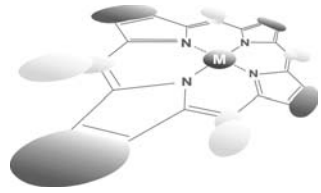
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2010; **14**: 335–342
DOI: 10.1142/S1088424610002136

Published at http://www.worldscinet.com/jpp/



Effects of methoxy-substituted metalloporphyrins in catalytic alkene epoxidation by *n*-Bu_4NHSO_5

Amineh Aghabali and Nasser Safari*◊

Chemistry Department, Shahid Beheshti University, G.C., Evin, Tehran 1983963113, Iran

Received 17 March 2009
Accepted 29 August 2009

ABSTRACT: TPPMnOAc and four different kinds of manganese tetraphenylporphyrin acetates were synthesized using different numbers of methoxy substituents in various positions of the phenyl rings. These porphyrins were used as catalysts in the epoxidation of various alkenes with tetra-*n*-butylammonium hydrogen monopersulfate (*n*-Bu_4NHSO_5) as the oxidant and imidazole as the axial base. The following order of catalytic activity was obtained: TPPMnOAc ≥ T(2,3-OMeP)PMnOAc > T(4-OMeP)PMnOAc > T(3,4-OMeP)PMnOAc > T(2,4,6-OMeP)PMnOAc. By studying the UV-vis spectra in the reaction solution, the stability of the applied methoxy porphyrins and the effect of this factor on obtained yields were investigated. Lower catalytic activity in some of the methoxy porphyrins emphasized steric effects and special hydrogen bonding among the reaction elements. However, the stability of T(2,3-OMeP)PMnOAc under our reaction condition was considerable and high activity was observed. By adding small amounts of alcohol to the reaction solution, the effect of the solvent mixture was previewed and steps were taken to identify the active intermediate of the catalyst in these conditions.

KEYWORDS: methoxy porphyrin, alkene epoxidation, oxone, imidazole.

INTRODUCTION

Efforts in simulating Cytochrome P450 and peroxidases systems have encouraged scientists to pay attention to synthetic metalloporphyrins and look more deeply into their efficiencies [1–8]. Metalloporphyrins were used in catalytic oxidation [9–11] including hydroxylation [12–16] and epoxidation [17–22] of hydrocarbons.

Changing the substitutional groups on the porphyrin rings results in different electronic and steric properties. Groves *et al.* were the first researchers to significantly mimic C-P450 using TPPFeCl in cyclohexene oxidation with PhIO [23]. These first-generation catalysts were found to suffer from rapid auto-oxidation degradation of the porphyrin ring. To overcome this problem, second-generation porphyrin catalysts containing electron-withdrawing substituents on the phenyl rings attached to the *meso*-position of the porphyrin were developed [24]. In addition, the substitutions near the metal center had the advantage of inhibiting the bimolecular self-destruction of porphyrin catalysts. In *ortho*-substituted tetraphenylporphyrin, (1) the bulky groups in *ortho* positions, (2) the more hindered rotation of axial base around the metal-nitrogen bond, and (3) van der Waals interactions between the *ortho* groups and the ligand, have been considered. The second-generation was more resistant to oxidative destruction but the electron deficiency on the phenyl ring could reduce the rate of the catalytic reaction. Therefore, there has been much research on catalyst modifications in order to optimize the selectivity, product distributions, catalyst stability and the rate of the oxidation processes [25–33].

The preliminary approach to mimicking the biochemical properties of hemoproteins also highlighted the importance of the axial ligand. These axial ligands, like nitrogen from histidine in peroxidase, are in the *trans* position of the catalytic site of the metalloenzymes and can protect the porphyrins from dimerization. The key role of π-bonding interactions and σ-donation of nitrogenous axial ligands in activating coordinated oxidant have been studied [34]. The shift of electron density from the dπ electron orbitals into π_x^* will facilitate heterolytic cleavage of the O-O

◊SPP full member in good standing

*Correspondence to: Nasser Safari, email: n-safari@cc.sbu.ac.ir, tel: +98 21-29902886, fax: +98 21-22431661

bond in the intermediate and the formation of metal-oxo species. This phenomenon leads to better single oxygen donation to substrates and more selective epoxide formations [35–37].

An extensive range of oxidants have been used as oxygen atom transfer reagents to metalloporphyrins, such as PhIO, H_2O_2, *m*-CPBA, hydroperoxides and air, [5, 19]. Furthermore, particular attention has been drawn to potassium monopersulfate, oxone [38]. HSO^-_5 has a non-symmetrical O-O bond that encourages metal-oxo formation [9].

Other examinations have shown that solvent can have a predominant effect on the mechanism and yield of the catalytic oxidation reactions. In this regard, insertion of protic solvents like alcohol in the epoxidation reaction media affects the total yields in catalytic oxidations with metalloporphyrins. Protic solvents act as general acid catalysts and facilitate the O-O bond cleavage. Hydrogen bonding between the alcohol and coordinated oxidant can also facilitate O-O cleavage and eases the formation of (Por)M=O species [31, 39–41].

The present work reports the results of alkenes epoxidation by *n*-Bu_4NHSO_5 with different manganese methoxy porphyrins as the catalysts and the nitrogenous base of imidazole as the co-catalyst. The effects of the position and plurality of the methoxy groups on the yields of epoxidation and the stability of catalyst were investigated. In the end, we tried to suggest the probable activated form of porphyrin while adding different amounts of alcohol to the reaction solution.

EXPERIMENTAL

Materials

Free-base porphyrins; tetraphenylporphyrin ($TPPH_2$), (5,10,15,20-tetrakis(2,4,6-trimethoxyphenyl)porphyrin), (5,10,15,20-tetrakis(2,3-dimethoxyphenyl)porphyrin), (5,10,15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin), (5,10,15,20-tetrakis(2,6-dimethoxyphenyl)porphyrin) and (5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin) were prepared using the Lindsey method [42]. Using this method, distilled pyrrol (7.2 mmol, 0.5 mL) and appropriate methoxy benzaldehyde (1.5 mmol) were added to a round-bottom flask containing one liter dried CH_2Cl_2 as the solvent and equipped with condenser and N_2 atmosphere. Boron trifluoride etherate (75 µl, 0.06 mmol) was added as the catalyst to the mixture. It was stirred for 24 hours at room temperature. To oxidize the produced porphyrinogen, the solution was refluxed with *p*-chloranil (5.5 mmol, 1.35 g) for two hours. Porphyrin formation was confirmed with UV-vis. All the synthesized porphyrins were purified with neutral alumina column chromatography. Porphyrins were metalated by $Mn(OAc)_2{\cdot}4H_2O$ according to the Adler procedure [43]. Imidazole was used as the nitrogenous base; related alkenes (cyclooctene, cyclohexene, *cis*-stilbene, styrene, 4-chloro styrene, 4-methoxy styrene, α-methyl styrene, 1-octene and 1-heptene) were all purchased from Fluka or Merck.

Since commercial potassium salt of oxone is not soluble in organic solvents [44], the corresponding soluble salt, tetrabutylammonium monopersulfate, was prepared using the following procedure. Tetra-*n*-butylammonium hydrogen sulfate (2.0 mg, 5.9 mmol) was dissolved in water (20 mL). Potassium monopersulfate (2 g, 6.5 mmol) was added to this solution and stirred until a colorless solution was obtained. This product was extracted with CH_2Cl_2 (40 mL) and the organic phase was dried on dehydrated Na_2SO_4 and filtered. After the evaporation of the solvent, the residue was washed with *n*-hexane (10 mL) and dried in vacuum. Because of the reducing oxidation ability of this oxidant and in order to obtain reproducible results, only freshly produced oxidant was used and it was kept in a refrigerator.

Tetra-*n*-butylammonium hydrogen periodate (*n*-Bu_4NIO_4) was also prepared following the procedure in the literature [45] with some modifications.

Oxidation reactions

Stock solutions of manganese porphyrins (3×10^{-3} M), imidazole (0.1 M) and alkenes (0.05 M) were prepared in CH_2Cl_2. In a 10 mL round-bottom flask the following were added in order: alkene (0.05 mmol, 1 mL), porphyrin catalyst (6×10^{-4} mmol, 0.2 mL), imidazole (from 10 to 100 mmol) and tetra-*n*-butylammonium hydrogen monopersulfate (0.104 mmol, 0.043 g) and the reaction solution was stirred for an appropriate amount of time and 0.5 µl of it was injected to GC. To identify the parent and by-products, authentic samples and standard solutions were used in internal standard method.

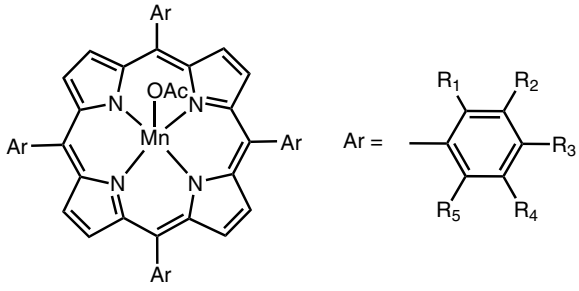
Instrumentation

Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx®-1 capillary column. UV-vis spectra were recorded in CH_2Cl_2 by a Shimadzu 2100 spectrophotometer.

RESULTS AND DISCUSSION

Alkene epoxidation

The metalloporphyrins presented in Fig. 1 were used for alkene epoxidation by *n*-Bu_4NHSO_5. Due to the significant role of the axial base in these reactions, the best molar ratio of imidazole to catalyst was optimized in the reaction condition (Fig. 2) and the molar ratio of 80:1 for imidazole:T(2,3-OMeP)PMnOAc was obtained. To be assured of the discovered optimum ratio, Im:Cat ratios were also examined with our other catalysts. Blockage of



	R_1	R_2	R_3	R_4	R_5
TPPMnOAc	H	H	H	H	H
T(4-OMeP)PMnOAc	H	H	OCH_3	H	H
T(3,4-OMeP)PMnOAc	H	OCH_3	OCH_3	H	H
T(2,3-OMeP)PMnOAc	OCH_3	OCH_3	H	H	H
T(2,6-OMeP)PMnOAc	OCH_3	H	H	H	OCH_3
T(2,4,6-OMeP)PMnOAc	OCH_3	H	OCH_3	H	OCH_3

Fig. 1. Structure of porphyrins used in our work

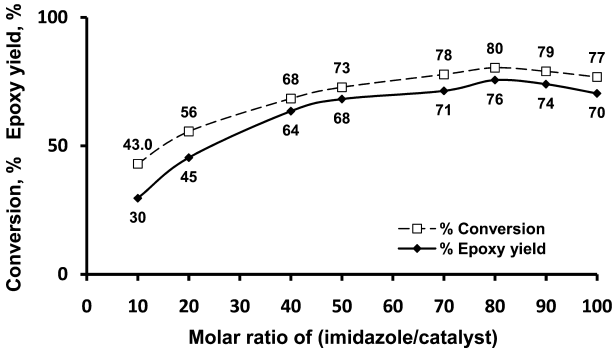


Fig. 2. Cyclooctene oxidation by different molar ratios of imidazole corresponding to T(2,3-OMeP)PMnOAc as catalyst with following ratios: (catalyst/imidazole/cyclooctene/oxidant: 1/X/83/164)

the catalytic site as $(Im)_2Mn(Por)$ formation and oxidation of imidazole instead of substrate are the reasons for lower catalytic activity at higher molar ratios of imidazole to catalyst.

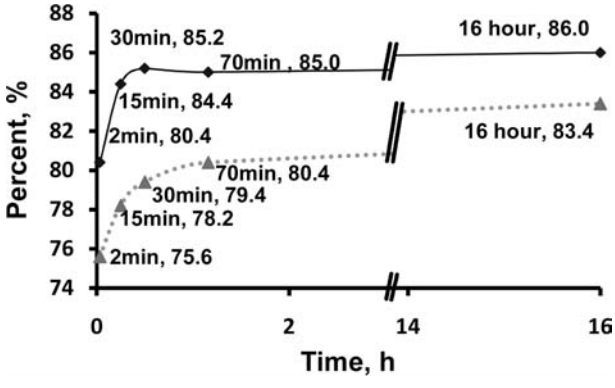


Fig 3. Percentage of conversion (solid line) and percentage of epoxy yield (dashed line) for cyclooctene epoxidation at different periods of time corresponding to T(2,3-OMe OMeP) PMnOAc as catalyst with following ratio: (catalyst/imidazole/cyclooctene/oxidant : 1/80/83/164). Reactions were carried out in triplicate and the averages are reported with ± (1–4)%

Sets of time periods were examined to find the best reaction time (Fig. 3). The most appropriate yields were obtained in 30 minutes and after this period, results were almost constant. These tests were carried with cyclooctene and T(2,3-OMeP) PMnOAc and were confirmed using our other catalysts and substrates.

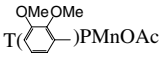
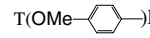
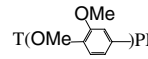
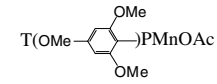
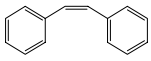
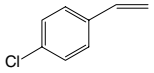
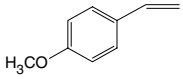
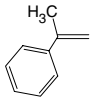
Using the amounts presented in Oxidation Reactions section, catalytic epoxidation of different alkenes was performed with synthesized manganese porphyrins. The final optimized molar ratio for Cat:Im:Substrate:Oxidant was 1:80:83:164. The reaction mixture was stirred at room temperature for 30 minutes in a tightly closed flask and then was examined with GC (Table 1). For a stepped approach to data interpretations, results were analyzed in rows or in columns of Table 1.

Effect of catalyst type

The rows of Table 1 show trends of the catalyst reactivity in the order: TPPMnOAc ≥ T(2,3-OMeP) PMnOAc > T(4-OMeP)PMnOAc > T(3,4-OMeP) PMnOAc > T(2,4,6-OMeP)PMnOAc .

T(2,3-OMeP)PMnOAc displayed high yields, rates and stabilities. It appears that some factors are manipulating the electron donation of substituted methoxy groups. We presumed that this quenching is related to the hydrogen bonding between the active part of the oxidant (HSO_5^-) and the methoxy groups. To substantiate this claim, we tried to use another oxidant which no longer has the capability of the named hydrogen bonding but which has a structure close to that of our major oxidant (n-Bu_4NHSO_5). For this purpose, n-Bu_4NIO_4 was used for cyclooctene oxidation in the presence of imidazole and all of our catalysts. The reactions were carried with optimized ratio of imidazole for about 24 hours and the results were compared with the other oxidant (Table 2). Here, the observed trend of the catalytic activity was as follows: T(4-OMeP)PMnOAc > TPPMnOAc > T(2,3-OMeP)PMnOAc > T(3,4-OMeP)PMnOAc > T(2,4,6-OMeP)PMnOAc. As expected, this order demonstrates a better catalytic activity for a porphyrin with an electron-donor methoxy group on the *para*-position of the phenyl ring. This property is related to the rich electron center in this methoxy porphyrin [34]. But likewise, the previous order of T(2,3-OMeP)PMnOAc > T(3,4-OMeP) PMnOAc > T(2,4,6-OMeP)PMnOAc was repeated. So it was suggested that some other factors, such as the steric effects, hydrogen bonding with the imidazole axial base and interactions of C-H of imidazole with the oxygen of the methoxy, should be considerable in these catalysts. In the latter, the possible interaction of electronegative elements such as oxygen or fluorine with the more highly alkylated carbons (like C-H adjacent to the donor site of imidazole) delocalizes electrons from C-H bonds into the low-lying C-F or C-O σ* orbitals [46]. These interactions has been previewed in catalytic ability of TPFPPMnOAc

Table 1. Conversion (epoxy yield) for different kinds of alkenes with various catalysts

Substrate	Catalyst				
	T()PMnOAc	T()PMnOAc	T(OMe )PMnOAc	T(OMe )PMnOAc	T(OMe )PMnOAc
	88.0 (79.1)	79.0 (70.0)	67.4 (57.2)	51.3 (43.9)	37.3 (30.3)
	83.6 (57.6) [2.0][a] [5.1][b]	82.9 (57.6) [2.7][a] [3.2][b]	62.9 (43.0) [0][a] [5.5][b]	58.5 (29.8) [1.4][a] [3.5][b]	28.3 (18.1) [0][a] [0][b]
	91.1 (87.8)	80.3 (73.0)	74.3 (60.9)	62.1 (54.4)	26.8 (21.8)
	79.6 (67.6)	76.7 (69.3)	63.6 (49.5)	56.0 (35.8)	38.0 (19.5)
	76.8 (75.2)	75.0 (72.0)	61.3 (60.6)	50.2 (41.0)	23.8 (23.4)
	100.0 (100.0)	98.0 (96.4)	93.0 (91.3)	64.0 (60.5)	25.9 (23.4)
	80.9 (80.9)	80.0 (73.0)	70.0 (62.1)	58.0 (49.9)	19.4 (19.4)
	25.0 (9.3)	31.5 (13.4)	16.1 (5.9)	21.5 (3.3)	18.1 (4.7)
	20.2 (4.8)	27.7 (9.7)	c	c	c

n-Bu_4NHSO_5 was used as oxidant and imidazole as co-catalyst. The molar ratio for catalyst/co-catalyst/substrate/oxidant is 1/80/83/164. Reactions were carried in triplicate and the averages are reported with ± (1–4)%. GC measurements were carried by internal standard method. [a] Percentage of 2-cyclohexene 1-ol. [b] Percentage of 2-cyclohexene 1-one. [c] Not detected.

Table 2. Cyclooctene oxidation in the presence of two different oxidants and all the applied catalysts

Catalyst	*n*-Bu_4NIO_4[a]		*n*-Bu_4NHSO_5[b]	
	Conversion, %	Epoxy yield, %	Conversion, %	Epoxy yield, %
TPPMnOAc	68.8	65.4	88.0	79.1
T(2,3-OMeP)PMnOAc	63.5	62.8	79.0	70.0
T(4-OMeP)PMnOAc	68.5	66.8	67.4	57.2
T(3,4-OMeP)PMnOAc	54.4	50.3	51.3	43.9
T(2,4,6-OMeP)PMnOAc	4.4	2.8	37.3	30.0
T(2,6-OMeP)PMnOAc	c	c	34.6	28.3

[a] Molar ratios: (catalyst/imidazole/substrate/n-Bu_4NIO_4: 1/10/83/164) and reaction time was 24 hours. [b] Molar ratios: (catalyst/imidazole/substrate/n-Bu_4NHSO_5: 1/80/83/164) and reaction time was 30 min. [c] Not detected.

near nitrogenous bases which generate better catalytic properties [38].

T(3,4-OMeP)PMnOAc. In this porphyrin, in spite of its good electronic condition, catalytic activity is reduced. Two points can be implied as the reasons. Firstly, the possible interactions between the methoxy groups of the catalyst and the oxidant provide a steric hindrance around the catalyst (Fig. 4) and less access to the metal center. Secondly, interactions between imidazole and the methoxy groups or imidazole and oxidants can reduce the mobility of imidazole around the catalyst and interfere with metal-imidazole species formation.

T(4-OMeP)PMnOAc. Because of fewer methoxy groups and also their *para* and farther positions from the center of the porphyrin, steric crowdedness cannot be of much effectiveness in this catalyst. This can be a reason for the higher catalytic activity of T(4-OMeP)PMnOAc compared to T(3,4-OMeP)PMnOAc.

T(2,3-OMeP)PMnOAc. Crowdedness cannot be the only effective factor in the catalytic activity of

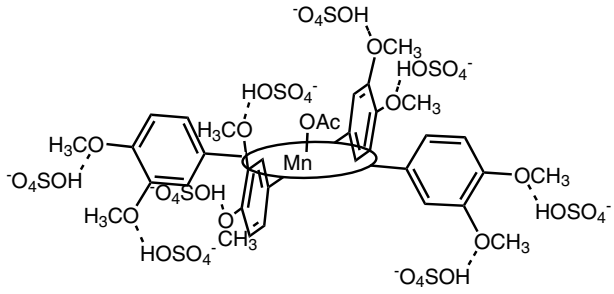


Fig. 4. Steric crowdedness around the metal center in T(3,4-OMeP)PMnOAc due to possible interactions between the active site of oxidant and methoxy groups of the porphyrin

T(2,3-OMeP)PMnOAc. As the distance of methoxy groups in T(2,3-OMeP)PMnOAc from the metal center is shorter, a more considerable decrease in the catalytic activity of T(2,3-OMeP)PMnOAc compared to T(3,4-OMeP)PMnOAc is expected. Some other factors are affecting this catalyst. First of all, due to the presence of substitutional groups with hydrogen bonding abilities in the *ortho*-position of the phenyl ring, some hydrogen bondings can occur between the N-H from imidazole and C-O: of the methoxy. This factor simplifies the imidazole approach to the metal core of T(2,3-OMeP)PMnOAc and encourages formation of (Im)(Por)Mn(OAc). The interactions between the C-H of imidazole and σ* orbital of C-O: in the *ortho*-position of the phenyl ring also eases the approach of the co-catalyst to the manganese, despite the steric crowdedness around it (Fig. 5a) [46]. The last reason can be related to the catalytic stability of this catalyst that will be presented in Catalyst Stability section.

T(2,4,6-OMeP)PMnOAc. The poor catalytic activity of this catalyst in contrast to other methoxy porphyrins may be related to the tendency of its eight *ortho* methoxies to interact with imidazole (as discussed for T(2,3-OMeP)PMnOAc). This can cause the rapid formation of bis-complexes of $(Im)_2Mn(Por)$ which transforms the catalyst into an inactive phase (Fig. 5b). The steric hindrance may be another prohibitive factor in the catalyst. Due to the oxidant capability for hydrogen bonding with the methoxy groups and the presence of eight (C-O:····HSO_5^-) interactions, steric crowdedness is remarkably increased around the metal center. The data in Table 2 for cyclooctene epoxidation with T(2,6-OMeP)PMnOAc can also confirm the claims for low catalytic activity of T(2,4,6-OMeP)PMnOAc.

Epoxidation of various alkenes

As can be seen in the columns of Table 1, steric effects and electronic properties of the alkenes are observable in yields of the reactions. Factors such as size of the substrate, the electron density on the double bond of the alkene and crowdedness around the catalyst are all effective in yields for each catalyst and a group of alkenes. The two following epoxidation orders have almost always happened for all catalysts: (4-methoxy styrene > α-methyl styrene > styrene > 4-chloro styrene) and (*cis*-stilbene > styrene). For instance, (*cis*-stilbene > styrene) shows better electron density on the *cis*-stilbene's double bond due to better electron donation from the two phenyl rings, an effect that has overcome the steric hindrance around *cis*-stilbene.

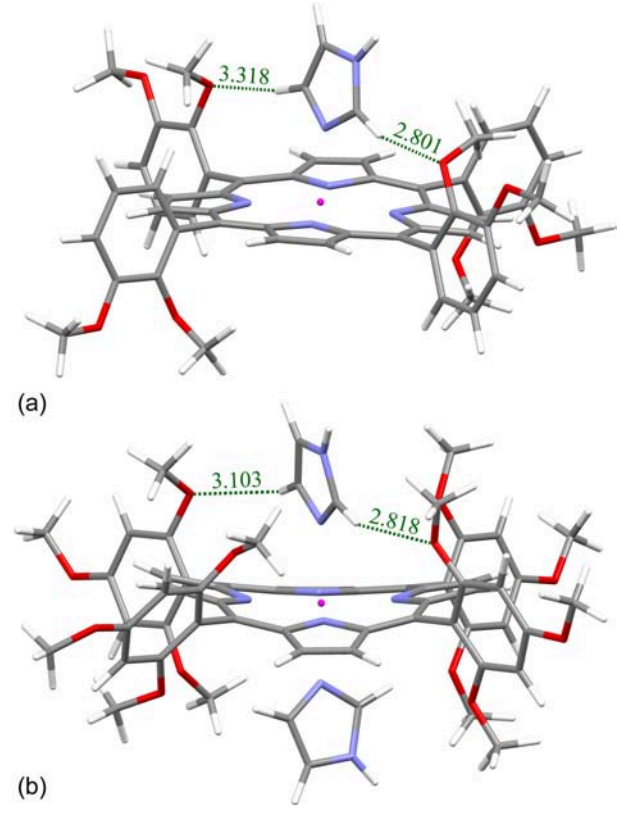


Fig. 5. Possible interactions between (a) imidazole and T(2,3-OMeP)PMnOAc, (b) imidazole and T(2,4,6-OMeP)PMnOAc. The structures are optimized with a semi-empirical PM3 calculation

Minimum conversions were observed in the linear alkenes of 1-ocetene and 1-heptene, which have the lowest electron densities and no conjugated π-bondings. However, T(2,3-OMeP)PMnOAc shows higher epoxy yield for linear alkenes compared to all other catalysts. Therefore, we claim that T(2,3-OMeP)PMnOAc is a good catalyst for epoxidation of less reactive alkenes.

Catalyst stability

Seeking the stability of the used catalysts, their UV-vis spectra were submitted (Fig. 6) and interpreted. In Fig. 6a, spectra of T(2,3-OMeP)PMnOAc and its changes in the presence of oxidant and {imidazole + oxidant} were recorded. After adding the oxidant to the catalyst solution, λ_{Soret} has 6 nm shifts, which is related to the formation of {(Por)Mn(OAc)(HSO_5)}. The absorbance intensity for the Soret band has not changed significantly, which can be interpreted as the stability of catalyst in this situation. When T(2,3-OMeP)PMnOAc faces the oxidant and imidazole in the solution (spectrum 3 in Fig. 6a),

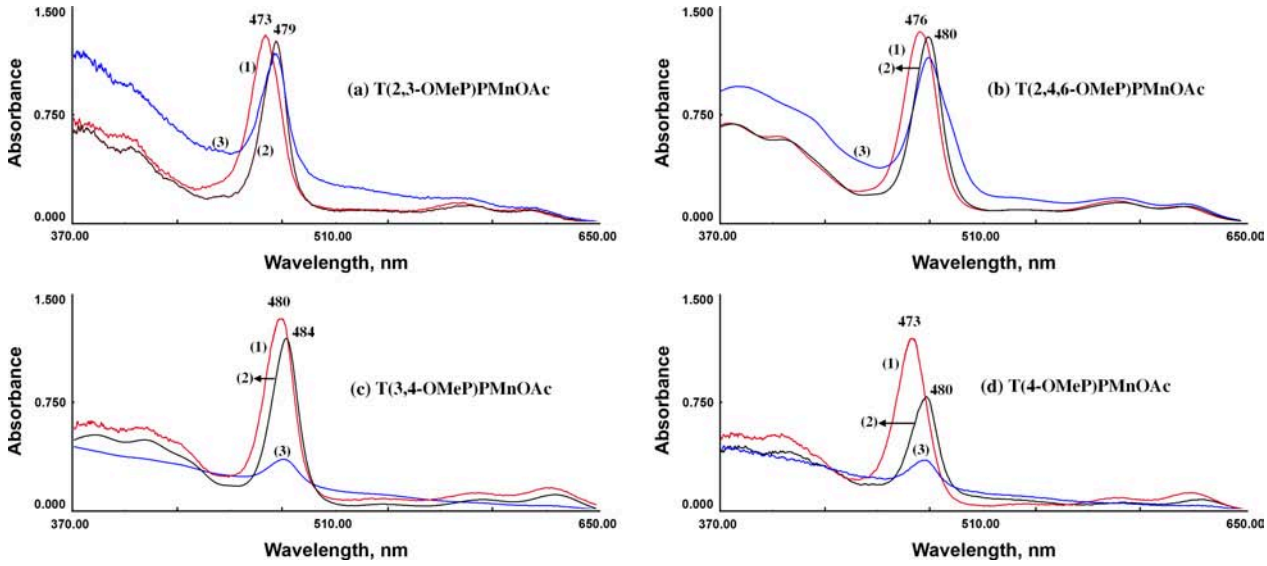


Fig. 6. The UV-vis spectra for following catalysts: (a) T(2,3-OMeP)PMnOAc, (b) T(2,4,6-OMeP)PMnOAc, (c) T(3,4-OMeP) PMnOAc, d) T(4-OMeP)PMnOAc. In spectra of each catalyst (1) represents catalyst solution (3.5×10^{-5} M), (2) relates to solution of catalyst (3.5×10^{-5} M) and oxidant, and (3) is the solution of three components: catalyst (3.5×10^{-5} M), oxidant and imidazole. The molar ratios used are the optimized ones in the epoxidation reaction. All the spectra were recorded in CH_2Cl_2 after 5 min

the intensity of the Soret does not decrease sharply. This demonstrates the stability of T(2,3-OMeP)PMnOAc due to the steric crowdedness around the *meso*-positions which are surrounded with *ortho*-methoxy groups. All the observations in Fig. 6a are repeated in Fig. 6b for T(2,4,6-OMeP)PMnOAc. After adding the oxidant to T(2,4,6-OMeP)PMnOAc, 4 nm shifts occur in the Soret band of the catalyst. The eight *ortho*-methoxies on phenyl rings shield the *meso*-position of this porphyrin. Therefore, the catalyst degradation is hindered and high stability is observed. This stability does not result in higher catalytic activities due to the formation of bis-imidazole complexes which were discussed previously. In Fig. 6c changes in the first and second spectra are the same as the previous discussed catalysts, but there is a sharp decrease in the absorption of the Soret band. This porphyrin has open areas around its *meso*-positions that cause its rapid degradation. This sharp decrease is also displayed in T(4-OMeP)PMnOAc (Fig. 6d). For this catalyst, we have the least crowdedness around the *meso*-position. So even after adding the oxidant to the catalyst, Soret band intensity decreases. Instability in T(3,4-OMeP)PMnOAc and T(4-OMeP)PMnOAc could be another reason for their lower catalytic activities in this system.

Additional observations

By-products. *Cis*-stilbene and cyclohexene had more than one product in the oxidation process (Fig. 7 and Table 1). Alcohol, ketone and epoxy are produced in cyclohexene epoxidation. Since total amounts of alcohol and ketone were less than 7% of the total conversion, epoxy selectivity is acceptable in these reactions.

Solvent effect. Adding small linear alcohols like CH_3OH with coordinating and hydrogen bonding abilities produce the metal-oxo (Mn=O) activated form of the catalyst more rapidly [39]. It is also believed that alcohols can act as general acid catalysts that motivate the heterolytic cleavage of the O-O bonds in the peroxo species and accelerates metal-oxo formation [31, 40]. On the other hand, better polarization in the solution, more stability of the activated porphyrin and its longer lifetime occur in the presence of the protic solvents [11].

Using small portions of CH_3OH in cyclooctene epoxidation with T(2,3-OMeP)PMnOAc produced an 8–12% increase in epoxy yields. Studying the UV-vis spectrum in CH_2Cl_2/CH_3OH solvent, a new broad band appeared in 424 nm (Fig. 8). This band is assigned to $[T(2,3\text{-OMeP})PMn(O)(Im)]^+$ active intermediate with long lifetime in this solvent mixture [47]. Addition of larger amounts of alcohol reduces the

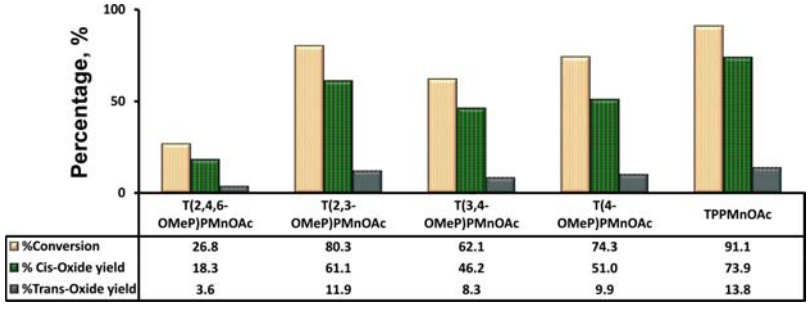


Fig. 7. By-products from epoxidation of *cis*-stilbene by different catalysts with *n*-Bu_4NHSO_5 as oxidant. The molar ratios were as follows: (catalyst/co-catalyst/substrate/oxidant: 1/80/83/164)

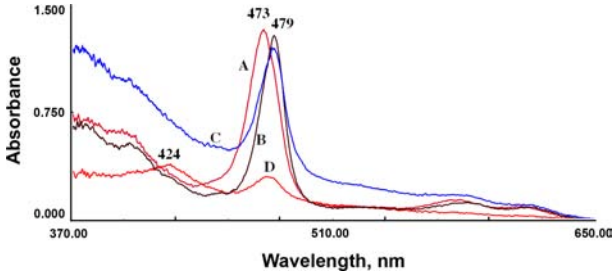


Fig. 8. UV-vis spectra for the interaction of T(2,3-OMeP)PMnOAc (A) in CH_2Cl_2; (B) in CH_2Cl_2 containing imidazole; (C) in CH_2Cl_2 containing imidazole and oxidant; (D) in CH_2Cl_2:CH_3OH with ratio of 16:1 and containing oxidant and imidazole. Spectra were recorded 5 min after adding the oxidant at room temperature

epoxidation product due to coordination of alcohol to the active site of the manganese porphyrin.

Solvent effects were also investigated for *cis*-stilbene, but there were no changes in the product distributions and after adding 200 μL of CH_3OH, ratios of *cis*/*trans*-stilbene oxide were almost constant.

CONCLUSION

Different manganese methoxy porphyrins were used as catalysts for alkene epoxidation in the presence of the imidazole nitrogenous base by *n*-Bu_4NHSO_5. The competition among steric and electronic properties of catalysts and substrates are effective in catalytic activities. Among the methoxy porphyrins used, T(2,3-OMeP)PMnOAc had the highest catalytic activity. The higher stability and yields of T(2,3-OMeP)PMnOAc in the catalytic process show that it is a good candidate in catalytic oxidations. This catalyst has shown higher proficiency for epoxidation of linear alkenes, in contrast to other applied catalysts. After using few amounts of small linear alcohol, CH_3OH, in the reaction media, the total yields increased and demonstrated Mn=O species as the main intermediate in CH_2Cl_2/CH_3OH mixed solution.

Acknowledgements

We would like to thank Graduate Study Councils of Shahid Beheshti University and the Catalyst Centre of Excellence (CCE) for financial support.

REFERENCES

1. Ortiz de Montellano PR. *Cytochrome P450: Structure, Mechanism, and Biochemistry*, Plenum Press: New York, 1995.
2. Dolphin D, Traylor TG and Xie LY. *Acc. Chem. Res.* 1997; **3**: 251–259.
3. Moro-oka Y and Akita M. *Catal. Today* 1998; **41**: 327–338.
4. Sono M, Roach MP, Coulter ED and Dawson JH. *Chem. Rev.* 1996; **96**: 2841–2888.
5. Gunter MJ and Turner P. *Coord. Chem. Rev.* 1991; **108**: 115–161.
6. Almarsson O and Bruice TC. *J. Am. Chem. Soc.* 1995; **117**: 4533–4544.
7. Traylor TG, Marsters Jr. JC, Nakano T and Dunlap BE. *J. Am. Chem. Soc.* 1985; **107**: 5537–5539.
8. Mansuy D. *Pure Appl. Chem.* 1987; **59**: 759–770.
9. *The Porphyrin Handbook*, Vol. 4, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: New York, 2000.
10. Sheldon RA. *Metalloporphyrins in Catalytic Oxidations*, Marcel Dekker: New York, 1994; pp 390.
11. Khavasi HR and Safari N. *J. Porphyrins Phthalocyanines* 2005; **9**: 75–81.
12. Traylor TG. *J. Am. Chem. Soc.* 1992; **114**: 1308–1312.
13. Groves JT and Viski P. *J. Org. Chem.* 1990; **55**: 3628–3634.
14. Guo C-C, Liu X-Q, Liu Y, Liu Q, Chu M-F and Zhang X-B. *J. Mol. Catal. A* 2003; **192**: 289–294.
15. Huang J-W, Huang W-Z, Mei W-J, Liu J, Hu S-G and Ji L-N. *J. Mol. Catal. A* 2000; **156**: 275–278.
16. Safari N, Bahadoran F, Hoseinzadeh MR and Ghiasi R. *J. Porphyrins Phthalocyanines* 2000; **4**: 285–291.
17. Groves JT and Nemo TE. *J. Am. Chem. Soc.* 1983; **105**: 5786–5791.
18. Traylor TG and Miksztal AR. *J. Am. Chem. Soc.* 1989; **111**: 7443–7448.
19. Campestrini S. *J. Mol. Catal. A* 2001; **171**: 37–42.
20. Haber J, Iwanejko R, Połtowicz J, Battioni P and Mansuy D. *J. Mol. Catal. A* 2000; **152**: 111–115.
21. Rose E, Quelquejeu M, Pandian RP, Lecas-Nawrocka A, Vilar A, Ricart G, Collman JP, Wang Z and Straumanis A. *Polyhedron* 2000; **19**: 581–586.
22. Cunningham ID, Danks TN, Hay JN, Hamerton I and Gunathilagan S. *Tetrahedron* 2001; **57**: 6847.
23. Groves JT, Nemo TE and Myres RS. *J. Am. Chem. Soc.* 1979; **101**: 1032–1033.
24. Chang CK and Ebina F. *J. Chem. Soc., Chem. Commun.* 1981: 778–779.
25. Ojima F, Kobayashi N and Osa T. *Bull. Chem. Soc. Jpn.* 1990; **63**: 1374–1380.
26. Nam W, Goh YM, Lee YJ, Lim MH and Kim C. *Inorg. Chem.* 1999; **38**: 3238–3240.
27. Cunningham ID, Danks TN, Hay JN, Hamerton I, Gunathilagan S and Janczak C. *J. Mol. Catal. A* 2002; **185**: 25–31.
28. Guo C-C, Song J-X, Chen X-B and Jiang G-F. *J. Mol. Catal. A* 2000; **157**: 31–40.
29. Schiavon MA, Iamamoto Y, Nascimento OR and Assis MdD. *J. Mol. Catal. A* 2001; **174**: 213–222.
30. Mandal AK, Khanna V and Iqbal J. *Tetrahedron Lett.* 1996; **37**: 3769–3772.
31. Khavasi HR, Davarani SSH and Safari N. *J. Mol. Catal. A* 2002; **188**: 115–122.
32. Khavasi HR and Safari N. *J. Mol. Catal. A* 2004; **220**: 127–132.

33. Safari N and Bahadoran F. *J. Mol. Catal. A* 2001; **171**: 115–121.
34. Mohajer D, Karimipour G and Bagherzadeh M. *New J. Chem.* 2004; **28**: 740–747.
35. Battioni P, Renuad JP, Bartoli JF, Reina-Artiles M, Fort M and Mansuy D. *J. Am. Chem. Soc.* 1988; **110**: 8462–8470.
36. Meunier B, De Carvalho ME, Bortolini O and Momenteau M. *Inorg. Chem.* 1988; **27**: 161–164.
37. de Sousa AN, de Carvalho MEMD and Idemori YM. *J. Mol. Catal. A* 2001; **169**: 1–10.
38. Mohajer D and Sadeghian L. *J. Mol. Catal. A* 2007; **272**: 191–197.
39. Mohajer D and Abbasi M. *Eur. J. Inorg. Chem.* 2008; 3218–3224.
40. Nam W, Lim MH, Lee MJ and Kim C. *J. Am. Chem. Soc.* 2000; **122**: 6641–6647.
41. Traylor TG and Xu F. *J. Am. Chem. Soc.* 1990; **112**: 178–186.
42. Lindsey JS, Hsu HC and Schreiman IC. *Tetrahedron Lett.* 1986; **27**: 4969–4970.
43. Adler AD, Long FR, Kampas F and Kim J. *J. Inorg. Nucl. Chem.* 1970; **32**: 2443–2445.
44. Wessel J and Crabtree RH. *J. Mol. Catal. A* 1996; **113**: 13–22.
45. Santaniello E, Manzocchi A and Farachi C. *Synthesis* 1980: 563–565.
46. Borden WT. *Chem. Commun.* 1998: 1919–1925.
47. Zhang R, Horner JH and Newcomb M. *J. Am. Chem. Soc.* 2005; **127**: 6573–6586.