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Manganeseporphyrin catalyzed cyclohexene epoxidation by iodosylbenzene The remarkable effect of the *meso*-phenyl *ortho*–OH substituent

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Abstract

Catalytic cyclohexene epoxidation with iodosylbenzene by the following Mn-porphyrins bearing *ortho* substituents on a *meso* group: MnTTP, $MnM_{2\text{-}OH}PTTP$(5-(2-hydroxyphenyl)-10,15,20-tritolylporphyrin) and $MnM_{2\text{-}Br}PTTP$(5-(2-(3-bromo-1-propoxy)phenyl)-10,15,20-tritolylporphyrin), has been studied. The effect of dioxygen and imidazole axial ligand on the yields of epoxide and allylic oxidation products, i.e. alcohol and ketone, was investigated. It was observed that the product selectivity is strongly dependent on the distribution of the Im/MnP species (M, MIm and MIm_2 obtained by spectrophotometric titrations). For MnTPP at Im/MnP = 1 the best epoxide yield associated with the maximum MIm concentration was observed. The presence of the –OH substituent produced a remarkable effect on the reactivity and catalytic properties of the porphyrin system, i.e. drastic reduction in allylic oxidation, slight increase on the epoxide yield, a decrease on the formation of the MnP/Im complexes and change of the reactivity of the Mn center with PhIO. These results are discussed in terms of a possible electronic interaction of the oxygen *ortho* substituent and the porphyrin ring.

Keywords: Manganeseporphyrin; Cyclohexene epoxidation; Iodosylbenzene; *Meso*-phenyl *ortho*–OH substituent

1. Introduction

Metalloenzymes accomplish reactions of oxidation of inactive substrates with high speed, selectivity and specificity [1,2]. The development of biomimetic systems to understand and reproduce the mechanism of highly selective enzymatic systems has been extensively investigated [1,2]. Among the several model systems, the ones considered most efficient are those based on Mn(III) porphyrins [3–6] and Fe(III) [4–9]. The active species in Fe- and Mn-porphyrins are high valence metal–oxo complexes, formally Fe(V)–oxo and Mn(V)–oxo [4–6,10]. Previous studies [11] revealed that the presence of substituents at *ortho* positions of the porphyrin rings increases the efficiency of the catalytic process, preventing autoxidative reactions and the aggregation of the catalyst. Simple metalloporphyrins like FeTPP or MnTPP, are easily destroyed by autoxidation, mainly when less reactive substrate such as alkanes are studied [12,13]. Therefore, the use of these metalloporphyrins as potential catalysts depends mainly on the modification of the porphyrin ring to make it more resistant to oxidative degradations [14,15]. The stability and the selectivity of these catalysts have been improved introducing

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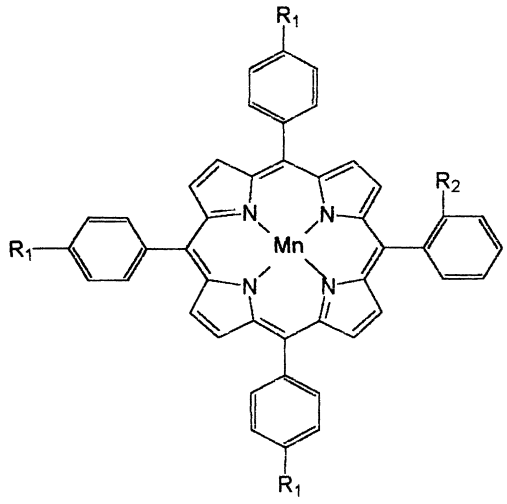


Porphyrin	R_1	R_2
MnTPP	H	H
$MnM_{2\text{-}OH}PTTP(Ac)$	CH_3	OH
$MnM_{2\text{-}Br}PTTP(Ac)$	CH_3	$O(CH_2)_3Br$

Fig. 1. Structure of the manganeseporphyrins studied.

bulky and/or electronegative substituents in the porphyrin ring, generally, in the *meso-ortho*-aryl positions [14–18].

Among the hydrocarbon porphyrin catalyzed oxidation reactions, olefin epoxidation has been the most studied. These studies have largely contributed for the characterization of intermediaries and the understanding of the reaction mechanisms. Besides the epoxide, allyl derivatives (alcohol and ketone) are important products of these reactions, whose formation seems to depend on the number of carbons of the substrate and the steric and/or electronic environment created by the porphyrin ring [19].

In this work, a systematic and comparative study of the catalytic epoxidation of cyclohexene by two monosubstituted Mn-porphyrins (Fig. 1) $MnM_{2\text{-}OH}PTTP(Ac)$ (5-(2-hydroxyphenyl)-10,15,20-tritolylporphyrinmanganese(III) acetate) and $MnM_{2\text{-}Br}PTTP(Ac)$ (5-(2-(3-bromo-1-propoxy)phenyl)-10,15,20-tritolylporphyrinmanganese(III) acetate) has been carried out. The effects of the substituent on the porphyrin ring, the presence of imidazole, and the presence of dioxygen have been investigated.

2. Experimental section

2.1. Materials

Dichloromethane (CH_2Cl_2) was distilled and stored under 3 Å molecular sieves. Cyclohexene was purified with a short activated alumina column. The purities were checked by gas chromatographic analyses. Iodosylbenzene was obtained by the hydrolysis of iodosylbenzenediacetate [20]. The samples were stored in a freezer and the purity was checked by iodometric assay.

MnTPP(Ac) was purchased from Strem Chemicals. UV–VIS (CH_2Cl_2): MnTPP(Ac)-(400) 476, 579, 617 nm. The free bases 5-(2-hydroxyphenyl)-10,-

15, 20-tritolylporphyrin-(1) [21–22] and 5-(2-(3-bromo- 1-propoxy)phenyl-10,15,20-tritolylporphyrin-(2) [22,23] were prepared as described by Little et al. [21,23]. Manganese insertion into the free base porphyrin was made by adapting the method described by Simonis et al. [24]. Acetate of 5-(2-hydroxyphenyl)-10,15,20-tritolylporphyrinmanganese(III)-($MnM_{2\text{-OH}}$PTTP(Ac)) and acetate of 5-(2-(3-bromo-1-propoxy)-phenyl)-10,15,20-tritolylporphyrin manganese(III)-($MnM_{2\text{-Br}}$PTTP(Ac)) were purified in a silica column, using a chloroform–ethanol 1:1 mixture and chloroform, respectively, as eluent. The purity of the porphyrins was checked by thin layer chromatography.

^{1}H NMR spectra were obtained with a Brucker DRX-400 Advance (400 MHz) spectrometer using $CDCl_3$ as the solvent and TMS as internal reference. ^{1}H NMR free base-(1): $\delta = 8.92$–8.84 (m, 8H, β-pyrrole); 8.08 (d, 6H, tolyl-2,6-protons); 7.54 (d, 6H, tolyl-3,5-protons); 5.12 (s, 1H, –OH); 2.65 (s, 9H, methyl); 7.21(m, 4H, Ar–H substituted). ^{1}H NMR free base-(2): $\delta = 8.82$–8.43 (m, 8H, β-pyrrole); 8.09 (d, 6H, tolyl-2,6-protons); 7.53 (d, 6H, tolyl-3,5-protons); 4.01 (m, 2H, $–CH_2–O$); 2.68 (s, 9H, methyl); 2.21 (t, 2H, $–CH_2Br–$); 1.46 (s, 2H, $–CH_2–$); 7.22(m, 4H, Ar–H substituted).

UV–VIS spectra were obtained on a Hewlett Packard Diode Array model 8453 spectrophotometer. $MnM_{2\text{-OH}}$PTTP(CH_2Cl_2): (402) 479, 583, 618 nm; $MnM_{2\text{-Br}}$PTTP(CH_2Cl_2): (403) 480, 584, 620 nm.

IR spectra were recorded on a Mattson FTIR model Galaxy 3000 spectrometer using KBr plates. Free base (1): OH ν_{stretch} at 3415 cm^{-1}; NH ν_{stretch} at 3300 cm^{-1}.

2.2. Oxidation reactions

The reactions were carried out in a 2.0 ml vial with an open top screw cap containing a silicon Teflon faced septum. In a typical reaction, 400 μl of dichloromethane and 200 μl of cyclohexene (1.97×10^{-3} mol) were added to the vial containing the solids iodosylbenzene (1.2×10^{-6} mol), and MnP (1.2×10^{-7} mol) with a molar ratio of catalyst:PhIO:cyclohexene of 1:10:16400. The mixture was stirred by ultrasound for 90 min (ultrasound laboratory cleaner Minisson–Thorthon, 40 W, 50–60 Hz) at 0°C (ice bath). The reaction was quenched by adding 50 μl of saturated sodium bisulfite, and 50 μl of saturated borax solution in dichloromethane. *n*-Octanol (100 μl) was used as internal standard for the GC analysis.

The effect of imidazole was studied with the addition of a 1.0×10^{-1} mol l^{-1} imidazole (Im) solution in dichloromethane to the vial to obtain different Im/MnP molar rations.

For the experiments in the absence of oxygen, the reaction flask was purged with N_2 for about 30 min before use. All reactions were repeated at least three times. The control reaction (blank) was carried out under the same conditions, in the absence of MnP.

2.3. Spectrophotometric titration

The spectrophotometric titrations were carried out with a stock solution of Mn-porphyrin in dichloromethane (10^{-5} mol l^{-1}); 50 μl of this solution was transferred to a glass cuvet containing 2.0 ml of solvent, thermostated at 25.0 ± 0.1°C. The spectrum of Mn-porphyrin was recorded and its initial concentration was corrected by the coefficient of absorption of Mn-porphyrin. Ligand aliquots (imidazole) were added consecutively to the cuvet with a microsyringe and the UV–VIS electronic spectra recorded. The end of the titration was determined when UV–VIS spectra variations ceased. The number of axial ligands, as well as the formation constants ($\log \beta$) were calculated based on the measured absorbances as a function of the volume of imidazole added. Both the model that best describes the system and the formation constants of the species present were determined by the software SQUAD [25]. The distribution curves of the species were simulated by the program SCECS [26].

2.4. Product analysis

The products were analyzed by gas chromatography using *n*-octanol as internal standard. The yields were based on iodosylbenzene. Gas chromatographic analyses were performed on a Shimadzu CG 17A FID detector with a Carbowax capillary column (30.0 m × 0.32 mm and film thickness 0.25 mm).

2.5. UV–VIS spectroscopic studies

To the vial containing PhIO (1.2×10^{-6} mol) and MnP (1.2×10^{-7} mol), 600 μl of CH_2Cl_2 were added. The mixture was stirred manually at 25°C for 1 min. A 50 μl aliquot of mixture was added to a 0.1 cm path length cell containing 2.0 ml of CH_2Cl_2. Consecutive spectra were recorded at different times.

3. Results

3.1. Cyclohexene epoxidation

Table 1 presents the results for the oxidation of cyclohexene with iodosylbenzene in the presence of Mn-porphyrins catalysts.

It can be observed for several experiments yields higher than 100% suggesting the incorporation of oxygen from O_2 into the products. For the reactions under nitrogen yields superior to 100% were also observed showing that the O_2 was not completely removed from the system. The catalytic tests carried out in the presence of the different Mn-porphyrins showed that the epoxide yield is not affected significantly by neither the porphyrin substituent nor the presence of oxygen. On the other hand, the yields of allylic oxidation products are strongly dependent on the O_2 atmosphere and the nature of the porphyrin substituent. Reactions under O_2 atmosphere even in the absence of the Mn-porphyrin produced large amounts of the allylic oxidation products especially the alcohol (blank experiment, Table 1). The presence of the catalysts MnTPP and $MnM_{2\text{-}Br}PTTP$ produced almost no change in the alcohol formation but a strong increase in the ketone yield. It is interesting to observe that the presence of the –OH substituent in the $MnM_{2\text{-}OH}PTTP$ catalyst resulted in a slight increase in the epoxide yield with a remarkable decrease on the formation of the allylic products especially the alcohol.

Table 1
Oxidation of cyclohexene with PhIO in CH_2Cl_2, using manganeseporphyrins as catalyst. Effect of the dioxygen[a]

Manganeseporphyrin	Yield (%)[b]		
	Epoxide	Alcohol	Ketone
Blank	5	110	72
MnTPP	50 (47)[c]	125 (22)	160 (31)
$MnM_{2\text{-}Br}PTTP$	49 (49)	118 (42)	131 (38)
$MnM_{2\text{-}OH}PTTP$	55 (55)	71 (20)	61 (15)

[a] Conditions: MnP 2.0×10^{-4} mol l^{-1}, PhIO 2.0×10^{-3} mol l^{-1}; 0°C; stirring by ultrasound for 90 min.

[b] Based on the starting PhIO with average error of ± 4% for the epoxide and ± 15% for the alcohol and ketone. Molar ratio PhIO/MnP = 10.

[c] Number in parentheses are the yields obtained under nitrogen atmosphere.

The results displayed in Table 1 might suggest the presence of at least three different reaction pathways: (1) the formation of the allylic oxidation products by the direct reaction with $PhIO/O_2$; and by a (2) Mn-porphyrin catalyzed process; and (3) a reaction leading to the formation of the epoxide. The reactions forming the allylic products are both strongly affected by the substituent and the presence of O_2. The pronounced effect of O_2 increasing the allylics yields might suggest the participation of free radicals in this reaction pathway [1,2,19]. On the other hand, the epoxide formation is less sensitive to these effects.

3.2. The effect of imidazole

Fig. 2a, b and c show the effect of the Im/Mn-porphyrin molar ratio on the reaction products yields.

It can be observed that the product yields are strongly dependent on the Im/MnP molar ratios tested. From Fig. 2a, b and c, it can be clearly seen that the catalysts MnTPP (Fig. 2a) and $MnM_{2\text{-}Br}PTTP$ (Fig. 2b) behave similarly in the entire Im/MnP molar ratio studied, producing mainly the ketone and the alcohol. The highest epoxide yields with low allylics were observed at the Im/MnP = 1. Further addition of Im resulted in an increase on the formation of allylics. On the other hand, the addition of imidazole to the $MnM_{2\text{-}OH}PTTP$ (Fig. 2c) catalyst at the molar ratio Im/MnP = 0.5 reduced the ketone and alcohol yields. For greater Im/MnP molar ratios no significant change in the allylics and a decrease in the epoxide yield was observed.

3.2.1. Titration of Mn-porphyrins with imidazole

In the presence of the imidazole ligand the Mn-porphyrin might exist in three different species in equilibrium: M, MIm and MIm_2 (where M = MnP

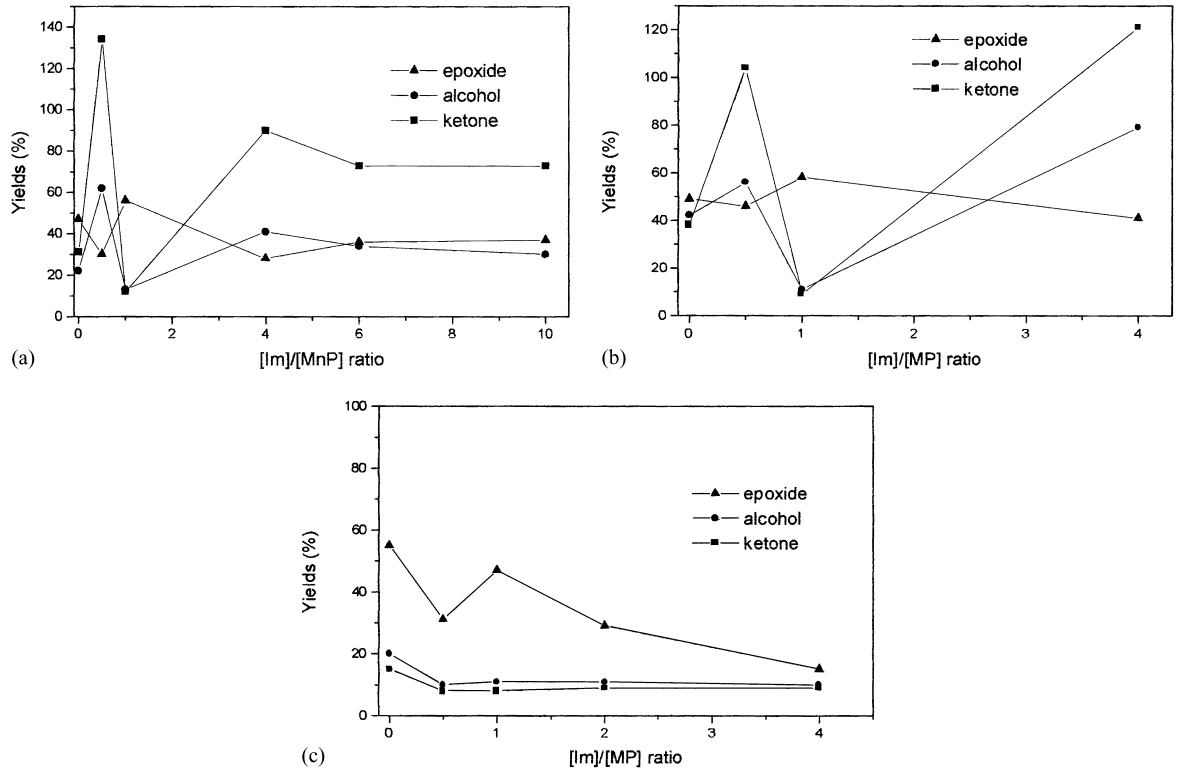
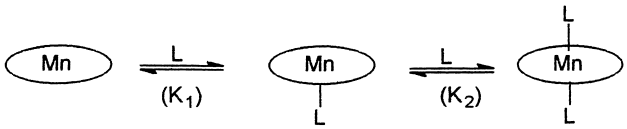


Fig. 2. Yields of epoxide, alcohol and ketone for the oxidation of cyclohexene with PhIO with different Im/MnP molar ratios, (a) catalyst MnTPP, (b) $MnM_{2\text{-}Br}PTTP$, and (c) $MnM_{2\text{-}OH}PTTP$.

and Im = imidazole, Eq. (1)).



$$K_1 = \beta_{11}$$
$$K_1 \times K_2 = \beta_{12} \quad (1)$$

In order to understand the effect of the Im/MnP molar ratio on the relative concentration of the different species present in the reaction, spectrophotometric titration of Mn-porphyrins with imidazole were carried out. The experimental values obtained for the equilibrium constants are displayed in Table 2.

Table 2 shows that the stability of the first complex formed MIm increases in the order $MnM_{2\text{-}OH}PTTP \ll MnM_{2\text{-}Br}PTTP <$ MnTPP. The imidazole complex of the MnTPP showed the highest stability. The introduction of the substituent $–OCH_2CH_2CH_2Br$ decreases the formation of the complex, especially the second complexation K_2. One can speculate that this low value of K_2 might be related to a possible steric effect by the bulky substituent $–OCH_2CH_2CH_2Br$ blocking one of the faces of the macrocycle and therefore, hindering the entrance of the second ligand.

The presence of the –OH substituent shows a much more pronounced effect strongly decreasing the formation of the complex with imidazole. As this –OH substituent causes no steric hindrance for the complexation one can consider that the electronic effect is the main responsible for this result. The acidic character of the –OH group may lead to the reaction with the

Table 2
Parameters supplied by the SQUAD program obtained in the titrations of Mn-porphyrins with Im in CH_2Cl_2

Mn-porphyrins	$\log \beta_{11}$	$\log \beta_{12}$	K_1	K_2	K_1/K_2
MnTPP	6.00±0.06	9.60±0.07	1.00×10^6	3.98×10^3	251
	(4.35±0.43)[a]	(7.45±0.04)[a]		(9.2×10^3)[b]	
$MnM_{2\text{-}Br}PTTP$	4.26 ± 0.05	6.59 ± 0.05	1.82×10^4	2.13×10^2	86
$MnM_{2\text{-}OH}PTTP$	2.83 ± 0.02	5.29 ± 0.02	6.76×10^2	2.88×10^2	2.4

[a] Reference [25] method SQUAD: $MnTPP(ClO_4)/Im/CH_2Cl_2$.
[b] Reference [27] method Benesi–Hildebrand: $MnTPP(Cl)/Im/CH_2Cl_2$.

basic molecule of imidazole forming HIm^+ and the substituent $–O^-$. This was confirmed by ^1H NMR and IR experiments with the $M_{2\text{-}OH}PTTP$ free base which showed that the –OH group observed at δ 5.12 ppm and 3415 cm^{-1} completely disappears upon addition of imidazole. Moreover, bands appear in δ 9.39 ppm and 3490 cm^{-1} assigning to HIm^+.

The distribution curve of the species for the Im/MnTPP system in CH_2Cl_2 is shown in Fig. 3. It can be observed that the maximum relative concentration of MIm species is reached for the Im/MnP molar ratio equal 1. In this molar ratio, there is ca. 87% of the MIm species and 13% of the M species. As the Im concentration increases, the MIm species strong decrease with the formation of the MIm_2 complex. Also, in Fig. 3 the epoxide yields for the different Im/MnTPP molar ratios are plotted. These results seem to suggest that the formation of epoxide depends mainly on the concentration of the M and MIm species. As Im is added to the reaction up to the Im/MnP molar ratio 0.5 the epoxide yield decreases probably due to a strong decrease on the concentration of the M species. For Im/MnP molar ratio 1 although the concentration of M further decreases, the concentration of MIm is maximum and the epoxide yield shows an increase. Further increase in the Im concentration results in a decrease of both M and MIm concentrations resulting in a decrease on the epoxide yield. The same behaviour was observed for the porphyrin $MnM_{2\text{-}Br}PTTP$ (data not shown).

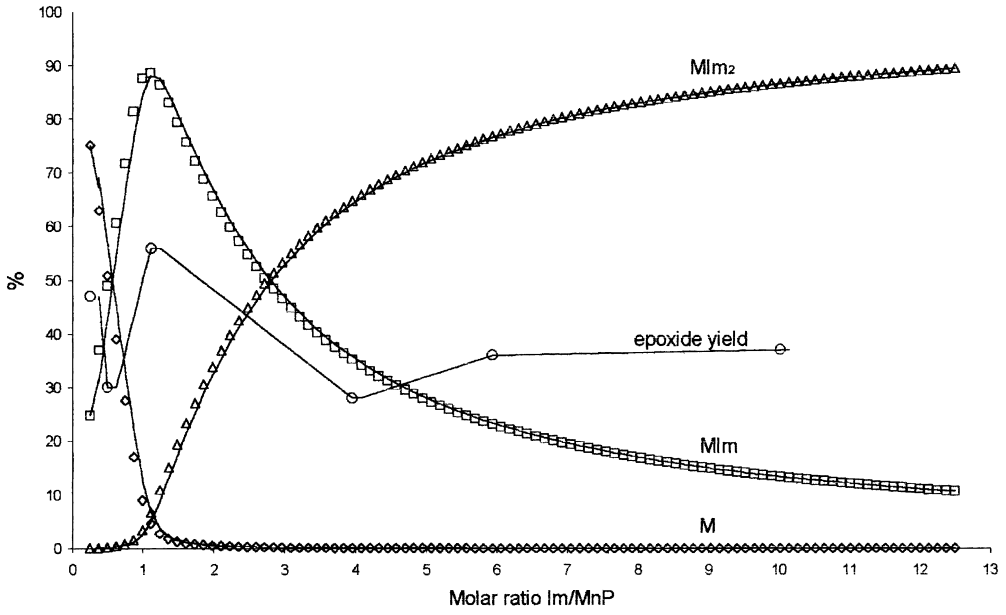


Fig. 3. Distribution curves of the species (M, MIm and MIm_2) for the system Im/MnTPP, in CH_2Cl_2; MnP 2.0×10^{-4} mol l^{-1}.

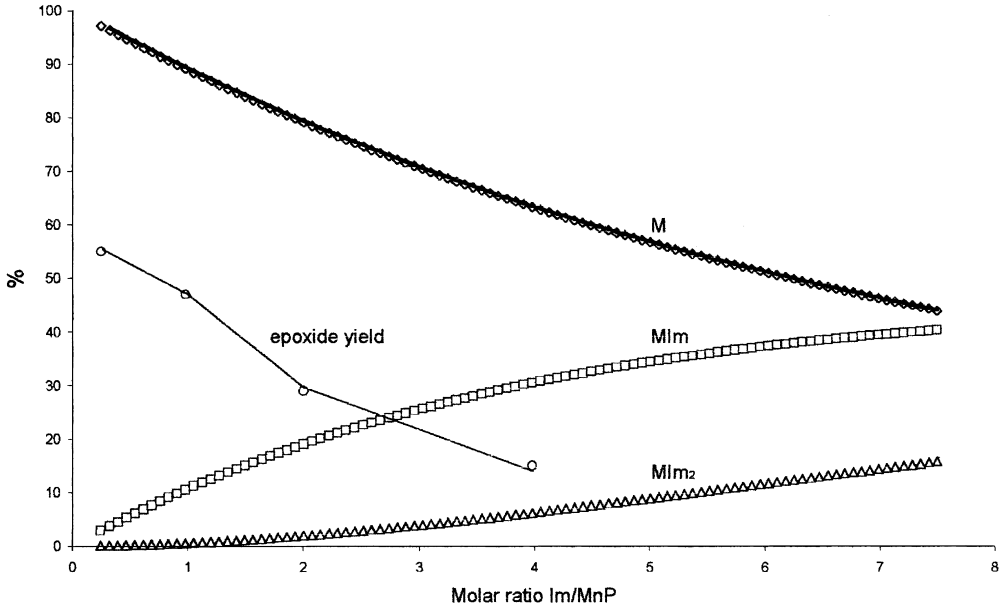


Fig. 4. Distribution curves of the M, MIm and MIm_2 species for the Im/$MnM_{2\text{-}OH}$PTTP system, in CH_2Cl_2; MnP 2.0×10^{-4} mol l^{-1}.

The distribution curves of the species M, MIm and MIm_2 for the system Im/$MnM_{2\text{-}OH}$PTTP (Fig. 4) are completely different compared to the other porphyrins. It can be observed that even for high Im/MnP molar ratios the concentration of M slowly decreases with the formation of MIm and very small amounts of MIm_2. In this case, the epoxide yield seems to decrease mainly with the concentration of the M species.

3.3. UV–VIS spectroscopic studies

The reaction of the different porphyrins at 25°C with PhIO in CH_2Cl_2 was monitored by UV–VIS spectroscopy. Fig. 5 shows the evolution of the spectrum after the MnTPP was mixed with PhIO.

The mixture of MnTPP and PhIO in CH_2Cl_2, after 1 min of reaction, shows a large band at 420 nm and the Soret absorption intensity at 478 nm decreases. The band at 420 nm has been reported in the literature and assigned to a Mn–oxo intermediate species [28]. The subsequent spectras showed a continuous recovery of the Soret band (478 nm) and the band in 420 nm shifts to a sharper band in 414 nm. If more PhIO was added to the mixture the same behaviour was observed with the decrease of the Soret absorption (which slowly increased) and the reappearance of the band at 420 nm which decreased with time. These results suggest that a Mn–oxo species is rapidly formed in the presence of PhIO and slowly reacts regenerating the original Mn-porphyrin. After a period of 20 h the solution changes the color and the band at 478 nm almost disappears indicating the destruction of the MnTPP. The same behaviour was observed for the porphyrin $MnM_{2\text{-}Br}$PTTP with a large band at 417 nm and the Soret absorption at 479 nm (data not shown). On the other hand, for the porphyrin $MnM_{2\text{-}OH}$PTTP no change in the electronic spectrum was observed in the first minutes after the addition of PhIO (Fig. 6) with the Soret band at 479 nm constant and no new absorption appearing. However, the rapid change in color and the disappearance of the Soret band at 479 nm suggests that an oxidizing species was indeed formed leading to the autoxidation of porphyrin. Apparently this active oxidizing species with the porphyrin $MnM_{2\text{-}OH}$PTTP is not detected under the experimental conditions used in this work due to its higher reactivity and shorter life time. In fact, kinetics experiments showed that during the oxidation of cyclohexene with PhIO in the presence of $MnM_{2\text{-}OH}$PTTP the epoxide is formed very

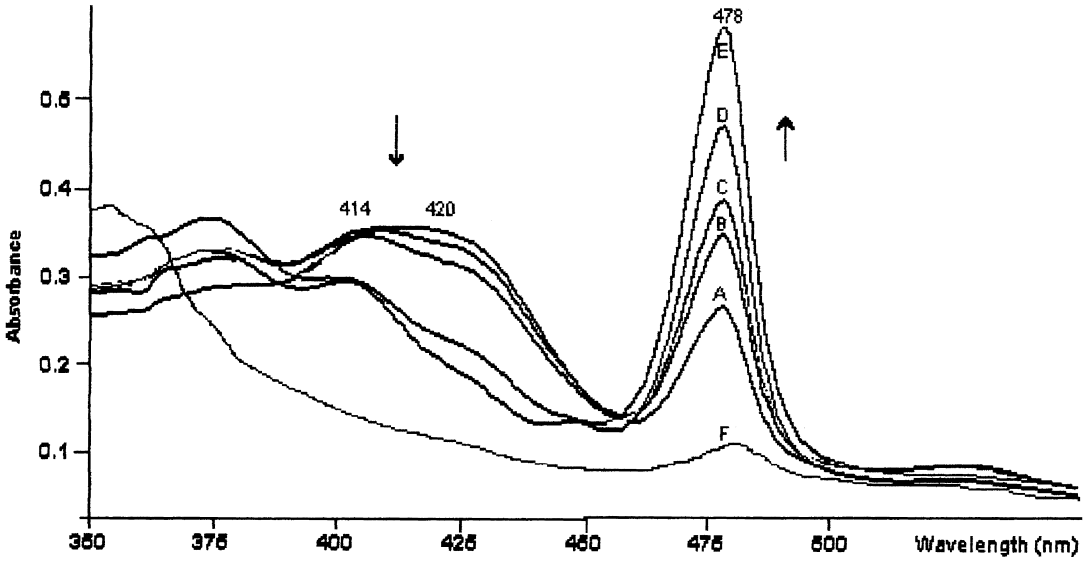


Fig. 5. Spectral changes observed during the reaction of MnTPP (4.9×10^{-6} mol l^{-1}) with PhIO (4.9×10^{-5} mol l^{-1}) in CH_2Cl_2 at 25°C at different times. A: after 1 min of reaction; B: after 2 min of reaction; C: after 4 min of reaction; D: after 9 min of reaction; E: after 120 min of reaction; F: after 20 h of reaction.

rapidly and stabilizes at approximately 10 min whereas for the catalyst MnTPP the reaction is much slower with the epoxide formation continuing up to ca. 50 min reaction.

4. Discussion

The data shown in Table 1 suggest that the porphyrin ring substituents do not affect significantly the epoxide

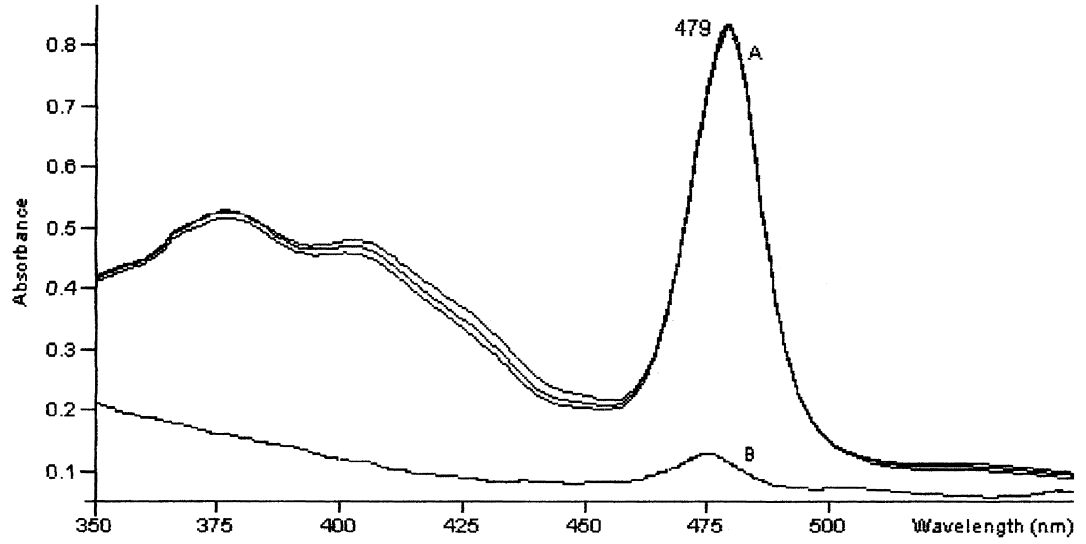


Fig. 6. Spectral changes observed during the reaction of $MnM_{2\text{-}OH}PTTP$ (4.9×10^{-6} mol l^{-1}) with PhIO (4.9×10^{-5} mol l^{-1}) in CH_2Cl_2 at 25°C in the time interval of 1–90 min (A) and after 20 h of reaction (B).

yield in the cyclohexene oxidation with PhIO. On the other hand, the presence of the substituent –OH in the porphyrin $MnM_{2\text{-}OH}PTTP$, produced a reduction in the formation of the ketone and alcohol whereas the catalysts MnTPP and $MnM_{2\text{-}Br}PTTP$ showed high yields of allylic products. The different catalytic behaviour of the $MnM_{2\text{-}OH}PTTP$ (Fig. 2c) compared to the other porphyrins was also observed for the reactions in the presence of the imidazole ligand. For the catalysts MnTPP (Fig. 2a) and $MnM_{2\text{-}Br}PTTP$ (Fig. 2b) the presence of the Im ligand strongly favours the formation of the allylics except for the Im/MnP molar ratio 1 where an optimum yield of epoxide is observed. On the other hand, for the catalyst $MnM_{2\text{-}OH}PTTP$ the addition of Im to the system will decrease and keep low the yields of allylics.

The spectrophotometric titrations with imidazole also revealed the different properties of the $MnM_{2\text{-}OH}PTTP$ compared to the MnTPP and $MnM_{2\text{-}Br}PTTP$ porphyrins. In the presence of the ligand Im the porphyrins MnTPP and $MnM_{2\text{-}Br}PTTP$ can rapidly complex to form the species MIm ($K_1 = 1.00 \times 10^6$ and $K_1 = 1.82 \times 10^4$, respectively). For the molar ratio Im/MnP = 1, the MnTPP shows a maximum MIm concentration which decreases for higher Im/MnP molar ratios to produce the MIm_2. On the other hand, the coordination of Im to the $MnM_{2\text{-}OH}PTTP$ ($K_1 = 6.76 \times 10^2$) occurs in a much lesser extension and the MIm species is formed only very slowly with the increase of the Im/$MnM_{2\text{-}OH}PTTP$ molar ratio.

Evidence for the reaction of PhIO with the porphyrins MnTPP (Fig. 5) and $MnM_{2\text{-}Br}PTTP$ was obtained from UV–VIS measurements. The results for the porphyrin $MnM_{2\text{-}OH}PTTP$ (Fig. 6) suggest that a more reactive active oxidizing species is formed and due to its shorter life time it cannot be detected by electronic spectroscopy under the experimental conditions employed.

As the –OH group causes no steric hindrance at the metallic center in $MnM_{2\text{-}OH}PTTP$ one can consider that the electronic effect is the main responsible for the results obtained in this work. The acidic nature of the phenolic –OH might form an *o*-phenoxide $–C_6H_4O^-$ group. This effect occurs in the presence of the basic imidazole ligand which can neutralize the acidic H. The poor interaction of Im with $MnM_{2\text{-}OH}PTTP$ ($K_1 = 6.76 \times 10^2$) as shown by the spectrophotometric titrations is likely related to the formation of $–C_6H_4O^-$ group. It is generally proposed in the literature [29] that low levels of allylic oxidation and high levels of epoxidation indicate an active intermediate containing two oxidizing equivalents localized in the vicinity of the center of the catalyst (Type-1 intermediate). Therefore, efficient epoxidations obtained with Mn-porphyrins are thought to involve an oxo–Mn(V) intermediate [29–32]. Basic ligands such as pyridine and imidazole are believed to favour the epoxide formation by stabilizing the Mn(V) state through charge donation to the metal [30,33,34]. Therefore, the similar epoxide yields observed for the different porphyrins suggests that the electronic interaction of the substituents with the Mn(V) center are not significant. Moreover, in these *meso*-porphyrins the phenyl moiety and the porphyrin ring are proposed to be mainly in a non-coplanar arrangement hindering a resonance-type interaction [35,36].

It is interesting to observe that the effect of –OH substituent on the Mn-porphyrin is much more pronounced for the allylic oxidation products whereas the epoxide formation was less affected. It has been suggested that the allylic oxidations in the presence of Mn-porphyrins are associated with an oxidizing equivalent located on the porphyrin ring in the form of a porphyrin π cation radical or an isoporphyrin derivative (Type-2 intermediate) [31,32]. Considering this assumption, it can be speculated whether the –OH or $–O^-$ substituent is interacting with this π cation radical on the porphyrin ring stabilizing it and therefore decreasing its reactivity towards the cyclohexene. An interesting example in the literature is the porphyrin oxo–Fe(IV)$TP_{2,4,6\text{-}Me}P(CH_3OH)$ which although has been characterized a Type-2 intermediate [37–39] it behaves more like a Type-1 intermediate. It was suggested for this Fe-porphyrin that the Me groups obstruct the *meso* position. As the a_{2u} macrocycle HOMO has lobes over the *meso* position and the pyrrole nitrogen this obstruction means that access to the macrocycle acceptor orbital is restricted to the pyrrole lobes. The pyrroles lobes are quite close to center of the porphyrin thus forcing the reaction to take place near to the metallic center. Therefore, the cation radical approximates a Type-1 intermediate [29,33,34]. One can expect that the *ortho* $–C_6H_4–OH$ group at *meso* position will exert similar effect. It can also be speculated that the orbitals of the –OH (or $–O^-$)

substituent might interact with the a_{2u} HOMO molecular orbital to change the reactivity of the π cation radical. Therefore, the step occurring in the outersphere of the metal where an electron is transferred from cyclohexene to form a $C_6H_{10}^{\bullet+}$ species in some extension is hindered. Therefore, the reaction of the $C_6H_{10}^{\bullet+}$ species with the Mn(IV)=O center to form Mn(III) and the alcohol is also inhibited [33,34,40–42].

5. Conclusions

The data presented in this work pointed a remarkable effect of the *ortho*–OH group on the physico-chemical properties of the phenyl-*meso* substituted porphyrins. This effect can be discussed in terms of a possible electronic interaction of the –OH or $–O^-$ group with the porphyrin system.

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