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Stereoelectronic effects of the *meso*-substituents on the catalytic performance of iron(III) *meso*-tetraarylporphyrins: Pyridyl and N-methylated pyridyl groups compared to phenyl, 4-methoxyphenyl and 4-sulfonatophenyl ones

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A B S T R A C T

The activity of a series of iron(III) *meso*-tetraarylporphyrins (aryl = phenyl, 4-methoxyphenyl, 4-sulfonatophenyl, 2-pyridyl, 3-pyridyl, 4-pyridyl and N-methyl-pyridyl counterparts) in the catalysis of oxidation reactions of olefins with tetra-n-butylammonium periodate (TBAP) or $NaIO_4$ in the presence of imidazole (ImH) has been studied. While the presence of ImH has no effect on the catalytic activity of the Fe-porphyrins containing pyridyl or N-methylated pyridyl substituents at the *meso*-positions, the catalytic performance of the other Fe-porphyrins significantly increased by the use of ImH in 5:1 molar ratio with respect to the catalyst. As was observed in the comparison of the Mn-porphyrins with pyridyl substituents, the oxidative stability of FeT(4-py)P(OAc) is remarkably higher than that of FeT(2-py)P(OAc) and FeT(3-py)P(OAc). Also, the same order of relative stability was found in the case of the N-methylated analogues. It is noteworthy that N-methylation of FeT(py)P(OAc) complexes led to the substantial decrease in their oxidative stability. Competitive oxidation of *cis*- and *trans*-stilbene, provides indirect evidence for the involvement of high valent Fe-oxo porphyrins as well as periodato iron porphyrins as the active oxidant in reactions catalyzed by the used iron porphyrins. However, the involvement of a high valent iron-oxo porphyrin species is more pronounced in the case of $FeTPPS_4(OAc)$, FeT(2-py)P(OAc), FeT(3-py)P(OAc), FeT(4-py)P(OAc) and the N-methylated analogues. Also, an unusual preference of *trans*-stilbene over *cis*-stilbene was observed in the competitive epoxidation reaction catalyzed by FeT(3-MePy)P(OAc) and FeT(4-MePy)P(OAc) which cannot be described by the *cis*/*trans* isomerization. Furthermore, significant *cis*/*trans* isomerization observed upon oxidation of *cis*-stilbene in the reaction catalyzed by FeT(2-MePy)P(OAc) indicates that steric effects due to the presence of methyl groups at the *ortho* positions of this complex are of minor importance. On the other hand, large differences were observed in the product distribution for oxidation reactions with TBAO performed in dichloromethane and aqueous solvent. In spite of the lack of close correlation between the catalytic activity of the Fe-porphyrins and the electronic properties of the *meso*-substituents, in comparison with the corresponding Mn-porphyrins, there is a better correlation between the catalytic activity of the Fe-porphyrins and the electronic effects of the *meso*-groups.

1. Introduction

After the first report on the use of iron porphyrins in oxidation of hydrocarbons with iodosylbenzene by Groves et al. in 1979, different aspects of the catalytic activity of metalloporphyrins have been studied and clarified [1–3]. One of the major results obtained by different studies is the general agreement on the higher catalytic activity of electron deficient metalloporphyrins relative to the electron rich ones [4]. On the other hand, there are many reports concerning the higher or nearly the same catalytic performance of metalloporphyrins with electron-donating groups compared to those bearing electron-withdrawing substituents [5–15]. Manganese porphyrin catalyzed oxidation of hydrocarbons with sodium periodate was pioneered by Mohajer and Tangestaninejad in 1993 [5]. After that, several studies have been carried out on the effects of nitrogen donors, solvent, *meso*- and/or β substituents and anionic axial bases on the efficiency of manganese porphyrins [5–7,13,15,16]. We have previously studied the catalytic activity of a series of *meso*- and/or β substituted electron-deficient and electron-rich manganese porphyrins in oxidation of various olefins with tetra-n-butylammonium periodate (TBAP) and iodosylbenzene (PhIO) and found a complex order of catalytic activity for the Mn-porphyrins. Interestingly, the electron rich Mn-porphyrins showed higher or similar

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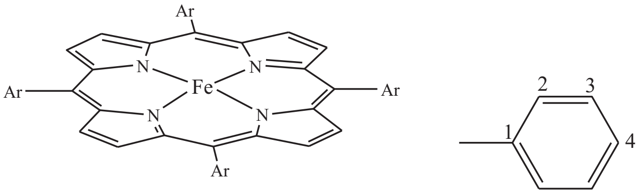


Ar =	Porphyrins	Fe-porphyrins
2-pyridyl	$H_2T(2\text{-py})P$	FeT(2-py)P(OAc) (**1**)
4-pyridyl	$H_2T(4\text{-py})P$	FeT(4-py)P(OAc) (**2**)
2-methylpyridyl	$H_2T(2\text{-Mepy})P$	FeT(2-Mepy)P(OAc) (**3**)
Phenyl	H_2TPP	FeTPP(OAc)(**4**)
4-methoxyphenyl	$H_2T(4\text{-}OCH_3)PP$	$FeT(4\text{-}OCH_3)PP(OAc)$ (**5**)
4-sulfonatophenyl	H_2TPPS_4	$FeTPPS_4(OAc)$ (**6**)
3-pyridyl	$H_2T(3\text{-py})P$	FeT(3-py)P(OAc) (**7**)
3-methylpyridyl	$H_2T(3\text{-Mepy})P$	FeT(3-Mepy)P(OAc) (**8**)
4-methylpyridyl	$H_2T(4\text{-Mepy})P$	FeT(4-Mepy)P(OAc) (**9**)

Fig. 1. Porphyrins and the iron(III) complexes used in this study.

catalytic efficiencies compared to the electron-deficient ones in oxidation of most of the used alkenes [13,14]. Also, the electronic effects of meso substituent on the activity of a series of electron-rich and electron-deficient manganese porphyrins containing (2-, 3-, 4-)pyridyl, 4-sulfonatophenyl, phenyl and 4-methoxyphenyl groups at the periphery of porphyrin for the catalysis of oxidation reaction of olefins with TBAP were studied in our recent work [16]. The results showed that apparently the well-known electronic effects of these substituents, have been used in organic chemistry to predict the product distribution and the kinetics of reactions as well as the linear free energy relationship, cannot be simply generalized to the groups attached to the *meso*- or β-positions of the manganese porphyrins. Due to the important role played by iron porphyrins in the catalysis of oxidation reactions in biological systems, also in order to judge whether this behavior is general or not in the series of iron porphyrins, a wide range of iron porphyrins (Fig. 1) and olefins have been used to investigate the influence of peripheral substitution on the oxidative degradation and catalytic activity of the iron porphyrins. Furthermore, in the present work, N-methylation of pyridyl substituents has been used to increase the electron deficiency of the porphyrin core of iron(III) *meso*-tetra(pyridyl)porphyrin complexes. The competitive oxidation of *cis*- and *trans*-stilbene has been used to gain insights on the nature of reactive species involved in the catalytic cycles [7,10,16]. Also, significant differences were found between the product distribution of oxidation reaction conducted in aqueous and non-aqueous conditions.

2. Experimental

2.1. Instrumental

^{1}H NMR spectra were obtained on a Bruker Avance DPX-400 MHz spectrometer. The absorption spectra were recorded on a Pharmacia Biotech Ultrospec 4000 UV-vis spectrophotometer. 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) or a packed column (Chromosorb WHP 80–100 Mesh, 4 mm × (1/4) m × 2 m) and a flame-ionization detector. ^{1}H NMR has been used to analyze the products in the case of *cis*- and *trans*-stilbene. All reactions were repeated at least three times.

2.2. Preparation of porphyrins

Meso-tetra(pyridyl)- [17,18], *meso*-tetraphenyl- [19], *meso*-tetra(4-OCH_3phenyl)- [19], *meso*-tetra(4-sulfonatophenyl)- [20,21], were prepared and purified according to the literature methods. The sulfonated *meso*-tetra(aryl)porphyrins were isolated as the tetra-n-butylammonium salts by extraction of the sulfonated porphyrin into dichloromethane using tetra-n-butylammonium bromide as the phase transfer catalyst. More details (UV–vis and ^{1}H NMR spectra data) have been described in our previous work [16]. N-methylated *meso*-tetra(pyridyl)porphyrins were prepared by refluxing the corresponding porphyrin with excess amounts of methyltosylate in dimethylformamide (DMF) and purified according to the literature [18,22]. $H_2T(2\text{-Mepy})P$: ^{1}H NMR (DMSO-d_6, 400 MHz): −2.995 (2H, br, s, NH), 9.681–9.696 ($4H_m$, adjacent to heteroatom, m), 8.860–8.964 ($4H_m$, m), 9.068–9.078 ($4H_o$, dd), 8.748–8.783 ($4H_p$, qn), 9.277 ($8H_\beta$, s), 4.039–4.15 (12H, $-CH_3$, s). UV–vis (λ/nm) in water: 412 (Soret), 508, 541, 578, 630. $H_2T(3\text{-Mepy})P$: ^{1}H NMR (DMSO-d_6, 400 MHz): −3.124 (2H, br, s, NH), 8.626–8.661 ($4H_m$, dd), 10.007 ($4H_o$, adjacent to heteroatom, s), 9.323 ($4H_o$, d), 9.579–9.594 ($4H_p$, d), 9.266 ($8H_\beta$, s), 4.698 (12H, $-CH_3$). UV–vis (λ/nm) in water: 415 (Soret), 512, 540, 577, 628. $H_2T(4\text{-Mepy})P$: ^{1}H NMR (DMSO-d_6, 400 MHz): −3.086 (2H, br, s, NH), 9.469–9.511 ($8H_m$, m), 8.993–9.009 ($8H_o$, d), 9.202 ($8H_\beta$, s), 4.741 (12H, $-CH_3$). UV–vis (λ/nm) in water: 420 (Soret), 515, 553, 582, 635.

2.3. Preparation of metalloporphyrins

Porphyrins were metalated with $FeCl_2{\cdot}4H_2O$ or $Fe(OAc)_2$ in refluxing DMF according to the method of Kobayashi et al. [23,24]. The progress of reaction was monitored by UV–vis spectroscopy (see supporting information for more details). With the exception of the iron porphyrins with anionic and cationic substituents, the other metalloporphyrins crystallized from the DMF solution upon cooling. In the case of the former, after the disappearance of the Soret band of the free base porphyrin (vide infra), DMF was evaporated in vacuo and further purification was performed on the crude product. The Soret (and visible bands, the data in the parentheses) of FeTPP(OAc), $FeT(4\text{-}OCH_3)PP(OAc)$, FeT(2-py)P(OAc), FeT(3-py)P(OAc), FeT(4-py)P(OAc), $FeTPPS_4(OAc)$ (as tetra-n-butylammonium salt), FeT(2-Mepy)P(OAc), FeT(3-Mepy)P(OAc) and FeT(4-Mepy)P(OAc) appears at 405 (λ_{max}, in CH_2Cl_2) (564, 606), 409 (λ_{max} in CH_2Cl_2) (569, 612), 404 (λ_{max}, in CH_2Cl_2) (563, 605), 409 (λ_{max}, in CH_2Cl_2) (498, 565, 607), 402 (λ_{max}, in CH_2Cl_2) (562, 603), 406 (λ_{max}, in CH_2Cl_2) (565, 604), 420 (λ_{max}, in DMF) (504, 558, 603), 421 (λ_{max}, in DMF) (490, 551, 637), 423 (λ_{max}, in DMF) (495, 548, 639) nm, respectively. The presence of unreacted porphyrin, especially in the case of iron porphyrins with λ_{max} values very close to those of the corresponding free base porphyrins, was monitored by gradual addition of a dilute solution of CF_3COOH to an aliquot of the reaction mixture and recording the UV–vis spectrum; the existence of free base porphyrin leads to the significant red shift of the Soret band due to the formation of the dication species [25].

2.4. General oxidation procedure

Stock solutions of the Fe-porphyrins (0.003 M) and ImH (0.5 M) were prepared in dichloromethane (or DMF for the cationic iron porphyrins). In a typical reaction, alkene (0.25 mmol), Fe-porphyrin (0.003 mmol, 1 ml) and ImH (X μl, vide infra) were added into a 10 ml round bottom flask containing 1 ml of dichloromethane. Then, 0.5 mmol (0.217 g) TBAP has been added. The mixture was stirred thoroughly for 4 h at ambient temperature. The optimized molar ratios of catalyst:ImH:alkene:TBAP are 1:0:85:170 in

Table 1
Effect of ImH on the catalytic activity of FeT(2-Py)P(OAc), FeT(4-Py)P(OAc), FeTPP(OAc), FeT(4-OCH_3)PP(OAc) and FeT(2-Mepy)P(OAc).[a]

	1:0	1:5	1:10
FeT(2-Py)P(OAc)[b]			
Conversion (%)	12.433	7.573	5.115
Epoxide yield (%)	12.433	7.573	5.115
FeT(4-Py)P(OAc)[c]			
Conversion (%)	41.842	25.855	19.358
Epoxide yield (%)	41.842	25.855	19.358
FeTPP(OAc)[d]			
Conversion (%)	29.378	15.612	7.150
Epoxide yield (%)	29.378	15.612	7.150
FeT(4-OCH_3)PP(OAc)[b]			
Conversion (%)	1.188	13.948	11.384
Epoxide yield (%)	1.188	13.948	11.384
FeT(2-Mepy)P(OAc)[c]			
Conversion (%)	Trace	32.756	20.990
Epoxide yield (%)	Trace	32.756	20.990

[a] The molar ratios of catalyst:ImH:olefin:TBAP (or $NaIO_4$ for the reactions performed in water) are 1:X:85:170; Reaction time was 4 h. Average of three runs.
[b] Oxidation of styrene in CH_2Cl_2.
[c] Oxidation of indene in CH_2Cl_2.
[d] Oxidation of indene in water.

reactions catalyzed by iron porphyrins with pyridyl substituents in dichloromethane and the N-methylated counterparts in water and 1:5(0.015 mmol, 30 μl):85:170 in the presence of the other iron porphyrins. With the exception of *cis*- and *trans*-stilbene, the progress of reaction was followed using TLC and GC analysis. After the required time, 5 ml diethyl ether was added to the flask and the reaction mixture passed through a short silica gel column to remove the unreacted tetra-n-butylammonium periodate and any remaining Fe-porphyrins. Low solubility of TBAP in ether leads to the precipitation of unreacted oxidant following the addition of ether to the reaction mixture. Also, the used Fe-porphyrins are slightly soluble in ether and are separated by chromatography through a short silica gel column. Oxidation of olefins with sodium periodate catalyzed by FeT(2-Mepy)P(OAc), FeT(3-Mepy)P(OAc) and FeT(4-Mepy)P(OAc) were performed in aqueous solution. Therefore, after stirring the reaction mixture for the required time at ambient temperature in air, extraction by CH_2Cl_2 was used to separate the products of reactions as well as the unreacted olefin. After drying the organic phase with $MgSO_4$, it was analyzed by GC.

2.5. Degradation of metalloporphyrins

Degradation of metalloporphyrins for a reaction time of 4 h was followed by UV–vis spectroscopy at the λ_{max} of the complexes. General procedure for the oxidation reactions and the molar ratios of catalyst, ImH, alkene and TBAP are as mentioned above (see [16] for more details).

3. Results and discussion

3.1. The optimized ImH/iron porphyrin ratios

The catalytic activity of metalloporphyrins has been found to be significantly dependent on the presence of nitrogen donors such as ImH. Previous studies have shown that in manganese porphyrin catalyzed oxidation of olefins the 1:10 ratio of the catalyst to ImH is the optimized condition [7,16]. However, the optimization of this molar ratio is needed to be done for the iron porphyrins. Accordingly, we have studied the influence of molar ratio of catalyst to ImH, in oxidation reactions conducted in the presence of the iron porphyrins. The effect of this parameter has been studied for all of the iron porphyrins but some of them are summarized in Table 1.

Table 2
The comparison of the catalytic activity of FeTPPCl and FeTPP(OAc) in oxidation of styrene in CH_2Cl_2.[a]

FeTPP(X)	Conversion (%)[b]	Epoxide yield (%)[b]	Epoxide selectivity (%)
X = OAc	12.963	12.963	100
X = Cl	6.270	6.270	100

[a] The molar ratios of catalyst:ImH:olefin:TBAP are 1:10:83:170.
[b] The average value of three independent experiments for a reaction time of 4 h.

3.1.1. FeT(2-, 3-, or 4-Py)P(OAc) and their N-methylated analogues

In spite of the significant increase in the catalytic activity of the iron and manganese [16] porphyrins (Table 1) with non-pyridyl substituents, caused by the presence of ImH, no co-catalytic activity has been found for ImH in reaction catalyzed by the iron porphyrins with pyridyl and N-methylated pyridyl substituents. Apparently, the formation of Fe(porphyrin)$(ImH)_2$ causes the decreased catalytic activity of the latter [7,26,27].

3.1.2. FeTPP(OAc), FeT(4-OCH_3)PP(OAc) and $FeTPPS_4$(OAc) (as tetra-n-butylammonium salt)

As was observed in the case of manganese porphyrins with the same meso substituents [16], the presence of ImH leads to a significance increase in the catalytic performance of these series of iron porphyrins (Table 1), although the maximum conversion is reached at a smaller molar ratio of ImH to the catalyst.

3.2. Counteranion effect

The nature of epoxidizing intermediates in iron porphyrin catalyzed epoxidation of olefins was shown to be markedly dependent on the ligating nature of the anionic ligands [28]. In a previous work, we have studied the effects of anionic counterion on the catalytic activity of the iron porphyrin of *meso*-tetra(n-propyl)porphyrin [27]. The catalytic activity of FeTPPX (X = Cl, OAc) is significantly influenced by the nature of counterion (Table 2).

3.3. Iron porphyrin catalyzed oxidation of olefins with TBAP

3.3.1. Oxidative stability of the Fe-porphyrins

According to the data of Table 3, stability of the iron porphyrins toward oxidative degradation under the reaction condition decreases as FeT(4-py)P(OAc) ≫ FeT(4-Mepy)P(OAc) > FeT(2-py)P(OAc) ~ FeT(3-py)P(OAc) > $FeTPPS_4$(OAc) > FeT(2-Mepy)P(OAc) > FeT(4-OCH_3)P(OAc) ~ FeTPP(OAc) > FeT(3-Mepy)P(OAc). Interestingly, FeT(4-py)P(OAc) and FeT(4-Mepy)P(OAc) are much more stable compared to the other members of the series which is in agreement with our previous findings on the relative stability of Mn-porphyrins with pyridyl and substituted phenyl groups [16].

Table 3
Degradation of the iron porphyrins under reaction conditions.[a]

Fe-porphyrins	Degradation (%)[b]	Fe-porphyrins	Degradation (%)[b]
FeT(2-py)P(OAc)[c]	28.6	$FeTPPS_4$(OAc)[d]	44.0
FeT(3-py)P(OAc)[c]	31.6	FeT(2-Mepy)P(OAc)[c,e]	71.5
FeT(4-py)P(OAc)[c]	6.4	FeT(3-Mepy)P(OAc)[c,e]	100.0
FeTPP(OAc)[d]	80.6	FeT(4-Mepy)P(OAc)[c,e]	10.8
FeT(4-OCH_3)P(OAc)[d]	80.0		

[a] See the footnotes of Table 1.
[b] On the basis of the absorbance changes (ΔA) at the λ_{max} of the Fe-porphyrins ($\Delta A/A$).
[c] The molar ratios of catalyst:ImH:styrene:TBAP are 1:0:83:170.
[d] The molar ratios of catalyst:ImH:styrene:TBAP are 1:5:83:170.
[e] For reaction conducted in water.

Furthermore, the present study indicates much higher oxidative stability of FeT(4-py)P(OAc) with respect to the N-methylated FeT(py)P(OAc), with the exception of FeT(4-Mepy)P(OAc). On the other hand, FeT(3-Mepy)P(OAc) has undergone the greatest degradation among the iron porphyrins. In comparison with the corresponding Mn-porphyrins [16], there are larger differences between the stability of the iron porphyrins. While the introduction of the $-SO_3$ groups at the phenyl substituents of FeTPP(OAc) causes the significant increase in the stability of the iron porphyrin, N-methylation of the iron *meso*-tetra(pyridyl)porphyrins does not necessarily increase the stability of the iron porphyrin. The order of stability of the iron *meso*-tetra(pyridyl)porphyrins is exactly the same as that was observed in the case of the manganese porphyrins with the same substituents. It is noteworthy that the order of stability of the N-methylated iron porphyrins is the same as was observed in the case of non-methylated iron and manganese [16] porphyrins. However, the comparable extent of degradation of FeT(4-OCH_3)P(OAc) and FeTPP(OAc) (also the manganese porphyrins [16]) implies that the substitution of phenyl groups with the $-OCH_3$ substituents has little or no effect on the stability of the metalloporphyrin. Finally, except for FeT(4-Mepy)P(OAc), the iron porphyrins with cationic N-methylated pyridyl substituents are found to be remarkably less stable than the corresponding non-methylated analogues. It should be noted that, compared to the aprotic solvents, the protic solvents such as water, are in favor of the formation of a high valent iron oxo species [7,29].

3.3.2. *Oxidation reactions in presence of the Fe-porphyrins*

With the exception of 4-methoxystyrene, FeTPP(OAc) catalyzed oxidation of olefins with TBAP gives the corresponding epoxide as the sole product (Table 4). Oxidation of the former gives some 4-methoxystyrene. The order of reactivity of different olefins is as follows: 4-methoxystyrene > indene ≫ cyclooctene > styrene ≥ cyclohexene ≥ *cis*-cyclooctene > α-methylstyrene ≫ 1-hexene (no reaction).

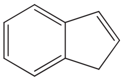
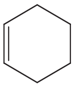
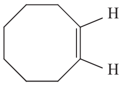
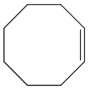
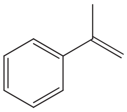
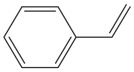
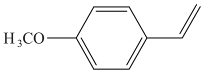
Also, in the presence of the other Fe-porphyrins, the following orders were observed:

FeTPPS$_4$(OAc) (Table S1): indene > cyclooctene > styrene > α-methylstyrene > *cis*-cyclooctene   cyclohexene ≫ 4-methoxystyrene ≫ 1-hexene (no reaction).
FeT(4-OCH_3)P(OAc) (Table S2): indene > 4-methoxystyrene ≫ styrene ∼ *cis*-cyclooctene ∼ cyclooctene ∼ cyclohexene ∼ α-methylstyrene ≫ 1-hexene (no reaction).
FeT(2-py)P(OAc) (Table S3): indene > styrene > cyclohexene ∼ α-methylstyrene ≥ *cis*-cyclooctene ≥ cyclooctene ≫ 4-methoxystyrene ≫ 1-hexene (no reaction).
FeT(3-py)P(OAc) (Table S4): cyclooctene > α-methylstyrene ≥ *cis*-cyclooctene ∼ indene > cyclohexene ≫ 4-methoxystyrene ≥ styrene ≫ 1-hexene (no reaction).
FeT(4-py)P(OAc) (Table S5): indene ≫ cyclohexene > styrene ≫ cyclooctene ∼ *cis*-cyclooctene > α-methylstyrene ∼ 4-methoxystyrene ∼ 1-hexene (no reaction).

Also, for the reactions performed in aqueous media:

FeT(2-CH_3Py)P(OAc) (Table S6): 4-methoxystyrene > α-methylstyrene > cyclohexene > styrene ≫ indene ≫ *cis*-cyclooctene ≥ cyclooctene ≫ 1-hexene (no reaction).
FeT(3-CH_3Py)P(OAc) (Table S7): 4-methoxystyrene > α-methylstyrene > cyclohexene > indene > styrene ≫ *cis*-cyclooctene ∼ cyclooctene ≫ 1-hexene (no reaction).
FeT(4-CH_3Py)P(OAc) (Table S8): 4-methoxystyrene > α-methylstyrene > styrene > cyclohexene > indene ≫ cyclooctene ≥ *cis*-cyclooctene ≫ 1-hexene (no reaction).

Table 4
Oxidation of olefins with TBAP in CH_2Cl_2 using FeTPP(OAc) as catalyst.[a]

Olefins	Conversion (%)[b]	Epoxide yield (%)[b]	Epoxide selectivity (%)
	29.616	29.616	100
	13.242	13.242	100
	12.961[c]	12.961	100
	16.725	16.725	100
	10.205	10.205	100
	13.948	13.948	100
	39.507	34.059	86[d]
	Trace	Trace	–

[a] The molar ratios of catalyst:ImH:olefin:TBAP are 1:5:83:170.
[b] For a reaction time of 4 h; the average value of three independent experiments.
[c] *cis*-Cyclooctene.
[d] 4-Methoxybenzaldehyde was the other product.

The observed order of reactivity of olefins depends on different factors such as: (i) the nature of active oxidant; (ii) degree of steric hindrance around the electrophilic oxygen atom of the active oxidant; (iii) stereoelectronic effects of the groups attached to the double bond; and (iv) degree of radical or carbocation character at the carbon atoms of the double bond involved in the oxidation reaction. In this regards, (i) high valent iron-oxo porphyrin species have been implicated as the key reactive intermediates in the catalytic cycles of dioxygen activation by heme and non-heme iron enzymes [10,30] and consequently are expected to be stronger oxidizing species compared to the corresponding (periodato)iron(III) porphyrin ones. More efficient oxidation of olefins with periodate observed in a mixed solvent of CH_2Cl_2 and *tert*-butanol [29] or wet CH_2Cl_2 [31] compared to the reactions conducted in CH_2Cl_2 was explained by the formation of high valent manganese oxo species in the presence of *tert*-butanol or water [7,29]; (ii) in the absence of bulky substituents at the meso positions, the steric hindrance around the electrophilic oxygen atom of an iron-oxo porphyrin moiety is usually less than that of a (periodato)iron(III) porphyrin one. Immediate formation of high valent Mn-oxo porphyrin species, in oxidation of olefins with TBAP carried out in CH_2Cl_2/H_2O mixed solvent was reported by Mohajer et al. [7]. Also, addition of small amounts of different alcohols to the reaction mixture leads to the formation of high valent Mn-oxo porphyrin moieties even in the case of MnTPP(OAc) [29]; (iv) radical and carbocation stabilizing substituents are expected to increase the reactivity of the olefins.

3.3.3. *The nature of active oxidant*

Epoxidation of *cis*- and *trans*-stilbene, in a competitive reaction, has been shown to be a useful probe to provide indirect

Table 5
Competitive oxidation of *cis*- and *trans*-stilbene in the presence of the Fe-porphyrins.[a,b]

Fe-porphyrins	*Cis–trans* isomerization[c]	*Cis/trans* epoxide[d]
FeT(2-py)P(OAc)	6.5	2.8 (3.1)
FeT(3-py)P(OAc)	17.0	3.3 (4.2)
FeT(4-py)P(OAc)	10.7	1.2 (1.5)
FeTPP(OAc)	2.0	8.3 (10.1)
FeT(4-OCH_3)P(OAc)	3.8	6.7 (7.1)
$FeTPPS_4$(OAc)	4.8	3.8 (4.0)
FeT(2-MePy)P(OAc)	34.7	0.3 (1.0)
FeT(3-MePy)P(OAc)	1.0	0.03 (0.04)
FeT(4-MePy)P(OAc)	16.0	0.12 (0.3)

[a] The molar ratios for (*cis*-stilbene, *trans*-stilbene):oxidant:ImH:catalyst are: (500, 500):170:0 or 5(see the footnotes of Table 3):1.

[b] Analyzed by ^1H NMR.

[c] Obtained by control reaction using *cis*-stilbene, TBAO:ImH:catalyst in 500:170:0 or 5 (see the footnotes of Table 3):1.

[d] The data in parentheses show the corrected *cis/trans* stilbene oxide considering the *cis* to *trans* isomerization upon the oxidation of *cis*-stilbene.

evidence on the nature of active oxidant in the metalloporphyrin catalyzed epoxidation of olefins in the absence of non-bulky *ortho*-substituents on the phenyl groups of *meso* tetraphenylporphyrins [7,10,16,29]. The results of competitive oxidation of *cis*- and *trans*-stilbene with TBAO in the presence of the Fe-porphyrins are summarized in Table 5.

According to the data of Table 5, the involvement of a high valent iron-oxo porphyrin species is more pronounced in the case of $FeTPPS_4$(OAc), FeT(2-py)P(OAc), FeT(3-py)P(OAc), FeT(4-py)P(OAc) and the N-methylated analogues. The observed ratio of 1.5 for the reaction catalyzed by FeT(4-py)P(OAc), indicates the nearly exclusive involvement of an iron-oxo moiety as the active oxidation intermediate [7,10]. In the case of FeTPP(OAc) and FeT(4-OCH_3)P(OAc), the results are in the favor of a periodato iron(III)porphyrin species. Also, a significant *cis*- to *trans* isomerization associated with the oxidation of *cis*-stilbene [7,27,28] was observed in oxidation of *cis*-stilbene with periodate in the presence of FeT(2-MePy)P(OAc), FeT(3-MePy)P(OAc) and to a lesser extent in the case of FeT(4-py)P(OAc). We have previously reported a high *cis*- to *trans* isomerization in oxidation of *cis*-stilbene with the same oxidant, using FeT(n-Pr)P(OAc) as catalyst [27]. These remarkable isomerizations seem to be in agreement with the involvement of a high-valent Fe-oxo species rather than a six coordinate periodato 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 around the electrophilic oxygen atom, i.e. a metal-oxo one. While the presence of bulky substituents at the *ortho* positions of the aryl groups of manganese *meso*-tetra(aryl)porphyrins has been shown to decrease the *cis/trans* isomerization [7], oxidation of *cis*-stilbene in the presence of FeT(2-MePy)P(OAc) is accompanied with significant degree of *cis/trans* isomerization. This observation is indicative of significant cleavage of the C—C double bond. On the other hand, the unusual preference of *trans*-stilbene over *cis*-stilbene observed in the competitive epoxidation reaction catalyzed by FeT(3-MePy)P(OAc) and FeT(4-MePy)P(OAc) cannot be explained by the *cis/trans* isomerization [27]. Nam et al. reported such an unexpected preference for *trans*-stilbene over *cis*-stilbene in the competitive epoxidations of *cis*- and *trans*-stilbenes catalyzed by Fe(TPFPP)Cl which was the most electron-deficient iron porphyrin complex of the used Fe-porphyrins [32].

Table 6
Oxidation of indene with TBAP catalyzed by the Fe-porphyrins.[a]

Fe-porphyrins	Conversion (%)	Epoxide yield (%)	Epoxide selectivity (%)
FeTPP(OAc)	29.616	29.616	100
FeT(4-OCH_3)PP(OAc)	32.756	32.756	100
FeT(4-SO_3H)PP(OAc)	30.857	30.857	100
FeT(2-Py)P(OAc)	38.102	38.102	100
FeT(3-Py)P(OAc)	12.285	12.285	100
FeT(4-Py)P(OAc)	41.842	41.842	100
FeT(2-CH_3Py)P(OAc)	29.378	29.378	100
FeT(3-CH_3Py)P(OAc)	47.701	47.701	100
FeT(4-CH_3Py)P(OAc)	51.025	51.025	100

[a] See the footnotes of Table 3 for details.

3.3.4. Relative catalytic activity of the Fe-porphyrins

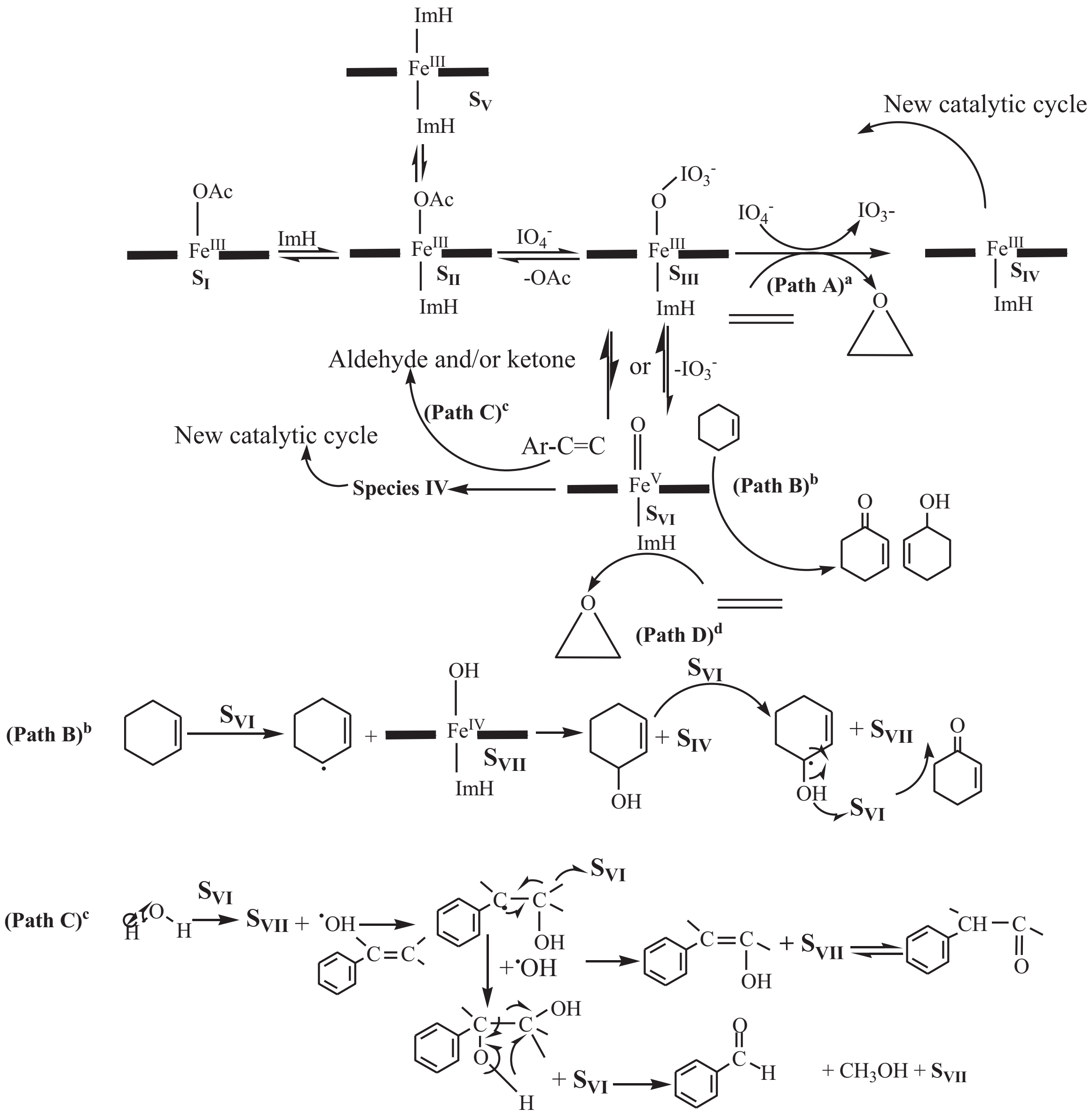
Oxidation of indene with TBAP in the presence of different Fe-porphyrins (Table 6) shows the following order of catalytic activity of the Fe-porphyrins:

Indene: FeT(4-CH_3Py)P(OAc) > FeT(3-CH_3Py)P(OAc) > FeT(4-Py)P(OAc) > FeT(2-Py)P(OAc) > FeT(4-OCH_3)PP(OAc) ≥ FeT(4-SO_3H)PP(OAc) ≥ FeTPP(OAc) ≥ FeT(2-CH_3Py)P(OAc) > FeT(3-Py)P(OAc).

Also, for the other olefins, the orders are as follows:

Styrene (Table S9): FeT(4-CH_3Py)P(OAc) > FeT(2-CH_3Py)P(OAc) ≫ FeT(3-CH_3Py)P(OAc) > FeT(4-SO_3H)PP(OAc) > FeTPP(OAc) ≥ FeT(2-Py)P(OAc) ≥ FeT(4-Py)P(OAc) > FeT(4-OCH_3)PP(OAc) > FeT(3-Py)P(OAc).
Cyclooctene (Table S10): FeT(3-CH_3Py)P(OAc) > FeT(4-SO_3H)PP(OAc) > FeTPP(OAc) > FeT(3-Py)P(OAc) > FeT(4-CH_3Py)P(OAc) > FeT(2-Py)P(OAc) > FeT(2-CH_3Py)P(OAc) > FeT(4-OCH_3)PP(OAc) > FeT(4-Py)P(OAc).
Cis-cyclooctene (Table S11): FeT(4-SO_3H)PP(OAc) > FeTPP(OAc) ≥ FeT(3-Py)P(OAc) > FeT(2-Py)P(OAc) > FeT(4-CH_3Py)P(OAc) ≥ FeT(2-CH_3Py)P(OAc) > FeT(4-OCH_3)PP(OAc) > FeT(3-CH_3Py)P(OAc) > FeT(4-Py)P(OAc).
Cyclohexene (Table S12): FeT(2-CH_3Py)P(OAc) > FeT(3-CH_3Py)P(OAc) > FeT(4-CH_3Py)P(OAc) > FeT(4-SO_3H)PP(OAc) ≥ FeTPP(OAc) ~ FeT(4-Py)P(OAc) > FeT(2-Py)P(OAc) ~ FeT(3-Py)P(OAc) > FeT(4-OCH_3)PP(OAc).
4-Methoxystyrene (Table S13): FeT(4-CH_3Py)P(OAc) ≥ FeT(3-CH_3Py)P(OAc) ≥ FeT(2-CH_3Py)P(OAc) ≫ FeTPP(OAc) > FeT(4-OCH_3)PP(OAc) > FeT(4-SO_3H)PP(OAc) > FeT(3-Py)P(OAc) ≥ FeT(2-Py)P(OAc) > FeT(4-Py)P(OAc).
α-Methylstyrene (Table S14): FeT(2-CH_3Py)P(OAc) > FeT(4-CH_3Py)P(OAc) ≥ FeT(3-CH_3Py)P(OAc) ≫ FeT(4-SO_3H)PP(OAc) > FeT(3-Py)P(OAc) > FeT(2-Py)P(OAc) ≥ FeTPP(OAc) > FeT(4-OCH_3)PP(OAc) > FeT(4-Py)P(OAc).

Although the result of degradation experiments showed low oxidative stability of FeT(2-Mepy)P(OAc) and FeT(3-Mepy)P(OAc) under reaction conditions, it is observed that a N-methylated FeT(Py)P(OAc) is usually the most efficient catalyst of the series. In oxidation of *cis*-cyclooctene, FeT(4-SO_3H)PP(OAc) shows higher catalytic activity relative to the other Fe-porphyrins. Also, while the Fe-porphyrins with cationic *meso*-substituents are more efficient with respect to the other catalysts in the oxidation of styrene, FeT(4-Mepy)P(OAc) and FeT(2-Mepy)P(OAc) are substantially more efficient than FeT(3-Mepy)P(OAc). In other words, there is no close correlation between the relative catalytic performance of the metalloporphyrins and the electronic properties of the *meso*-substituents as well as the oxidative stability of the catalysts. Also, there is large difference between the degree of dependence of the catalytic activity of Fe-porphyrins to the electronic effects of the *meso*-substituents in oxidation of various olefins. In this regard, FeT(4-SO_3H)PP(OAc) with more electron deficient groups at the *meso* positions compared to FeTPP(OAc) is not necessarily a better catalyst relative to the latter (compare their relative activity



Scheme 1. Proposed mechanism for oxidation of different olefins with TBAP; different active oxidant species (S$_{III}$ and S$_{VI}$) and paths (A–D) are suggested to be involved in the oxidation reactions. [a]A six coordinate periodato Fe(III) complex (i.e. S$_{III}$) is the active oxidant intermediate. [b–d]Reactions performed with involvement of a high valent iron(V) oxo porphyrin species (i.e. S$_{VI}$) or iron(IV)–oxo porphyrin π-cation radicals (see Section 3.3.3 for the nature of active oxidants). In path C, H abstraction from H_2O to S$_{VI}$ has been suggested to be responsible of the formation of OH radical.

in oxidation of α-methylstyrene, indene and 4-methoxystyrene). In comparison of the Fe-porphyrins with phenyl and pyridyl substituents it is found that in spite of the higher oxidative stability of the latter (Table 3), with the exception of indene, the former is a more efficient catalyst in the oxidation of the other olefins. Also, FeT(4-OCH$_3$)PP(OAc) with better electron donating groups relative to those with pyridyl substituents has been usually more efficient than the latter. However, in comparison with the corresponding Mn-porphyrins [16], there is a better correlation between the catalytic activity of the Fe-porphyrins and the electronic properties of the *meso*-substituents. The order of catalytic performance of the Mn-porphyrins with pyridyl substituents was found to decrease as MnT(4-Py)P(OAc) > MnT(2- or 4-Py)P(OAc). Also, an unusual oxidative stability was observed for the former [16]. In the case of the Fe-porphyrins, although a similar trend of oxidative stability was observed, but the different relative activity was found for the three Fe-porphyrins in oxidation of different olefins. It is noteworthy that FeT(4-Py)P(OAc) shows no catalytic activity for the oxidation of 4-methoxystyrene and α-methylstyrene (see Tables S13 and S14).

From the steric point of view, the steric hindrance due to the presence of bulky methyl groups at the *ortho* positions [6,13] of FeT(2-Mepy)P(OAc) was expected to decrease its catalytic activity, compared to that of FeT(4-Mepy)P(OAc) and FeT(3-Mepy)P(OAc). The comparison of conversion rates of the reactions catalyzed by the three complexes shows that with the exception of indene and cyclooctene (Tables 6 and S10), in the case of the other olefins FeT(2-Mepy)P(OAc) has a catalytic activity greater than that of FeT(3-Mepy)P(OAc) and comparable with that of FeT(4-Mepy)P(OAc). Accordingly, the steric hindrance caused by the methyl groups seems to have little effects on the catalytic performance of the complex. It should be noted that the introduction of bulky substituents at the *ortho* positions of *meso*-tetraarylporphyrins has been used as a strategy to improve the stability of metalloporphyrins in oxidative condition [33].

However, the oxidative degradation of FeT(2-Mepy)P(OAc) is greater than FeT(4-Mepy)P(OAc) and the three FeT(py)P(OAc) complexes. Also, the observed significant *cis*- to *trans* isomerization associated with the oxidation of *cis*-stilbene in the presence of FeT(2-Mepy)P(OAc) shows the negligible steric hindrance of the *ortho* methyl groups; the formation of *trans*-stilbene oxide as the thermodynamically more stable isomer in oxidation of *cis*-stilbene requires a free rotation about the alkene C—C bond which is expected to be more feasible in the case of the metalloporphyrins with less steric strain [7].

3.3.5. *Proposed mechanism*

According to the results of the competitive oxidation of *cis*- and *trans*-stilbene, utilized to elucidate the nature of the active oxidation species as well as the ratio of the high valent iron oxo porphyrin species and the six coordinate periodato complex, Fe(porphyrin)(ImH)(IO_4), as the active oxidants, the product distribution observed in the presence of the used catalysts and the mechanistic studies performed on the iron porphyrin catalyzed oxidation of hydrocarbons [34,35] a possible mechanism (Scheme 1) is proposed for the oxidation of different olefins with periodate in aqueous and non-aqueous conditions. Paths A and D show the formation of epoxide with the involvement of the Fe(porphyrin)(ImH)(IO_4) species or a high valent iron oxo porphyrin intermediate, respectively. The formation of allyl alcohol (in the case of cyclohexene), aldehyde and ketone may be explained by a radical mechanism initiated by high valent iron oxo species [33,34] through H abstraction from olefins or water. Formation of S_V which leads to the occupation of the fifth and sixth coordination sites of the iron(III) atom causes the catalyst deactivation [7,26,27]. H_2O has been suggested (path C) to produce $^\bullet$OH radical in reaction with high valent iron(V) oxo porphyrin species (S_{VI}). However, the reduced form of this intermediate, i.e. (porphyrin)(ImH)iron(IV)—OH species may also be considered as the source of $^\bullet$OH radical, needed for the formation of aldehyde and ketone products; homolytic cleavage of the iron(IV)—OH bond gives $^\bullet$OH radical and the catalyst precursor (S_{IV}).

3.3.6. *A comparison between the catalytic activity of the iron and manganese porphyrins*

Very recently, we have reported the oxidation of different olefins with TBAP in the presence of the manganese complexes of the title porphyrins, with the exception of the N-methylated *meso*-tetra(pyridyl)porphyrins [16]. In comparison with the results obtained with the manganese porphyrins (i) FeT(2-, 3- or 4-py)P(OAc), FeTPP(OAc) and FeT(4-OCH$_3$)P(OAc) are more stable toward oxidative degradation than the manganese counterparts, although FeT(4-py)P(OAc) and MnT(4-py)P(OAc) have a comparable high stability relative to the other metalloporphyrins. Also, FeTPPS$_4$(OAc) is as stable as the manganese complex; (ii) similar to that observed in the case of the manganese porphyrin series, FeT(4-py)P(OAc) and the N-methylated analogue are the most stable iron porphyrins among the series; (iii) greater differences were observed between the oxidative stability of FeT(2-, 3- or 4-py)P(OAc) and FeT(phenyl- or 4-methoxyphenyl)P(OAc), compared to that observed between the manganese ones; (iv) in spite of the crucial role of ImH on the catalytic performance of the manganese porphyrins [16] and iron porphyrins with phenyl, 4-sulfonatophenyl and 4-methoxyphenyl at the *meso* positions, the presence of ImH has a negative effect on the activity of FeT(2-, 3- or 4-Py)P(OAc) and the N-methylated analogues; (v) the manganese porphyrins are generally more efficient catalysts than the iron ones. However, the iron and manganese porphyrins with pyridyl substituents may have comparable catalytic activities; (vi) similar to that observed in the case of the manganese porphyrins, there is no close correlation between the stereoelectronic properties of the *meso* substituents and their catalytic activity.

4. Conclusions

In this study, the influence of the electronic properties of the *meso*-substituents and the molar ratio of ImH/catalyst on the catalytic activity of a series of iron porphyrin in oxidation of olefins with TBAP was studied and the following results were obtained: (i) ImH showed no co-catalytic activity in oxidation reactions catalyzed by Fe-porphyrins containing pyridyl or N-methylated pyridyl substituents at the *meso*-positions; (ii) in spite of the significant increase in the catalytic performance of the other Fe-porphyrins due to the presence of ImH, the maximum catalytic efficiency achieved with a smaller molar ratio of ImH to catalyst (i.e. the 5:1 molar ratio of ImH to catalyst) compared to that in the case of the corresponding Mn-porphyrins (i.e. 10:1); (iii) as was observed in the comparison of the Mn-porphyrins with pyridyl substituents, the oxidative stability of FeT(4-py)P(OAc) is remarkably higher than that of FeT(2-py)P(OAc) and FeT(3-py)P(OAc). Also, the same trend was found in the comparison of the N-methylated analogues. However, N-methylation of FeT(2-, 3- or 4-py)P(OAc) led to the substantial decrease in their oxidative stability; (v) in spite of the lack of close correlation between the catalytic activity of the Fe-porphyrins and the electronic properties of the *meso*-substituents, in comparison with the corresponding Mn-porphyrins, there is a better correlation between the catalytic activity of the Fe-porphyrins and the electronic effects of the *meso*-groups; (vi) the competitive oxidation of *cis*- and *trans*-stilbene, gave evidence of the involvement of high valent Fe-oxo porphyrins as well as periodato iron porphyrins as the active oxidants in reactions catalyzed by the used iron porphyrins. However, the involvement of a high valent iron-oxo porphyrin species is more pronounced in the case of FeTPPS$_4$(OAc), FeT(2-py)P(OAc), FeT(3-py)P(OAc), FeT(4-py)P(OAc) and the N-methylated analogues; (vii) an unusual preference of *trans*-stilbene over *cis*-stilbene observed in the competitive epoxidation reaction catalyzed by FeT(3-MePy)P(OAc) and FeT(4-MePy)P(OAc) which cannot be described by the *cis*/*trans* isomerization; (viii) large difference has been observed in the product distribution for oxidation reactions with TBAO performed in dichloromethane and aqueous solvent; while in dichloromethane, the oxidation of olefins gave the corresponding epoxide as the sole (or nearly the exclusive) product, running the reaction in water led to the formation of aldehyde and/or ketone as the major product; (ix) N-methylation of FeT(py)P(OAc) at the *ortho* position seems to have little steric effects on the catalytic activity of the Fe-porphyrin as well as the degree of *cis*/*trans* isomerization in the oxidation of *cis*-stilbene.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.11.003.

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