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Kinetics and mechanistic studies on the formation and reactivity of high valent MnO porphyrin species: mono-ortho or parasubstituted porphyrins versus a di-ortho-substituted one

Rahele Nasrollahi and Saeed Zakavi*

The high valent $Mn^{V}(O)$ ($\lambda_{max} \approx 407 \text{ nm}$) and $Mn^{V}(O)$ ($\lambda_{max} \approx 421 \text{ nm}$) species of a series of electron-rich and electrondeficient meso-tetra(aryl)porphyrins (aryl = phenyl, 2-chlorophenyl, 2-nitrophenyl, 2-methylphenyl, 2-bromophenyl, 2,6dichlorophenyl 4-methoxyphenyl, 4-methylphenyl, 4-chlorophenyl and 4-pyridyl) were prepared through the reaction of their corresponding manganese porphyrins with Oxone in dichloromethane at a relatively low temperature (273 K). While the high valent Mn(O) intermediates of the para-substituted porphyrins were significantly degraded under reaction conditions, the corresponding species of the ortho substituted porphyrins showed high oxidative stability up to 20 min. Interestingly, the high valent Mn(O) of the mono-ortho-substituted meso-tetra(phenyl)porphyrins were as stable as that of meso-tetra(2,6-dichlorophenyl)porphyrins. The presence of imidazole (ImH) was found to play crucial roles in the formation and reactivity of the high valent Mn(O) species. The kinetics and mechanism of the oxidation of olefins with the high valent Mn^V(O) porphyrin intermediate were studied and the second order rate constants were evaluated under pseudo-first-order conditions. Also, the Mn^{IV}(O) species showed a reactivity comparable with that of the corresponding MnV(O) species. The observation of a Hammet constant of $\rho = -0.48$ in the oxidation of para-substituted styrenes is in accord with an electrophilic mechanism.

Introduction

Catalytic, electron-transfer and structural properties of heme and non-heme high valent metal-oxo species have been the subject of extensive computational and experimental investigations over the past decades. From the catalytic point of view, these species are used to mimic the active site of cytochrome P450 (CYP) enzymes.¹⁻⁵ A high valent oxo-iron(IV) porphyrin π cation radical is known to be involved in the catalytic cycle of CYP ^{3,6-7}. While there are simple alkyl and alkenyl substituents at the porphyrin periphery of CYP enzymes, the active site is surrounded by protein residues which can efficiently protect the substrate-free ferric resting state of CYP from the oxidative degradation by the high valent iron-oxo intermediate ⁸. Over the past decades, synthetic metalloporphyrins with different meso and/or β substituents have been used to mimic the active site of CYP.⁸ In contrast to

the high valent iron oxo porphyrin intermediates, the nature of manganese(V)-oxo porphyrins has been debatable until Groves et al. reported the UV-Vis and ¹H NMR spectra of Mn(O) porphyrins in aqueous solution.^{9,10} After this report, the high valent manganese oxo porphyrin intermediate of a wide range of electron-deficient manganese porphyrins was characterized by Nam et al. by Raman and X-ray absorption spectroscopy/extended X-ray absorption fine structure spectroscopy (XAS/EXAFS).¹¹ Also, the latter was used in different biomimetic organic transformations ¹². A literature survey reveals that the high valent metal-oxo complexes of metalloporphyrins with electron demanding or sterically hindered substituents at the porphyrin periphery are sufficiently stable which allows the study of their catalytic activity at relatively high temperatures. Accordingly, most of the previous studies on the high valent metal-oxo species devoted to this family of metalloporphyrins^{1,2,5,9-14}.

The coordination of axial ligands in the trans position of the metal-oxo group of heme enzymes plays crucial roles in the reactivity of the enzymes^{15,16}. In this study, the presence of imidazole (ImH) was found to play crucial roles in the stabilization and reactivity of the high valent manganese(IV and V)-oxo porphyrin intermediates. The oxidation of organic compounds with Oxone and its organic derivatives catalyzed

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by manganese and iron porphyrins have been studied in details ¹⁷⁻²⁴. However, there are limited reports on the kinetics of these reactions. Very recently, we have reported kinetic and mechanistic studies of the oxidation of alcohols with highvalent manganese oxo species formed by the reaction of meso-tetrakis(2,6-dichlorophenyl)porphyrinatomanganese(III) acetate, [MnT(DCl)PP(OAc)] and tetra-n-butylammonium oxone (TBAO)³². In the present study, the formation of high valent metal-oxo species for the manganese complexes of meso-tetra(aryl)porphyrins (aryl = phenyl, 2-chlorophenyl, 2methylphenyl, 2-bromophenyl, 4-chlorophenyl. 4methoxyphenyl and 4-pyridyl) was evidenced by UV-vis spectroscopy studies at a relatively low temperature. The main objective of the present work is to study the formation and reactivity of the high valent manganese oxo intermediates of structurally simple, low cost and easily synthesized porphyrins. Furthermore, the latter will be compared with the well known high valent MnO porphyrin species of the sterically hindered and electron-deficient porphyrin, H₂T(DCI)PP. The results of the present study show that mono-ortho-substituted mesotetra(phenyl)porphyrins can readily form stable high valent manganese^(IV) and manganese^(V)-oxo intermediates through reaction with TBAO at 273 K. Furthermore, the kinetics of oxidation of styrenes with the high valent Mn(O) porphyrin species of different Mn-porphyrins were investigated to elucidate the influence of the meso substituents on the reactivity of the high valent Mn(O) species. Also, the high valent species were used for the oxidation of a wide range of organic compounds including indene, cyclohexene, cyclohexane, toluene, methyl phenyl sulfide and aniline.



Ar=	Porphyrins	Mn-porphyrins
Phenyl	H ₂ TPP	MnTPP(OAc)
2-Methylphenyl	H ₂ T(2-CH ₃)PP	MnT(2-CH ₃)PP(OAc)
2-Brphenyl	H ₂ T(2-Br)PP	MnT(2-Br)PP(OAc)
2-Clphenyl	H ₂ T(2-CI)PP	MnT(2-Cl)PP(OAc)
2-NO2phenyl	H ₂ T(2-NO ₂)PP	MnT(2-NO ₂)PP(OAc)
2,6-dichlorophenyl	H ₂ T(2,6-DCI)PP	MnT(DCI)PP(OAc)
4-PyridylPhenyl	H ₂ T(4-Py)PP	MnT(4-py)PP(OAc)
4-OMePhenyl	H ₂ T(4-OMe)PP	MnT(4-OMe)PP(OAc)
4-MePhenyl	H ₂ T(4-Me)PP	MnT(4-Me)PP(OAc)
4-Clphenyl	H ₂ T(4-Cl)PP	MnT(4-Cl)PP(OAc)

Figure 1. Manganese porphyrins used in this study

Experimental

Preparation of porphyrins and metalloporphyrins

Meso-tetraphenylporphyr	in, H ₂ TPP,	meso-tetrakis(4-
methoxyphenyl)porphyrin	, H ₂ T(4-OMe)PP	meso-tetrakis(4-
methylphenyl)porphyrin,	H ₂ T(4-Me)PP	meso-tetrakis(4-
chlorophenyl)porphyrin,	H ₂ T(4-Cl)PP	meso-tetrakis(4-
pyridyl)porphyrin,	H ₂ T(4-Py)PP	meso-tetrakis(2-

chlorophenyl)porphyrin,	H ₂ T(2-Cl)PP	meso-tetrakis(2-
methylphenyl)porphyrin,	H ₂ T(2-Me)P	P meso-tetrakis(2-
bromophenyl)porphyrin,	H₂T(2-Br)PF	p meso-tetrakis(2-
nitrophenyl)porphyrin,	H ₂ T(2-NO ₂)PP,	Meso-tetrakis(2,6-
dichlorophenyl)porphyrin,	H ₂ TDCIPP an	d the corresponding
manganese porphyrins ha	ave been prepa	ared according to the
Literature ²⁵⁻²⁸ . TBAO was	prepared by a	a previously published
method modified by N	1eunier et al.	²⁹ (See Supporting
Information for more expe	erimental detai	ls).

Results and discussion

High valent metal-oxo porphyrins complexes are strong active oxidants that are involved in the oxidation reactions performed by strong terminal oxidants such as iodosylbenzene, meta-chloroperbenzoic acid and TBAO catalyzed by metalloporphyrins ^{2,30-37}. However, due to the high reactivity of these species at room or near room temperature, they should be studied at low temperatures. In the case of para-substituted porphyrins, the high valent metaloxo intermediates are stable only at very low temperatures. Moreover, the extensive oxidative degradation of the catalyst precursor by high valent metal-oxo complex may be prevented at low temperatures. On the other hand, the presence of sterically hindered and/or electron-withdrawing substituents at the meso positions may be utilized to overcome the oxidative degradation of the porphyrinic catalysts. It is noteworthy that the presence of bulky substituents at the ortho position increases the dihedral angle between the aryl substituents and the porphyrins mean plane ³⁸. This in turn decreases the resonance interaction between the aryl group and porphyrins π systems and leads to an increase in the electron-deficient character of the aromatic macrocycle. Accordingly, the introduction of bulky electron-releasing groups at the ortho positions may be also employed to increase the electron-deficiency of Mn-porphyrins. Meot-Ner et al. showed that the presence of methyl group at the ortho position of meso-tetra(phenyl)porphyrin makes it as electrondeficient as meso-tetra(4-cyanophenyl)porphyrin³⁹. Also, the electron-deficient character of ortho substituted mesotetra(aryl)porphyrins was revealed by UV-vis spectroscopy of their dications ^{40,41}. In this study, a series of Mn-porphyrins with bulky substituents at the para and ortho position were used to prepare the corresponding high valent Mn(O) porphyrin species at a relatively low temperature. Interestingly, the high valent Mn(O) intermediates of the ortho substituted porphyrins were remarkably stable regardless of the electron-withdrawing or electron-releasing properties of the ortho position. The formation of high-valent $Mn^{(IV \text{ or } V)}(O)$ porphyrin species from their manganese(III) counterparts is accompanied with the appearance of an absorption band at lower wavelengths and therefore UV-vis spectroscopy has been extensively employed to provide evidence on the formation of these species ⁴²⁻⁴⁴. According to the literature, the position of the blue shifted band in the UV-vis spectrum of these species depends on the meso substituents and therefore the band due to the high valent species was observed at 407 to

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Figure 2. UV-vis spectra of the Mn-porphyrins, their ImH (1:15 molar ratio to the catalyst) complexes and the corresponding $Mn^{V}(O)$ (\approx 1:500 ratio to the catalyst) and $Mn^{V}(O)$ species (\approx 1:1000 ratio to the catalyst) species in dichloromethane at 273 K.

413 and 420-425 nm for the ${\rm Mn}^{\rm V}({\rm O})$ and ${\rm Mn}^{\rm IV}({\rm O})$ species, respectively $^{34,45\text{-}53}$

The UV-vis spectra of the high valent Mn(O) porphyrins compexes ($Mn^{IV}(O)$ or $Mn^{V}(O)$) of different Mn-porphyrins at 273 K are shown in Figure 2. It should be noted that the formation of two types of high valent manganese oxo porphyrins, $Mn^{V}(O)$ and $Mn^{V}(O)$, occurred in the presence of different excess amounts of TBAO; as seen in Figure 2, When TBAO was added to this solution in 1:500 molar ratio with respect to the catalyst, an absorption band appeared at \approx 421 nm that was attributed to the (ImH)Mn^{IV}(O)porphyrin; The addition of larger excess amounts of TBAO (1:1000), led to disappearance of the bands at \approx 421 nm and the appearance of a band at \approx 407 nm. The latter band belongs to the (ImH)Mn^v(O)porphyrin. Decay of this species gives an absorption band at ca. 477 nm that is attributed to the six coordinate (ImH)Mn^{III}(P)(OOSO₃H) intermediate. In the case of (ImH)MnT(DCI)PP(OAc) (Supporting information, Figure S1) the addition of TBAO to this solution in CH₂Cl₂ in 1:500 molar ratio with respect to the catalyst, two absorption bands appeared at 474 and 421 nm that are attributed to (ImH)Mn^{III}T(DCI)PP(OOSO₃H) and (ImH)Mn^{IV}(O)T(DCI)PP species, respectively (blue curve). The use of TBAO in larger

excess amounts (1:1000), led to the disappearance of the absorption bands at 474 and 421 nm and appearance of a band at 407 nm due to $[(ImH)Mn^{V}(O)T(DCI)PP]^{+}(orange curve)$. It is noteworthy that significantly less amounts of TBAO were needed for the completeness of the reaction in the case of the more electron-rich Mn-porphyrins such as MnTPP(OAc). This observation is probably due to the higher Mn(V)/Mn(III) reduction potential (Scheme 1) of the more electron-deficient Mn-porphyrins^{54,55}.

$$Mn^{III}(P) + Oxone \xrightarrow{k_{f}} Mn^{V}(P) + HSO_{4}^{-}$$
$$K = k_{f} / k_{r}$$
$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = -RTInK$$
$$\Delta G = -nEF^{o}$$

 $E^{e} = E^{e} (HSO_{5} / HSO_{4}) - E^{e} (Mn^{V} / Mn^{V})$

Scheme 1. The presence of an equilibrium between the Mn(III) and Mn(V) species of various Mn-porphyrins caused by the difference between their Mn(V)/Mn(III) reduction potential.

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UV-vis spectral data of Mn-porphyrins, their ImH complexes and the corresponding high valent Mn(O) complexes in dichloromethane at 273 K are collected in Table 1. As seen in Table 1, the position of the Soret and Q bands ^{56,57} of the used Mn-porphyrins only slightly depends on the type of meso substituents. This observation is in accord with the nearly perpendicular orientation of the meso aryl substituents with the porphyrins mean plane in metalloporphyrins^{40,58,59}.

It is noteworthy that the HOMO-LUMO gap in porphyrins and metalloporphyrins is determined by the dihedral angle between the meso substituents and porphyrin mean plane and the out-of-plane deformation of porphyrins macrocycle ³⁸. For a series of Mn-porphyrins with different meso substituents the extent of coplanarity of meso substituents and porphyrin π systems influencing the resonance interaction between the two π systems determines the electron-rich or electron-deficient nature of the metalloporphyrin ³⁹.

According to the literature, high valent Mn(O) porphyrin intermediate has been prepared using different oxidants such as *m*-chloroperbenzoic acid, iodosylarenes, hydrogen peroxide, Oxone and iodobenzene diacetate ^{2,31-36} under various reaction conditions. However, most of these species are highly reactive toward oxidizable organic and inorganic substrate and solvents and therefore have been prepared and studied in situ. In this regard, the introduction of electron-withdrawing and/or sterically hindered substituents at the ortho position may be utilized to enhance their stability so that the species may be studied at high temperatures as 273 K. Also, the catalyst precursor of electron deficient and sterically hindered metalloporphyrins would be more stable with respect to the oxidative attack by the corresponding high valent metal-oxo.

As seen from Table 1, the UV-vis spectra of the high valent Mn(O) species consists of two absorption bands at the Soret and Q bands region. First of all, the addition of ImH to the

solution of the Mn-porphyrins in CH₂Cl₂ and its coordination to the Mn(III) centre led to a little or no shift in the absoprtion bands. The use of large eccess amount of TBAO (≈1:1000 molar ratio) resulted in the formation of high valent $Mn^{v}(O)$ complexes with the absorption maxima in the range of 406-413 nm. When TBAO was added in ca. 1:500 molar ratio with respect to the catalyst, two absorption bands appeared in the 474-479 range of 417-424 and nm, due to (ImH)Mn^{IV}(O)porphyrin and (ImH)Mn^{III}(P)(OOSO₃H) species, respectively.

The absorption maxima of the six coordinate species of the used Mn-porphyrins is observed at slightly higher wavelengths relative to that of the corresponding Mn-porphyrin. The presence of ImH was crucial for the formation of the high valent metal-oxo species. Also, the high valent metal-oxo intermediates was completely stable up to 20 min at 273 K.

Interestingly at the solution of the Mn-porphyrins with ortho substituents such as $MnT(2-NO_2)PP(OAc)$ the band for $Mn^V(O)$ or $Mn^{IV}(O)$ was rapidly and completely replaced with the band of six coordinated compound. In other word, no catalyst degradation was observed. On the other hand, the addition of TBAO to the solution of the Mn-porphyrins with no ortho substituents, MnT(4-CI)PP(OAc), MnT(4-Me)PP(OAc), MnT(4-OMe)PP(OAc) and MnT(4-Py)PP(OAc) in dichloromethane led to disappearance of the Soret band at ca. 470 nm and the appearance of a blue shifted band at ca. 410 nm.

Table 1. UV-vis spectral data of Mn-porphyrins, their ImH complexes and the corresponding high valent Mn(O) porphyrin complexes in dichloromethane at 273 K.

		Soret b	and			Q(0,1)band	Q(0,0) band	Q(0,0)band
		(λ/nm	n)			(λ/nm)	(λ/nm)	(λ/nm)
Mn- Porphyrins	Catalyst precursor	ImH complex	Mn ^v (O) species	Mn ^{IV} (O) species	Six Coordinate Peroxymonosulfate complex ^a	Catalyst p	precursor	Mn ^{IV} (O) and Mn ^V (O) ^b
MnTPP(OAc)	470	470	410		477	577	612	526
MnT(2-NO ₂)PP(OAc)	473	473	411		479	580	614	524
MnT(2-Me)PP(OAc)	470	470	406	417	477	576	611	523
MnT(2-Cl)PP(OAc)	470	470	406	417	477	576	607	518
MnT(4-Cl)PP(OAc)	470	470	412	422	477	577	611	527
MnT(4-Py)PP(OAc)	476	475	410	424	476	580	611	520
MnT(DCI)PP(OAc)	471	468	407	421	474	576	607	518
MnT(2-Br)PP(OAc)	472	472	409	423	478	576	609	518
MnT(4-OMe)PP(OAc)	472	473	413		478	579	618	530
MnT(4-Me)PP(OAc)	471	471	409		478	579	614	529

^[a] (ImH)Mn^{III} (Porphyrin) (OOSO₃H). ^[b] The Q(0,0) bands of Mn^{IV} (O) and Mn^V (O) species appear at nearly the same wavelengths.

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Figure 2, no absorption band due to the catalyst precursor was observed after disappearance of the band at 410 nm that confirms the oxidative decomposition of the catalyst precursor that is In accord with that Mn-porphyrins with no electronwithdrawing or bulky substituents are readily decomposed in the presence of TBAO by an intermolecular oxidative degradation mechanism and therefore the oxidative degradation of MnT(4-OMe)PP(OAc) as the most electron-rich metalloporphyrins of the series occurred much faster than the other para-substituted Mn-porphyrins by oxidative attack by the corresponding high valent metal-oxospecies. It is noteworthy that due to the remarkably high reactivity of the metal-oxo species, these species are often studied at low temperature to prevent their reaction with oxidizable substrates such as the catalyst precursor and water impurity of commonly used solvents. However, the band for $Mn^{v}(O)$ or Mn^{IV}(O) nm was rapidly replaced with the band of six coordinated compound. The experiments were also conducted in acetonitrile and very similar results were obtained.

Interestingly, the other ortho substituted Mn-porphyrins MnT(2-NO₂)PP(OAc), MnT(2-Br)PP(OAc), MnT(2-CI)PP(OAc) and MnT(2-Me)PP(OAc) were more stable than that of the para substituted Mn-porphyrins. Furthermore, the high valent metal-oxo complexes of the ortho mono-substituted Mn-porphyrins showed an oxidative stability comparable with that of MnT(DCI)PP(OAc). Accordingly, the previous may be used instead of the latter in kinetic and mechanistic studies on the high valent Mn(O) porphyrin species. It should be noted that the porphyrins free base of the former may be synthesized and purified and metallated with more simple and efficient procedures as well as low cost reagents.

Spectral changes upon the formation of high valent intermediates

The high valent Mn(O) intermediate of MnT(DCI)PP(OAc) has been also synthesized by the oxidation of this complex with m-CPBA under alkaline conditions. The Soret and Q bands of $[(ImH)Mn^{V}(O)T(DCI)PP]^{\dagger}$ and $[(ImH)Mn^{V}(O)T(DCI)PP]^{\dagger}$ were observed at 444 and 560 nm, respectively⁶⁰. In the present study, the corresponding absorption bands of the high valent intermediates formed in the presence of ImH appeared at 407 and 520 nm, respectively (Table 1). The presence of ImH was crucial for the formation of the latter; the addition of a large excess amount of TBAO to the solution of MnT(2-NO₂)PP(OAc) in dichloromethane. in the absence of ImH gave no band due to the high valent metal-oxo complex (Figure 3). Interestingly, the addition of ImH to this solution caused the appearance of an absorption band at 411 nm. This observation was attributed to the multiple roles played by ImH in the formation and reactivity of the active oxidants upon the activation of different terminal oxidants by Mn-porphyrins. It should be noted that the coordination of ImH to the metal centre facilitates departure of the leaving group i.e. HSO₄.



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Figure 3. The addition of a large excess amount of TBAO to the solution of MnT(2-NO₂)PP(OAc) in dichloromethane in the absence of ImH (red curve). The spectrum after the addition of ImH to this solution (green curve).

Furthermore, the hydrogen bond formation between ImH and the leaving group can also be involved in the formation of the high valent Mn(O) species, due to the stabilization of the anionic leaving group in non-polar solvents such as dichloromethane. (Scheme 2). Accordingly, the presence of ImH led to the blue shift of the Soret and Q bands. It is noteworthy that the high valent Mn(O) intermediate prepared under alkaline conditions was not able to oxidize olefins, evidenced by no change in the UV-vis spectra upon the addition of substrate ⁶⁰. However, the high valent Mn(O) complexes prepared in the presence of ImH readily oxidized indene and other olefins. Very recently we have shown that the presence of ImH is crucial for the oxidation of electron-rich with electrondeficient alcohols and the $[(ImH)Mn^{V}(O)T(DCI)PP]^{+}$. These observations in combination with the spectral changes upon the addition of ImH to the solution of MnT(DCI)PP(OAc) provide evidence for the coordination of ImH to the Mn(V) centre of the active oxidant (Scheme 3).



Scheme 2. Coordination of ImH to metal centre of metalloporphyrins and hydrogen bond formation between the leaving group and ImH facilitate the formation of high valent Mn(O) species.

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Effect of catalyst:ImH molar ratio

The rate of formation of the high-valent Mn(O) species determined by the initial rate method, was found to be dependent on the catalyst:ImH molar ratio (Figure 4). The maximum rate was obtained in the ca. 1:15 molar ratio.



Figure 4. Initial rate of $[(ImH)Mn^{V}(O)T(DCI)PP]^{*}$ formation against ImH to catalyst molar ratio.

Although the catalytic activity of Mn-porphyrins strongly enhances in the presence of $ImH^{31,61-63}$, $MnIII(Porphyrin)(ImH)_2$ species can readily form in the case of high concentrations of ImH^{64} (Scheme 3). In other words, an optimum molar ratio of catalyst:ImH should be used to prevent the formation of the latter.

$$\begin{array}{c} MnT(DCl)PP(OAc) & \underbrace{ImH}_{} (ImH)Mn^{III}T(DCl)PP)(OAc) \\ \\ \underbrace{ImH}_{} (ImH)_2Mn^{III}T(DCl)PP)(OAc) \end{array}$$

Scheme 3. Formation of inactive species formed by occupation the sixth coordination site of $\mathsf{Mn}(\mathsf{III})$ centre.

Table 2. The observed rate constants for oxidation of Indene and cyclohexene by Mnporphyrins and TBAO.

Mn-porphyrins	Observed	Mn-porphyrins	Observed
	rate constants		rate constants
	(× 103 M-1s-1) ^a		(× 103 M-1s-1) ^b
MnT(2-Cl)PP	6.85	MnT(2-Cl)PP	0.81
MnT(2-CH3)PP	3.05	MnT(2-CH3)PP	1.83
MnT(2-Br)PP	2.15	MnT(2-Br)PP	1.49

a and b are for the oxidation of Indene and cyclohexene, respectively.

Kinetic and mechanistic studies

Reactivity of different high valent manganese oxo species in the oxidation of indene and cyclohexene

In order to study the influence of the groups substituted at the phenyl substituents of meso-tetra(phenyl)porphyrins on the reactivity of the corresponding high valent Mn(O) porphyrins species, the rate of oxidation of indene and cyclohexene to the corresponding epoxides was studied by these species through

pseudo-first order conditions (Supporting Information, Figure 5, 6 and Figure S2).





Figure 5. UV-vis spectral changes upon the oxidation of a) cyclohexene and b) indene (2.25 × 10³ M) with [(ImH)Mn^V(O)T(2-Me)PP]*(4.5×10^{5} M) in ≈ 5 min.



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Figure 6. a) The results of observed rate constants for the oxidation of indene (a) and cyclohexene (b) with $(ImH)Mn^{v}(O)P$ in dichloromethane at 273 K.

It is noteworthy that due to high degree of catalyst degradation in the case of MnTPP(OAc) and the parasubstituted analogues, the oxidation reactions were studied using MnT(2-Cl)PP(OAc), MnT(2-Me)PP(OAc) and MnT(2-Br)PP(OAc) as catalyst (Table 2).

As seen in Table 2, the order of reactivity of the manganese oxo species decreased as MnT(2-CI)PP(OAc) > MnT(2-Me)PP(OAc) > MnT(2-Br)PP(OAc) > MnT(2-Br)PP(OAc) > MnT(2-CI)PP(OAc) for the oxidation of indene and cyclohexene, respectively.

The observed order of reactivity may be explained on the basis of the electronic and steric effects of the substrate and high valent Mn(O) porphyrins species; the formation of high valent Mn(O) species leads to a significant decrease in the steric effects around the reaction centre in comparison with the (Porphyrin)Mn(HSO₅)(ImH) species. However, a steric hindrance should be considered due to the presence of bulky meso-substituents^{65,66}. Also, the presence of phenyl adjacent to the reaction centre of indene increases the steric hindrance around the C=C bond of indene compared to that of cyclohexene. In the case of cyclohexene, the reverse order of reactivity of the high valent Mn(O) species cannot be explained on the basis of the steric hindrance at the meso positions. This observation may be due to the decreased reactivity of the active oxidants of the electron-deficient manganese porphyrins in comparison with those of the electron-rich ones⁶⁷⁻⁶⁹.

Mohajer et al. showed that manganese mesotetra(aryl)porphyrins with perfluorophenyl, 2,6-dichlorophenyl and 2,4,6-trimethylphenyl substituents are remarkably less reactive than MnTPP(OAc) for the oxidation a wide range of olefins³¹.



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Figure 7. a) UV-vis spectrum of MnT(DCI)PP(OAc) in $CH_2Cl_2 (\lambda_{max} = 471 \text{ nm}, \text{ black curve})$. The spectrum after the addition of ImH in 1:15 molar ratio (ImH)(Mn^{III}T(DCI)PP, $\lambda_{max} = 468 \text{ nm}, \text{ red curve})$, and that after the addition of excess amount of TBAO on (ImH)Mn^{III}(DCI)PP ($\lambda_{max} = 407 \text{ nm}, \text{ blue curve})$; b)UV-vis spectral changes monitored upon the reaction of [(ImH)Mn^V(O)(TDCIPP)]^{*} (4.5 × 10⁻⁵ M) with styrene (2.25 × 10⁻³ M). The Inset demonstrates the plot of absorbance vs time at 407 and 474 nm for [(ImH)Mn^V(O)T(DCI)PP]^{*} and (ImH)Mn^{III}(OOSO₃H)T(DCI)PP]^{*}.

In order to investigate the Kinetic and mechanism of the reactions of $[(ImH)Mn^{V}(O)T(DCI)PP]^{+}$, the kinetics of oxidation of styrene was studied under pseudo-first-order conditions. As was observed in the case of the ortho mono-substituted Mnporphyrins the addition of ImH led to slight shift in the position of absorption maxima of MnT(DCI)PP(OAc). (Figure 7a),

Also, the formation of high valent Mn(O) intermediate was evident from the large blue shift of the Soret band from 468 to 407 nm (Figure 7a). The reaction of styrene with the high valent metal-oxocomplexes obeyed the second order rate equation.

Rate = $k_2[(ImH)Mn^V(O)T(DCI)PP)[Styrene]$ Rate = $k_{obs}[(ImH)Mn^V(O)T(DCI)PP]$.

Figure 7b shows the UV-vis spectral changes monitored upon the reaction of [(ImH)MnV(O)T(DCI)PP]⁺ with styrene. The absorption changes at the λ_{max} of the high valent Mn(O) species were used to study the kinetics of the oxidation of para-substituted styrenes to the corresponding epoxides (Figure 7b The UV-vis spectral changes for other para

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substituted styrenes are shown in Supporting information, Figure S3. The non-linear curve fitting, $[A_t = A_{\infty} - (A_{\infty} - A_0)exp($ kobst)] plotted versus the time gave the kobs values (Supporting information, Figure S4). As seen in Figures S4 and S5 in the supporting information, an induction period was observed for the oxidation of styrene and other olefins (Supporting information, Figure S5). This observation seems to be due to the presence of hydrogen bond forming molecules such as ImH and water adjacent to the active site of the metal-oxo species; previous studies demonstrate that the coordination of ImH to the metal centre is crucial for the reactivity of the high valent metal-oxo intermediate. However, ImH can also facilitate the formation of the high valent metal-oxo complex through the formation of hydrogen bond with the leaving group of the oxidant assisting leaving group (HSO₄⁻) departure. On the other hand, ImH and other hydrogen bond donor molecules such as water and alcohols stabilize the high valent metal-oxo species through hydrogen bond formation with the formed manganese oxo intermediate (Scheme S1)^{31, 70-72}

Accordingly, these molecules should be removed from the active site to allow substrates access the electrophilic oxygen atom of the active oxidant. The latter is similar to the departure of water molecules from the active site of CYP following the arrival of substrate in the active site^{8, 73, 74}.

The kinetics of reaction was studied using different concentrations of styrene (Figure 8.) to obtain the second order rate constants (K_2). As seen from Figure 8, the increase in the concentration of styrene led to no change in the second order kinetics of the reaction. However, continuous increase in the K_{obs} values was observed.



Figure 8. Pseudo-first-order rate constants (k_{obs} / s^{-1}) against the concentration of para substituted styrenes in reaction with [(ImH)Mn^V(O)T(DCI)PP]^{*}.

Table 3 shows the second order rate constant values for the oxidation of para-substituted styrenes with $[(ImH)Mn^{V}(O)T(DCI)PP)]^{*}$.

Also the Hammett treatment of the oxidation data is shown in Figure 9. A slope (ρ) of -0.48 is consistent with an electrophilic mechanism⁷⁵⁻⁷⁷ that shows the remarkable dependence of the rate of the reaction on the electronic properties of the substrate.

Table 3. Second order rate constants (k₂) for alkenes

Olefins	Second order rate constants
	$k_2 (\times 10^3 M^{-1} s^{-1})$
Styrene	2.25
4-Methoxystyrene	4.94
4-Methylstyrene	4.27
4-Chlorostyrene	3.08



Figure 9. Hammett plot for the oxidation of para substituted styrenes with $\left[({\rm ImH}){\rm Mn}^V(O)T(DCI)PP\right]^*.$

As seen from Figure 2, high valent $Mn^{(IV)}O$ porphyrin (Soret band ~ 417 nm) may be also prepared by using TBAO in lesser molar ratios of catalyst to TBAO. Interestingly, the $Mn^{(IV)}oxo$ species was also able to oxidize olefins with a rate comparable with that of the Mn(V)oxo counterpart. The changes in the Soret band of the Mn(IV)oxo species of MnT(2-CI)PP(OAc) upon the addition of indene are shown in Supporting information, Figure S6. It should be noted that the latter was much less reactive than the $Mn^{(V)}oxo$ species towards the oxidation of alcohols. Also, the $Mn^{(IV)}Oxo$ species was completely unreactive for with respect to the oxidation of electron-deficient alcohols²⁵.

In all the experiments relevant to the study of the kinetics of oxidation of olefins, the substrate was added to the reaction mixture after the formation of the high valent $Mn^{V}(O)$ or $Mn^{IV}(O)$ complexes. In a control experiment, TBAO was added to a solution containing MnTPP(OAc), ImH and styrene and the changes in the absorption spectrum were recorded. Interestingly, no absorption band due to the formation of a high valent Mn(O) was observed. Furthermore, the band due to (ImH)Mn(Porphyrin)(HSO₅) at 477 nm (Supporting information, Figure S7) was gradually disappeared confirming degradation of the catalyst precursor. In other words, the high reactivity of the Mn(O) species led to the rapid oxidation of styrene and oxidative degradation of the catalyst.

Competitive oxidation of stilbenes has been used to provide indirect evidence on the nature of the active oxidant in metalloporphyrin catalyzed oxidation of olefins; for the Mnporphyrins with no steric hindrance at the meso positions, a *cis*

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to trans stilbene oxide ratio of ca. 1 has been observed in the case of the involvement of a high valent Mn(O) intermediate as the active oxidant. In the presence of a six coordinate (ImH)Mn(Porphyrin)(HSO₅) species, the steric hindrance around the active oxidant leads to the higher reactivity of cisstilbene relative to trans stilbene and therefore deviation from ca. 1 is observed for the competitive reaction.





Furthermore, the presence of sterically hindered substituents at the meso position also lead to a cis to trans stilbene oxide ratio greater than 1; in the case of MnT(2,4,6trimethyl)phenylporphyrin acetate a value of ca. 3.5 was observed for the oxidation of stilbenes with high valent Mn(O) complex. ^{31,78,79}. In this study, the use of MnT(TDCI)PP(OAc) and TBAO in 1:200 molar ratio gave no band due to the formation of a high valent Mn(O) species. In other words, the six coordinate (ImH)MnT(DCI)PP(HSO₅) was the exclusive active oxidant. The oxidation of cis and trans-stilbenes under this condition gave a value of 6 for the molar ratio of cis to trans-stilbene oxides. On the other hand, when the reactions were repeated using the catalyst and TBAO in 1:1000 molar ratio, a cis to trans-stilbene oxide value of 3 was observed. It should be noted that under this molar ratio, $[(ImH)Mn^{V}(O)T(DCI)PP]^{+}$ (λ_{max} = 407 nm) was the sole active oxidant, evident from the UV-vis spectrum of the reaction mixture. Accordingly, the results confirm that the competitive oxidation may be used to distinguish between the high valent Mn(O) intermediate and six coordinate intermediates as the active oxidants.

The formation of different intermediates upon the addition of ImH and TBAO to the solution of Mn-porphyrins in dichloromethane is summarized in Scheme 4.

Reactivity of the Mn^V(O) species towards the oxidation of other substrates

The high valent metal-oxo complexes are usually employed for the oxidation of different organic substrates^{36, 83}. In order to study the reactivity of the high valent $Mn^{V}(O)$ species towards the oxidation of other organic compounds, the oxidation of New Journal of Chemistry Accepted Manuscrip

substrates with $[(ImH)Mn^{\vee}(O)(TDCI)PP]^{+},$ various and Mn^v(O)T(2-Me)PP(OAc) was studied (Supporting information, Figures S8 and S9). The results show that the high valent Mn(O) intermediates of these Mn-porphyrins are able to oxidize a wide range of organic compounds at 273 K. Furthermore, the meso substituents has no significant effect on the reactivity of the high valent Mn(O) complexes.

Conclusion

The high valent Mn(O) species of mono-ortho substituted meso-tetra(phenyl)porphyrins with Cl, methyl, nitro or Br at the ortho position were prepared using TBAO as the terminal oxidant and ImH as co-catalyst at 273 K. The high valent $Mn^{V}(O)$ and $Mn^{IV}(O)$ intermediates were stable up to ca. 20 min. in the absence of organic substrate. In other words, the presence of bulky ortho substituents with a size equal to or greater than that of chlorine atom leads to the formation of a stable high valent Mn(O) complex. Also, the addition of water to the dichloromethane solution of these species led to no detectable change in the intensity of the absorption band due to the high valent $Mn^{V}(O)$ and $Mn^{IV}(O)$ intermediates at ca. 407 and 421 nm, respectively. Moreover, the formation, reactivity and stability of the high valent Mn(O) species remarkably depended on the presence of ImH. The kinetic studies on the oxidation of olefins with the former showed that the k_{obs} (k₂[olefin]) values were only slightly dependent on the nature of the ortho substituents. Interestingly, the high valent Mn(O) complexes of the mono-ortho-substituted Mnporphyrins showed a stability similar to that of the corresponding species of meso-tetra(2,6dichloro)phenylporphyrin. Also, the oxidative stability of the catalyst precursor of the former was very similar to the latter within a reaction time of ca. 20 min. It is noteworthy that the kinetics of the oxidation reaction conducted with the $Mn^{v}(O)$ of meso-tetra(2,6-dichloro)phenylporphyrin was comparable with that of the mono-ortho-substituted counterparts. Furthermore, the Mn^{IV}(O) species were as reactive as the $Mn^{v}(O)$ analogues. On the other hand, the Soret band due to the high valent Mn(O) species of para-substituted mesotetra(phenyl)porphyrins was observed only at the first seconds of the reaction at 273 K and guickly disappeared without the apperance of the absorption band of the catalyst precursor. Also, high degress of catalyst degradation were observed for their catalyst precursor. It should be noted that the formation of the high valent intermediates of the latter occurred at lower concentrations of TBAO, in comparison with the ortho substituted manganse porphyrins. The high valent Mn(O) complexes were also sufficiently reactive toward the oxidation of a wide range of organic substrates including methyl phenyl sulfide, aniline, benzyl alcohol, toluene and cyclohexane.

Conflicts of interest

There are no conflicts to declare.

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High valent manganese oxo species of a series of electron-rich and electron-deficient mesotetra(aryl)porphyrins (aryl = phenyl, 2-chlorophenyl, 2-nitrophenyl, 2-methylphenyl, 2-bromophenyl, 2,6-dichlorophenyl 4-methoxyphenyl, 4-methylphenyl, 4-chlorophenyl and 4-pyridyl) were prepared at 273 K.

