catalytic activity of Mn(TPP)Cl **1** in the presence of imidazole is better than in the Mn(TPP)IPG system (Table 3).

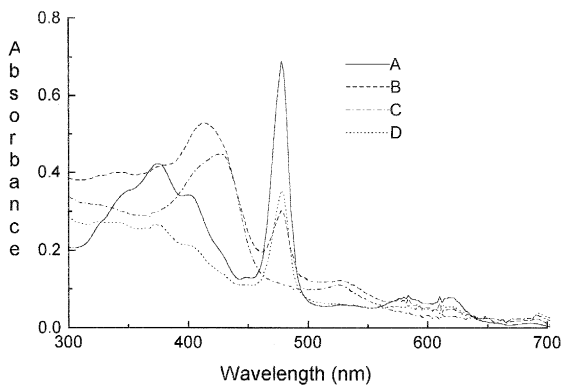



Fig. 4. UV–Vis spectra at 25°C of: (A) Mn(TPP)Cl ($1.0\times10^{-4}$ mol $L^{-1}$) with Imidazole ($1.0\times10^{-4}$ mol $L^{-1}$) in DCM. (B) After addition of PhIO (150 $\mu$L of solution $1.2\times10^{-2}$ mol $L^{-1}$) in DCM to a solution of Mn(TPP)Cl (150 $\mu$L of solution $2.0\times10^{-4}$ mol $L^{-1}$) containing imidazole ($2.0\times10^{-4}$ mol $L^{-1}$). (C) B after 60 s of reaction. (D) B after 20 min of reaction.

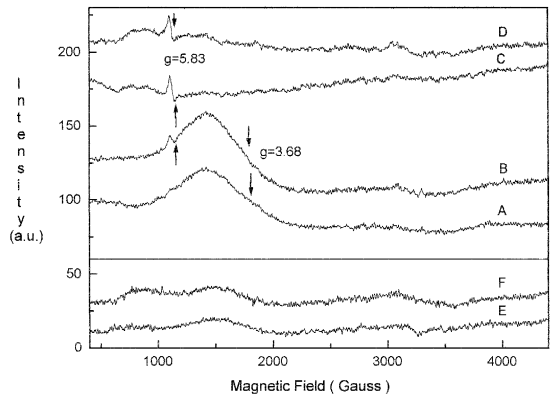



Fig. 5. EPR spectra of (A) MnTPPCl (200 $\mu$L of solution $1.0\times10^{-4}$ mol $L^{-1}$) with substrate (100 $\mu$L of cyclohexane) and $1.86\times10^{-6}$ mol of PhIO (B) After 30 min of reaction (C) B after 2 h of reaction. (D) B after 3 h of reaction. (E) MnTPPCl (200 $\mu$L of solution $1.0\times10^{-4}$ mol $L^{-1}$) with imidazole ($1.0\times10^{-4}$ mol $L^{-1}$) and substrate (100 $\mu$L of cyclohexane) and $1.9\times10^{-6}$ mol of PhIO. (F) B after 30 min of reaction.

Contrary to Mn(TPP)Cl, the catalytic activity of MnP with highly electrophylic substituents such as Mn(TDCPP)Cl **3** and Mn(TFPP)Cl **4** in the presence of imidazole is not as efficient as when they are supported on IPG. With these MnP, the bis imidazole complexes are stable [30], while in the IPG supported system, the 6th position is free in the catalytic site. For the unsubstituted Mn(TPP)Cl **1** though, even in the homogeneous system it is only pentacoordinated to imidazole and the catalytic site is available for the reaction with PhIO, and thus high efficiency is observed.

The EPR spectra of the reaction between Mn(TPP)Cl **1** and PhIO in the presence of substrate (cyclohexane) shows the formation of $Mn^{IV}(O)P^{\cdot+}$ species (Fig. 5A) with $g = 3.68$. After a long time of reaction (150 min) we also observed the appearance of a signal at 5.83 (Fig. 5C). Hill et al. [31] assigned this signal to $Mn^{II}P$ and it was interpreted as a result of a radicalar mechanism reaction promoted by $Mn^{IV}(O)P^{\cdot+}$, leading to the formation of a hy-

droxymanganese(IV) porphyrin complex, $Mn^{IV}(OH)P$, through hydrogen abstraction from the substrate. The reaction between $Mn^{III}$TPPCl **1** and free alkyl radicals produces the observed $Mn^{II}P$ and RX.

In the presence of imidazole and substrate the reaction is very fast and $Mn^{IV}(O)P$ species is detected in very low amounts and $Mn^{II}P$ is not detected (Fig. 5E and F). This means that the radicalar mechanism does not occur in this condition. In this way, the presence of imidazole is expected to promote the formation of $Mn^{V}(O)P$ which fastly oxidizes the substrate, and the EPR spectra (Fig. 5F) after 30 min of reaction does not show significative changes, which is in agreement with $Mn^{III}P$ recovery.

### *3.5.2. Mn(TDCPP)Cl*

In the reaction of PhIO with Mn(TDCPP)Cl **3** we observed the disappearance of the band at 478 nm, which means that the $Mn^{III}P$ is being consumed (Fig. 6B). The disappearance of $Mn^{III}P$ is followed by the formation of a large amount of $Mn^{IV}(O)P^{\cdot+}$ species, which presents a band at 420 nm (Fig. 6C). This spectrum also shows a small band at 408 nm, related to $Mn^{V}(O)P$ species formed in a small amount. Fig. 6D gives evidence of the disappearance of the $Mn^{V}(O)P$ species and shows that the $Mn^{IV}(O)P^{\cdot+}$ species remains in solution. After 2 h and 50 min, the catalyst $Mn^{III}P$ is partially recovered and after 24 h we can observe a 90% recovery. The poor catalytic activity observed for Mn(TDCPP)Cl **3** (Table 3) confirms that $Mn^{V}(O)P$ species is not formed in large amount. This homogeneous system contrasts with the heterogenized system, Mn(TDCPP)IPG, where high yields and selectivity towards C-ol were obtained in the cyclohexane hydroxylation (Table 3). In fact, it has been observed [29] that in the reaction of Mn(TDCPP)IPG with PhIO, only the $Mn^{V}(O)P$ species is formed (band at 409 nm).

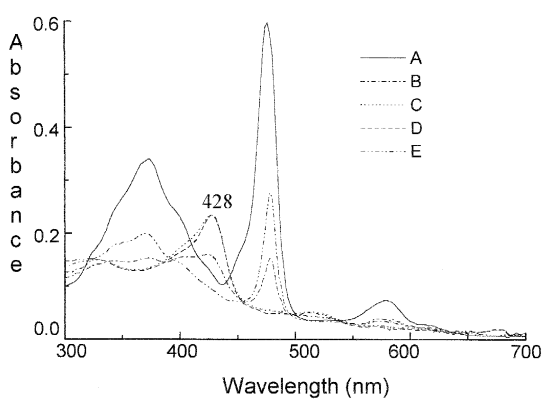



Fig. 6. UV–Vis spectra at 25°C of: (A) Mn(TDCPP)Cl (300 $\mu$L of $1.0\times10^{-4}$ mol $L^{-1}$) in DCM. (B) After addition of PhIO (150 $\mu$L of solution $1.2\times10^{-2}$ mol $L^{-1}$) in DCM to a solution of Mn(TDCPP)Cl (150 $\mu$L of solution $2.0\times10^{-4}$ mol $L^{-1}$) (C) B after 60 s reaction. (D) B after 7 min of reaction. (E) B after 2 h and 50 min of reaction.

## 4. Conclusions

The best conditions obtained for the higher efficiency of 1 and 2 were in the presence of imidazole, whereas with 3 and 4 the efficiency was not improved because the halogen-substituted MnP form very stable bis-imidazole complexes. Anchoring of such MnP on IPG results in better catalytic activity because in this case the catalyst is mono-coordinated to the imidazole from the support, which leaves the 6th coordination available for reaction with PhIO. The efficiency of 3 and 4 in homogeneous system was highly improved by adding trifluorosulphonate acid, which act as a weak coordinating ligand and cocatalyst. In a general way catalysts 2 and 4 showed higher efficiency.

The intermediate studies confirmed the catalytic results. The $Mn^{V}(O)P$ species detected by UV–Vis is always related to the more efficient catalyst system and the EPR results also explain the different catalytic activities for Mn(TPP)Cl systems in the presence and absence of imidazole. Mn(TDCPP)Cl showed to be less efficient for alkane hydroxylation and $Mn^{IV}(O)P$ was evidenced as the intermediate species.

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