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Catalytic activity of Mn(III) and Fe(III) complexes of *meso*-tetra(*n*-propyl)porphyrin in oxidation of olefins: *Meso*-alkyl substituent in comparison with the alkenyl and aryl ones

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A B S T R A C T

Catalytic activity of Mn(III) and Fe(III) complexes of *meso*-tetra(*n*-propyl)porphyrin, MnT(*n*-Pr)P(X) and FeT(*n*-Pr)P(X) (X = Cl, SCN, OAc) in oxidation of olefins with tetra-*n*-butylammonium periodate at room temperature has been studied. The influence of different parameters including the molar ratio of catalyst to imidazole, type of counter ion (X) and oxidative stability of metalloporphyrins on the efficiency of the catalysts was investigated. The results of competitive oxidation of *cis*- and *trans*-stilbene suggest the presence of a high-valent Mn-oxo as the predominant oxidant species in equilibrium with a six coordinate complex, MnT(*n*-Pr)P(ImH)(IO_4) in the case of MnT(*n*-Pr)P(OAc). An unusual preference for *trans*-stilbene over *cis*-stilbene was observed in the reaction catalyzed by FeT(*n*-Pr)P(OAc). Control reaction indicated a significant *cis*- to *trans*-isomerization (81%) in oxidation of *cis*-stilbene catalyzed by FeT(*n*-Pr)P(OAc) which may explain the observed unusual *cis* to *trans*-stilbene oxide ratio. While oxidation of cyclooctene and styrene led to the exclusive formation of the corresponding epoxides, oxidation of cyclohexene gave 2-cyclohexe-1-ol and cyclohexene oxide as the products. However, the results of this study clearly demonstrate the key role played by the group substituted at the *meso* positions of metalloporphyrins on their catalytic activity, apart from the electron-donating or electron-withdrawing properties of the substituents.

1. Introduction

Since 1970’s very efficient chemical model systems based on metalloporphyrins, able to reproduce the catalytic functions of cytochrome P450 (CYP)-dependent monooxygenases, have been developed [1]. In spite of the absence of any substituents at the *meso*-positions of the cofactor of CYP enzymes, majority of designed model compounds are metalloporphyrins with aryl substituents at this position [2]. It has been well known that the metalloporphyrins bearing nonbulky or electron-rich groups at the periphery of the porphyrin macrocycle suffer from the instability caused by the oxidative degradation during the oxidation reactions [3]. In CYP enzymes, the active site is surrounded by protein residues which protects the rest of catalyst from oxidative degradation by the high valent iron-oxo intermediate [4,5]. Substitution of the *meso*-aryls with electron-deficient groups, introduction of bulky substituents at the *ortho*-positions of *meso*-tetraarylporphyrins and using excess amounts of substrate are among the main strategies have been utilized to overcome the problems associated with the stability of metalloporphyrins [3,6,7]. We have recently reported the oxidation of olefins with tetra-*n*-butylammonium hydrogen monopersulfate catalyzed by the Mn(III) complex of a *meso*-tetra(alkenyl)porphyrin (alkenyl = cinnamyl) as catalyst [8]. Oxidation of hydrocarbons with tetra-*n*-butylammonium periodate (TBAP) in the presence of Mn(III) complexes of *meso*-tetraarylporphyrins has been extensively studied by Mohajer et al. [9–11]. In a very recent work, we have studied the relative catalytic activity of a series of electron-rich and electron-deficient Mn(III) porphyrins in oxidation of olefins with TBAP [12]. In the present work, the catalytic activity of Mn(III) and Fe(III) complexes of *meso*-tetra(*n*-propyl)porphyrin, H_2T(*n*-Pr)P, for oxidation of olefins (Scheme 1) with TBAP has been studied. To our knowledge, it is the first report on using the metal complexes of a nonhalogenated *meso*-tetraalkylporphyrin in metalloporphyrin catalyzed oxidation of olefins. The competitive oxidation of *cis*- and *trans*-stilbene has been used to elucidate the nature of the active intermediate of the reaction [13,14].

2. Experimental

2.1. Preparation and metallation of H_2T(n-Pr)P

H_2T(*n*-Pr)P was prepared and purified according to the method of Neya and Funasaki [15] MnT(*n*-Pr)P(OAc), MnT(*n*-Pr)PCl, MnT

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(n-Pr)P(SCN), FeT(n-Pr)P(OAc), FeT(n-Pr)P(Cl) and FeT(n-Pr)P(SCN) have been synthesized and purified using the literature methods [16,17]. The progress of metallation reaction was followed by UV–Vis spectroscopy. While the wavelengths of the *Q* bands are completely different from those of the free base porphyrin, there is a small shift in the position of the Soret band of $H_2T(n\text{-}Pr)P$ upon metallation with Fe(III). Accordingly, to ensure the absence of free base porphyrin, at different time intervals a small aliquot was withdrawn, diluted with dichloromethane and treated with a dilute solution of CF_3COOH in CH_2Cl_2. The presence of $H_2T(n\text{-}Pr)P$, leads to the appearance of new bands at 422.4 and 631.0 nm in the UV–Vis spectrum due to the Soret and Q(0,0) bands of the $H_2T(n\text{-}Pr)P(CF_3COOH)_2$ [18,19]. The Soret and Q (λ/nm) bands (the data in parentheses) of the complexes appear at 476 (542, 597, 631), 482 (545, 604, 636), 487 (545, 603, 637), 420 (517, 581, 679, 725), 419 (517, 579, 671, 728), 416 nm (522, 582, 676, 737 nm), respectively. The spectra of MnT(n-Pr)P(OAc) and FeT(n-Pr)P(SCN) are shown in Figs. 1 and 2.

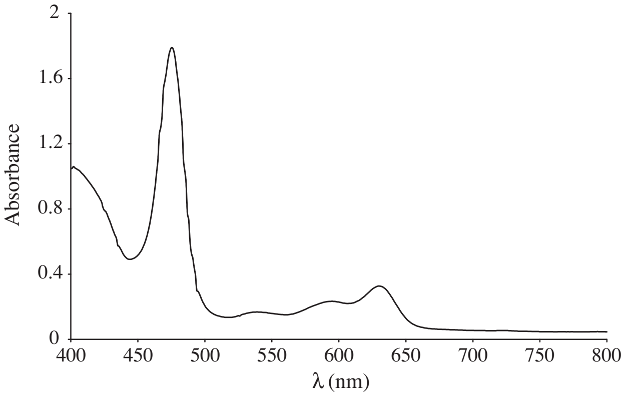
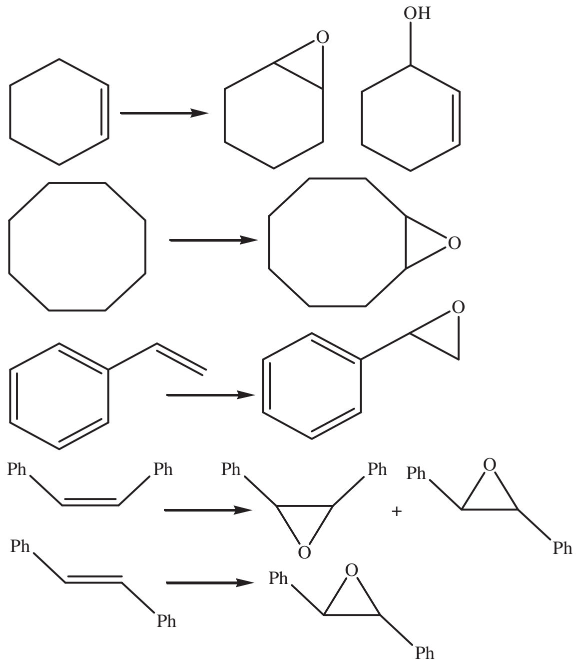


Fig. 1. UV–Vis spectra of MnT(n-Pr)P(OAc) in CH_2Cl_2.

2.2. General oxidation procedure

Oxidation of olefins was carried out using the procedure developed by Mohajer et al. [10] with some modifications to overcome the lower oxidative stability of the metal complexes of *meso*-tetraalkylporphyrins relative to that of *meso*-tetraarylporphyrins; alkene, oxidant, imidazole and catalyst have been used in 1000:170:10:1 molar ratios, respectively. All catalytic reactions performed in air at ambient temperature. With the exception of *cis*- and *trans*-stilbene, all reactions were analyzed by a Varian-3800 gas chromatograph equipped with a HP-5 capillary column (phenylmethyl siloxane 30 m × 320 μm × 0.25 μm) and flame-ionization detector. All reactions were repeated three times. Addition of 10 ml ether to the reaction mixture led to the precipitation of unreacted TBAP. The reaction mixture was passed through a short silicagel column to remove the remaining metalloporphyrin before injection into the GC. It should be noted that in a non-stoichiometric reaction, the limiting reagent (here, TBAP) should be used to calculate the expected yields and conversions. Accordingly, the molar ratio of TBAP to the olefin i.e. 170/1000 × 100% = 17 mol % corresponds to a conversion of 100% based on the starting oxidant. Other values are calculated considering the value of 17% for the 100% conversion.



Scheme 1. The products obtained in oxidation of olefins with TBAP catalyzed by MnT(n-pr)P(X) and FeT(n-pr)P(X) (X = SCN, OAc, Cl).

3. Results and discussion

3.1. Stability of catalyst

MnT(n-Pr)P(OAc) and FeT(n-Pr)P(SCN) have no electron-withdrawing or bulky substituents on the periphery of the porphyrin ring. Accordingly, the complexes are subject to oxidative degradation in reaction conditions. Using a very large excess of substrate is one of the main strategies commonly employed with the aim of reducing catalyst degradation in reactions catalyzed by metalloporphyrins [3,6,7]. In this regard, we have used oxidant and olefin in 1:6 molar ratios. It should be noted the use of much higher ratios of oxidant:olefin such as 1:40 [20], 1:1640 [21], 1:60 [22] has been avoided in this work to ensure the contribution of catalyst stability to the observed catalytic efficiency of the metalloporphyrins. Changes in the UV–Vis spectrum of MnT(n-Pr)P(OAc) in dichloromethane containing imidazole (ImH) in 1:10 molar ratio at various time intervals after the addition of TBAP are shown in Fig. 3. The results demonstrate that approximately 64% of the metalloporphyrin has been degraded 10 min after the addition of TBAP. In the same conditions, 46% of FeT(n-Pr)P(SCN) has been degraded (Fig. 4). However, after ca. 10 min, the rate of degradation of catalyst (FeT(n-Pr)P(SCN) or MnT(n-Pr)P(SCN)) decreases significantly

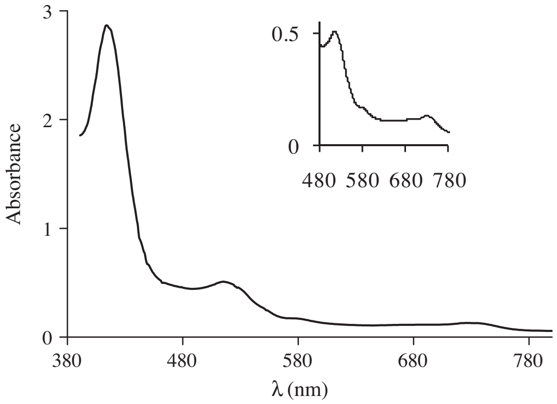


Fig. 2. UV–Vis spectra of FeT(n-Pr)P(OAc) in CH_2Cl_2 (the inset shows the Q bands region).

so that the reaction proceeds in the presence of a nearly constant concentration of the catalyst (Figs. 3 and 4). According to the UV–Vis spectrum of the reaction mixture after 4 h, ca. 30% of MnT(*n*-Pr)P(SCN) remained at the end of reaction (Fig. 3, inset). It is notable that in the case of FeT(*n*-Pr)P(SCN), the Soret band shifts to longer wavelengths from this point (Fig. 4) which may be attributed to the formation of a FeT(*n*-Pr)P$(ImH)_2$ species.

3.2. Effect of different parameters on the catalytic activity of MnT(n-Pr)P(X) and FeT(n-Pr)P(X)

3.2.1. Effect of ImH

Catalytic activity of metalloporphyrins is usually improved by the presence of nitrogen donors especially ImH. This five-membered planar ring can act as both hydrogen-bond acceptor and hydrogen-bond donor. Accordingly, electron-donation to the metal center of catalyst [10], hydrogen bond formation with the leaving group of coordinated oxidant and possibly the stabilization of high-valent metal-oxo species are the main roles played by the nitrogen donors. According to the data of Tables 1–4, the presence of ImH leads to a more significant enhancement of conversion in reaction catalyzed by MnT(*n*-Pr)P(OAc) compared to the other MnT(*n*-Pr)P(X) and FeT(*n*-Pr)P(X) complexes. This observation may be explained on the basis of the ability of acetate ion to form stronger hydrogen bonds with ImH relative to Cl^- or SCN^- anions which makes it a better leaving group. Also, the optimized molar ratio of catalyst to ImH is different for MnT(*n*-Pr)P(X) with various X; it is 1:10 for MnT(*n*-Pr)P(OAc) and MnT(*n*-Pr)P(SCN) and 1:20 for MnT(*n*-Pr)P(Cl). Interestingly, using the molar ratio of 1:50 (Table 1) in reaction catalyzed by MnT(*n*-Pr)P(OAc) leads to the formation of 2-cyclohexe-1-ol as the sole product.

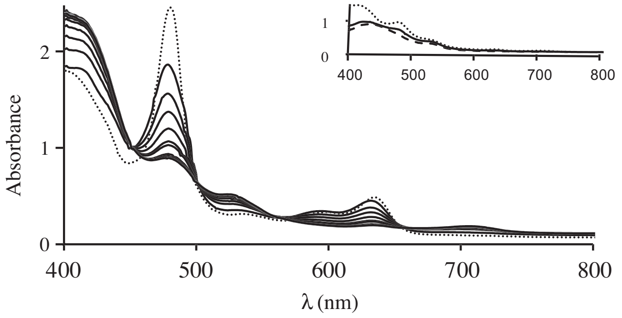


Fig. 3. UV–Vis spectrum of MnT(*n*-Pr)P(OAc) in dichloromethane (dotted curve) and its change upon addition of ImH, cyclooctene and TBAP within 1.5 min time intervals up to 10 min. The inset shows the spectrum after 30 min (dotted curve) and after 4 h (dashed curve).

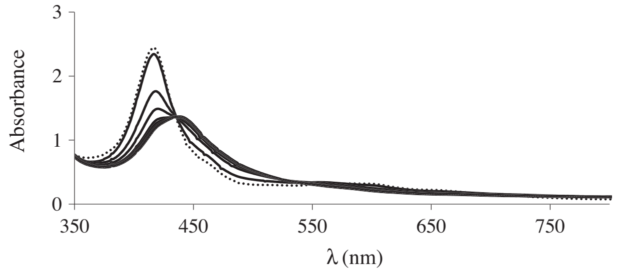


Fig. 4. UV–Vis spectrum of a solution of FeT(*n*-Pr)P(OAc) in dichloromethane (dotted curve) and its change upon addition of ImH, cyclooctene and TBAP within 1.5 min time intervals up to 10 min.

3.2.2. Effect of anionic counter ion (X)

MnT(*n*-Pr)P(X) and FeT(*n*-Pr)P(X) with different counter ions (X = Cl, SCN, OAc) have been used as catalyst for oxidation of cyclohexene with TBAP (Table 5). MnT(*n*-Pr)P(OAc) shows the best catalytic performance compared to the other MnT(*n*-Pr)P(X) and FeT(*n*-Pr)P(X). While changing the counter ion from chloride to acetate had no effect on the product selectivity, the conversion increased significantly upon this change. On the other hand, FeT(*n*-Pr)P(Cl) is more efficient than FeT(*n*-Pr)P(OAc) and FeT (*n*-Pr)P(SCN). Counter-ion dependence of the catalytic activity of the used metalloporphyrins and the remarkable influence of ImH on the performance of the catalysts (*vide supra*) suggest the involvement of metal-X bond breaking and the coordination of ImH to the metal center in the mechanism of reaction.

3.3. The nature of active oxidant

Competitive oxidation of *cis*- and *trans*-stilbene has been used as an indirect method to elucidate the nature of active oxidant in reaction catalyzed by metalloporphyrins in the absence of bulky substituents at the periphery of porphyrin [10,13,14]. The competitive reaction has been performed in the presence of MnT(*n*-Pr)P(OAc) and FeT(*n*-Pr)P(OAc). A value of 2.5 (Table 6) for the ratio

Table 1
Effect of ImH on the catalytic activity of MnT(*n*-Pr)P(OAc) in the oxidation of cyclohexene with TBAP in dichloromethane.[a]

MnT(*n*-Pr)P(OAc):ImH	Conversion (%)[b]	Epoxide yield (%)	Selectivity (%)[c]
1:0	trace	trace	
1:10	31.0	12.0	39.0
1:20	32.1	12.3	38.0
1:30	12.0	6.6	55.0
1:50	19.0	trace	0.0

[a] The molar ratio for alkene:oxidant:catalyst is 1000:170:1.
[b] Based on the starting TBAP.
[c] 2-Cyclohexe-1-ol is the other product.

Table 2
Effect of ImH on the catalytic activity of MnT(*n*-Pr)P(SCN) in the oxidation of cyclohexene with TBAP in dichloromethane.[a]

MnT(*n*-Pr)P(SCN):ImH	Conversion (%)[b]	Epoxide yield (%)	Selectivity (%)[c]
1:0	trace	trace	
1:10	12.0	2.8	23.3
1:20	12.0	2.5	20.8
1:30	14.0	2.3	16.4
1:50	11.0	2.3	21.0

[a] The molar ratio for alkene:oxidant:catalyst is 1000:170:1.
[b] Based on the starting TBAP.
[c] 2-Cyclohexe-1-ol is the other product.

Table 3
Effect of ImH on the catalytic activity of MnT(*n*-Pr)P(Cl) in the oxidation of cyclohexene with TBAP in dichloromethane.[a]

MnT(*n*-Pr)P(Cl):ImH	Conversion (%)[b]	Epoxide yield (%)	Selectivity (%)[c]
1:0	trace	trace	
1:10	12.8	5.0	39.1
1:20	17.0	6.0	35.3
1:30	13.1	4.0	30.5
1:50	11	3.0	27.3

[a] The molar ratio for alkene:oxidant:catalyst is 1000:170:1.
[b] Based on the starting TBAP.
[c] 2-Cyclohexe-1-ol is the other product.

Table 4
Effect of ImH on the catalytic activity of FeT(*n*-Pr)P(OAc) in the oxidation of cyclohexene with TBAP in dichloromethane.[a]

FeT(*n*-Pr)P(OAc):ImH	Conversion (%)[b]	Epoxide yield (%)	Selectivity (%)[c]
1:0	trace	trace	
1:10	12.8	2.0	15.6
1:20	8.1	2.1	26.0
1:30	15.3	3.6	23.5
1:50	8.0	1.0	12.5

[a] The molar ratio for alkene:oxidant:catalyst is 1000:170:1.
[b] Based on the starting TBAP.
[c] 2-Cyclohexe-1-ol is the other product.

Table 5
Counter ion effect on the efficiency of MnT(*n*-Pr)P(X) and FeT(*n*-Pr)P(X) in the oxidation of cyclohexene with TBAP in dichloromethane at room temperature.[a,b]

Catalyst	Conversion (%)	Epoxide yield (%)	Epoxide selectivity (%)
FeT(*n*-Pr)P(Cl)	24.7	2.3	9.5
FeT(*n*-Pr)P(SCN)	9.7	1.0	10.3
FeT(*n*-Pr)P(OAc)	12.9	2.0	15.6
MnT(*n*-Pr)P(Cl)	12.8	5.0	39.0
MnT(*n*-Pr)P(SCN)	11.7	2.8	24.0
MnT(*n*-Pr)P(OAc)	31.0	12.0	38.7

[a] The molar ratio for alkene:oxidant:ImH:catalyst is 1000:170:10:1.
[b] For a reaction time of 4 h, based on the starting TBAP.

Table 6
Competetive oxidation of *cis*- and *trans*-stilbene with TBAP in the presence of MnT(*n*-Pr)P(OAc) and FeT(*n*-Pr)P(OAc) in dichloromethane at room temperature.[a,b]

Catalyst	*Cis* to *trans* isomerization of *cis*-stilbene (%)[c]	*Cis*/*trans*
MnT(*n*-Pr)P(OAc)	24	2.5 (3.6)[d]
FeT(*n*-Pr)P(OAc)	81	0.3 (5.8)[d]

[a] The molar ratio for (*cis*-stilbene, *trans*-stilbene):oxidant:ImH:catalyst is (500, 500):170:10:1.
[b] Analyzed by ^{1}H NMR.
[c] The control reaction using *cis*-stilbene.
[d] The corrected *cis*/*trans* ratio considering the *cis* to *trans* isomerization of *cis*-stilbene (see the text).

of *cis*-stilbene oxide to the *trans* one in reaction catalyzed by MnT(*n*-Pr)P(OAc) suggests that the high-valent Mn-oxo is the predominant oxidant species in the catalytic cycle. On the other hand, oxidation of *cis*-stilbene in the presence of metalloporphyrins with non-bulky substituents at the *ortho* position of *meso*-aryl groups is usually accompanied with partial *cis* to *trans* isomerization of the product [8,10]. This in turn would result in giving false product ratios in the competitive epoxidation reactions [13,14]. Control reaction with *cis*-stilbene in the presence of MnT(*n*-Pr)P(OAc) in the same reaction conditions showed a *cis* to *trans* isomerization of 24% in the products. Accordingly, the correct value for the ratio of *cis* to *trans*-stilbene oxide will be 3.6 instead of 2.5. This ratio shows the involvement of a six coordinate MnT(*n*-Pr)P(ImH)(IO_4) species in addition to a high-valent Mn-oxo one as the reactive intermediates responsible for oxygen atom transfer. In the case of FeT(*n*-Pr)P(OAc), the observed ratio (0.3) apparently shows the unexpected preference of *trans*-stilbene over *cis*-stilbene which has been previously reported in the case of the iron(IV) oxo cation radical of electron-deficient porphyrins [13]. Interestingly, oxidation of *cis*-stilbene with TBAP using FeT(*n*-Pr)P(OAc) as catalyst in the same reaction conditions gave *cis*- and *trans*-stilbene oxide in 1.0:4.3 molar ratios (Table 6) corresponding to a ca. 81% *cis* to *trans* isomerization. Therefore, the correct value for the ratio of *cis*- to *trans*-stilbene oxide is 5.8. Accordingly, the unusual ratio of *cis*- to *trans*-stilbene oxide in competitive reaction catalyzed by FeT(*n*-Pr)P(OAc) is probably due to the significant *cis*–*trans* isomerization rather than the preference of *trans*-stilbene to the *cis*-isomer. On the other hand, this remarkable isomerization seems to be in agreement with the involvement of a high-valent Fe-oxo species rather than a six coordinate FeT(*n*-Pr)P(ImH)(IO_4) one as the active oxidant; rotation about the C–C bond is expected to be more feasible in the presence of an active oxidant with less steric hindrance about the electrophilic oxygen atom i.e. a metal-oxo one.

Table 7
Oxidation of cyclooctene and styrene with FeT(*n*-Pr)(OAc) and MnT(*n*-pr)(OAc).[a]

Catalyst	Olefin	Yield of epoxide (%)[b,c]
MnT(*n*-Pr)P(OAc)	cyclooctene	33.6
FeT(*n*-Pr)P(OAc)	cyclooctene	24.7
MnT(*n*-Pr)P(OAc)	styrene	37.7
FeT(*n*-Pr)P(OAc)	styrene	33.5

[a] The molar ratio for alkene:oxidant:catalyst is 1000:170:1.
[b] For a reaction time of 4 h, based on the starting TBAP.
[c] The epoxide has been obtained as the sole product.

On the other hand, the remarkably greater *cis* to *trans* isomerization in oxidation of *cis*-stilbene with TBAP in the presence of FeT(*n*-Pr)P(OAc) (81%) compared to MnT(*n*-Pr)P(OAc) (24%) reveals a significantly enhanced cleavage of the carbon–carbon π-bond of the olefin in the transition state of the reaction catalyzed by the former in comparison with the latter. It should be noted that the formation of *trans*-stilbene oxide as the thermodynamically more stable product [10,23] with respect to the *cis*-isomer, requires a rotation about the C=C bond at some intermediate step [24,25].

3.4. Oxidation of styrene and cyclooctene

Oxidation of styrene and cyclooctene with TBAP in the presence of FeT(*n*-Pr)(OAc) and MnT(*n*-Pr)(OAc) gives the corresponding epoxide as the sole product (Table 7). As was observed in oxidation of cyclohexene, the Mn-porphyrin is a more efficient catalyst compared to the iron counterpart. However, in the case of cyclooctene and styrene, the difference between the efficiency of the two metalloporphyrins decreases so that in oxidation of styrene FeT(*n*-Pr)(OAc) is as efficient as the Mn(III) analogous.

The results of this study in comparison with other previous studies [8–12] clearly show that the presence of aryl or alkenyl [8] substituents at the *meso* positions of metalloporphyrins, apart from the electron-donating or electron-withdrawing ability of the substituents, is the basic electronic requirement for such complexes to act as efficient catalyst precursors for mild oxidation of organic compounds. Otherwise, the introduction of strong electron withdrawing groups at the alkyl residues of *meso*-tetraalkylporphyrins substituents is necessary [26]. In a previous work, we have shown the higher catalytic performance of Mn(III) complex of a *meso*-tetra(alkenyl)porphyrin compared to that of *meso*-tetraphenylporphyrin in oxidation of olefins with oxone [8].

Further work is now in progress to explore the effect of branched chain alkyl substituents on the catalytic activity of the metal complexes of *meso*-tetraalkylporphyrins in oxidation of olefins with different terminal oxidants.

4. Conclusions

In summary, the catalytic activity of a series of Mn(III) and Fe(III) complexes of H$_2$T(*n*-Pr)P bearing various anionic counter ions in oxidation of olefins with TBAP has been studied and the influence of different reaction parameters on the efficiency of the metalloporphyrins was investigated. Competitive oxidation of *cis*- and *trans*-stilbene in the presence of MnT(*n*-Pr)(OAc) and FeT(*n*-Pr)(OAc) supports the involvement of high valent metal oxo species as well as the six coordinate FeT(*n*-Pr)P(ImH)(IO_4) and MnT(*n*-Pr)P(ImH)(IO_4) complexes as the reactive intermediates responsible for oxygen atom transfer. However, the results suggest that the high valent metal oxo species has higher contribution compared to the six coordinate one. The unusual ratio of *cis*- to *trans*-stilbene oxide observed in competitive reaction catalyzed by FeT(*n*-Pr)P(OAc) is in agreement with the significant *cis*–*trans* isomerization observed in oxidation of *cis*-stilbene in the presence of the same catalyst.

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