Regular Article

INORGANIC CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
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Inorg. Chem. Res., *Vol. 2, No. 1, 16-25, June 2019*
DOI: 10.22036/icr.2019.127896.1042

Hydrogen Bond Control of Active Oxidizing Species in Manganese Porphyrin Hydroxylation Catalysts

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(Received 20 April 2018, Accepted 13 May 2019)

Some *meso*-tetra aryl porphyrinato manganese(III) acetate or chloride complexes including *meso*-tetraphenyl porphyrinato manganese(III) chloride (TPPMnCl), *meso*-tetrakis(2,3-dimethoxyphenyl)porphyrinato manganese(III) acetate, (T(2,3-OMeP)PMnOAc) and *meso*-tetrakis(pentaflourophenyl)porphyrinato manganese(III) acetate (TPFPPMnOAc) were synthesized. These porphyrins were used as catalyst in the oxidation of various alkanes in the presence of pyridine and imidazole as axial ligands. It was revealed that the catalytic activity depends on the existence of hydrogen bonding between the axial base and the substituents on the ortho position of the phenyl ring, in addition to usual electronic and steric effects. Therefore, T(2,3-OMeP)PMnOAc and TPFPPMnOAc exhibited higher catalytic activity than TPPMnCl owing to the presence of such hydrogen bonding between substitutions on the periphery of the porphyrin ring and coordinated axial ligand. Also, the selectivity of these two Manganese porphyrins significantly varies in the presence of pyridine and imidazole for the alkane hydroxylation and is reversed for the alkene epoxidation, suggesting different active oxidizing agent produced by pyridine and imidazole

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Keywords: Manganese porphyrin, Hydroxylation, Hydrogen bonding, Active oxidizing species, Axial ligand

INTRODUCTION

Activation and functionalization of relatively inert C-H bond of alkanes to valuable products is in particular interest in industry due to the abundance of these precursors in nature, especially in crude oil and natural gas [1-4]. Oxygen insertion into C-H bonds is thermodynamically favorable but due to the inert nature of C-H bond, it needs very difficult conditions such as high temperature and pressure requirement [5]. Therefore, development of an effective method for oxidation of these inert bonds is important from both industrial and synthetic aspects [6]. In order to overcome this problem, highly active-oxidizing agents are needed [7].

Nature has employed a family of heme-thiolate ligated enzymes named cytochrome P-450 for this purpose. These enzymes have an iron(III) protoporphyrin IX in their active site that can activate dioxygen and transfer it to camphor. It is believed that an $[Fe^{IV}(O)(por^{\bullet})]^{+}$ species generated during enzymatic catalytic cycle is the active oxidizing species, so enzyme can oxidize inert C-H bonds at physiologic conditions by such an extraordinary powerful oxidizing species through a radical pathway (rebound mechanism) [8], Fig. 1.

Metalloporphyrins including iron, manganese and ruthenium porphyrins organize a unique family of catalysts which mimic Cytochrome enzymes are able to provide such a high reactivity for alkane oxidation in nearly mild condition by using strong oxidizing agents. Alkane oxidation catalyzed by synthetic metalloporphyrins has been widely studied over the last decades [9-14]. In particular, manganese porphyrins were early identified as efficient hydroxylation catalysts [15-18]. Groves *et al*. were the first researchers that used TPPFeCl in hydroxylation of alkanes with PhIO [19,20]. This catalyst undergoes rapid auto-oxidation degradation on porphyrin ring. Therefore, many

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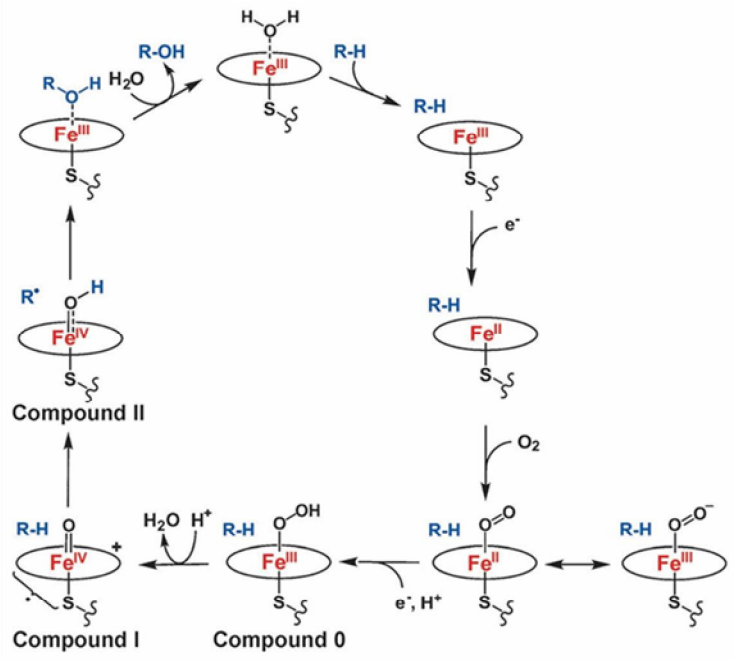
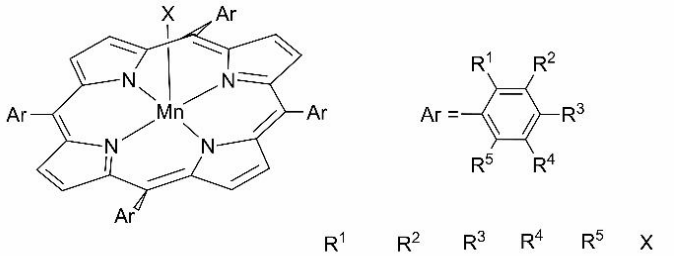


Fig. 1. The catalytic cycle of Cyt. P450 monooxygenases (R-H is the substrate) [8].



	R^1	R^2	R^3	R^4	R^5	X
Mn(2,3-OMeP)P(OAc)	OCH_3	OCH_3	H	H	H	OAc
MnTPFPPOAc	F	F	F	F	F	OAc
MnTPPCl	H	H	H	H	H	Cl

Fig. 2. Structures of the substituted manganese(III) tetraphenylporphyrins used in this work.

studies have been carried out on factors affecting these catalysts reactivity in order to improve the stability of the catalyst, product yields, selectivity and rate of oxidation reactions [21-27]. It is found that the reactivity of metalloporphyrin complexes depends on the central metal [28,29], the substituents on the porphyrin periphery [30-32] and the axially coordinated [33-35] ligand.

It is believed that axial ligand has a crucial role on cleavage the O-O bond through hydrogen bond interactions in the enzyme pocket that called "push-pull" effect [36]. There have also been theoretical studies investigating the effect of weak interactions such as hydrogen bonding between axial ligand and porphyrin periphery that affecting the active intermediate nature [37]. Our previous works on alkene epoxidation have shown that among the different methoxy and hydroxy substituted manganese porphyrins, existence of methoxy or hydroxy substitutents on *ortho* position of phenyl ring increased reactivity of catalyst due

to the their capability for hydrogen bonding formation with axial ligand [30,38]. Moreover, a recent deeper study on alkene epoxidation in the presence of meso-tetrakis (2,3-dimethoxyphenyl) porphyrinato manganese(III) acetate, T(2,3-OMeP)PMnOAc, and different nitrogenous axial bases was performed by us [39]. Our results led us to a clue to active oxidizing species in catalytic cycle which its spin state depends on such a hydrogen bonding formation with axial ligand. We proposed that active oxidizing species may be $^{5}[Mn^{IV}(O)(por^{\bullet+})(py)]$ in the presence of pyridine and a mixture of $^{1}[Mn^{V}(O)(por)(Im)]^{+}/^{5}[Mn^{IV}(O)(por^{\bullet+})(Im)]$ and probably $[Mn^{IV}(O)(por)(Im)]$ in the presence of imidazole axial base on the basis of UV-Vis spectra, product distribution and DFT studies.

Due to this reactivity and low selectivity of [(T(2,3-OMeP)PMn(O)(Py)] catalyst in alkene epoxidation compare to that [(T(2,3-OMeP)PMn(O)(Im)], we extend our study to alkene epoxidation by catalysts in Fig. 2. Hydroxylated product formation, conversion and selectivity accompanied by further DFT calculation clarify our previous conclusion about effect of hydrogen bonding and the active oxidizing nature affected by axial ligand and oxidant by periphery of the porphyrins.

EXPERIMENTAL

Instrumentation

All reagents were purchased from Sigma-Aldrich and Merck chemical companies and used without further purification. Gas Chromatography (GC) analyses were performed on the Agilent Technology 7890A which was equipped with HP-1 capillary column and FID detector. Formation of porphyrins tracked by their electronic absorption spectra recorded on a double beam Shimadzu 2100 spectrophotometer in CH_2Cl_2.

Materials

Free base porphyrins including 5,10,15,20-tetraphenylporphyrin (H_2TPP), 5,10,15,20-tetrakis(2,3-dimethoxyphenyl)porphyrin ($H_2T(2,3\text{-}OMeP)P$), 5,10,15,20-tetrakis(pentaflourophenyl)porphyrin (H_2TPFPP) were prepared by the Lindsey method [40] and metallated according to literature methods to yield corresponding T(2,3-OMeP)PMnOAc and TPFPPMnOAc [41,42]. Tetra-*n*-butylammoniummonopersulfate (*n*-Bu_4NHSO_5) and Iodosylbenzene (PhIO) were also synthesized according to the literature [43,44].

Notice: To obtain reproducible results, only freshly synthesized oxidants were used.

Hydroxylation Reactions

All reactions were performed after preparing the stock solutions of substrates and catalysts in CH_2Cl_2 as follows: substrate solution (1 ml, 0.05 M) was poured in a 5 ml volumetric flask. n-Bu_4NHSO_5 (0.043 g) or PhIO (0.022 g) was adjoined after adding the nitrogenous bases solution (0.48 ml, 0.1 M), (liquid bases were added directly to the reaction flask). Finally a typical oxidation reaction was started by addition of catalyst solution (0.2 ml, 3×10^{-3} M). The reaction mixture was stirred at room temperature and after 30 min, the reaction solution (0.2 µl) was injected into GC system.

Notice: The conversion and yield of the all reactions were calculated using external standard and calibration curves.

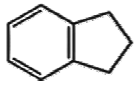
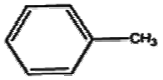
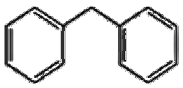
DFT Calculations

The computational study performed on the complexes $[(TPFPP)Mn^{V}(O)(Py)]^{+}$, $[(TPFPP)Mn^{V}(O)(Im)]^{+}$ were accomplished with DFT [45] using the Gaussian 98 A.9 program suite. OPBE/6-31G* method was used for the optimization of all structures and in all of cases, the energies were corrected by single point calculation with a larger basis set 6-311+G** for all the atoms that taken from the frequency calculations.

RESULTS AND DISCUSSION

Hydroxylation of alkanes was studied in the presence of some manganese porphyrin complexes (Fig. 2) by n-Bu_4NHSO_5 and PhIO as oxidant, and pyridine and imidazole as axial ligand in dichloromethane. Optimized reaction time and molar ratios of the components were set as our recent work for alkene epoxidations [39] (catalyst/axial ligand/substrate/oxidant: 1/80/83/164 and optimized reaction time was 30 min). Table 1 shows the hydroxylation results in the presence of n-Bu_4NHSO_5 oxidant. This table shows two main trends: 1) for all substrates, hydroxylation

Table 1. Conversion (Yield) Percentage of Alkane Oxidations by *n*-Bu_4NHSO_5 in the Presence of Different Axial Ligands and Catalyst[a]

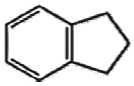
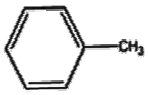
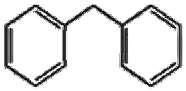
Substrate	Products	Axial ligands			
		Pyridine		Imidazole	
		Catalyst			
		(TPFPP)MnOAc	T(2,3-OMeP)PMnOAc	(TPFPP)MnOAc	T(2,3-OMeP)PMnOAc
	1-Adamantanol	58.7 (44.7)	36.1 (10.6)	62 (18.4)	48.9 (8.4)
	2-Adamantanol	(9.9)	(4.8)	(3.8)	(2.1)
	1-Indanol	45.9 (35.6)	44.9 (30.7)	49.5 (27.8)	49.2 (11.9)
	1-Indanone	(9.3)	(12.8)	-	(9.1)
	Cyclooctanol	32.9 (16.3)	20.7 (5.8)	36.2 (10.9)	30.6 (3.4)
	Cyclooctanone	(5.5)	(9.6)	(3.9)	(2.9)
	Cyclohexanol	13 (4.2)	10.6 (3.6)	36.2 (2.6)	48.9 -
	Cyclohexanone	-	-	-	-
	Benzyl alcohol	14.6 (4.4)	12.4 (3.7)	30.4 (2.8)	20.5 -
	Benzaldehyde	-	-	-	-
	Benzophenone	10 (5.5)	8.5 (4.1)	30.9 (3.6)	25.7 (1.9)

[a]The reactions were all triplicated at room temperature, in CH_2Cl_2 and the average data are reported. GC injections were carried out after 30 minutes. The molar ratios for {catalyst/ axial ligand/substrate/oxidant} are {1/80/83/164}. To analyze the results, external standard method was used.

yield is much higher for pyridine than that of imidazole while conversion is higher in the presence of imidazole; in the other word, pyridine is more selective for the hydroxylation reactions to that of imidazole; 2) both T(2,3-OMeP)PMnOAc and TPFPPMnOAc catalysts show very close reactivity for alkane hydroxylation except in the case of adamantane.

A more close look at Table 1 reveals that conversion percent for adamantane by TPFPPMnOAc is considerably higher than T(2,3-OMeP)PMnOAc (58.7 to 36.1). This difference in conversion percent may arise from steric crowdedness resulted by ortho methoxy substitution and adamantane. For indane, the similarity of conversion percent is seen for pyridine and imidazole axial ligands. Another feature in Table 1 is relatively low amount of hydroxylation product or low selectivity in the presence of imidazole axial base. To note the same reaction condition were employed by same catalytic system and reaction condition for alkene epoxidation and results showed that selectivity is reversed and imidazole axial base are

Table 2. Conversion (Oxidation Yield) Percentage in Hydroxylation of Various Alkanes by PhIO in the Presence of Different Axial Ligands and Catalyst[a]

Substrate	Products	Axial ligands			
		Pyridine		Imidazole	
		Catalyst			
		TPFPPMnOAc	T(2,3-OMeP)PMnOAc	TPFPPMnOAc	T(2,3-OMeP)PMnOAc
	1-Adamantanol	29.7 (22.4)	18.5 (10.6)	37.4 (18.1)	30.5 (9.2)
	2-Adamantanol	(4)	(3.4)	(3.2)	(1.7)
	1-Indanol	38.9 (29.6)	25 (7.3)	40.5 (20.8)	38.4 (9.9)
	1-Indanone	(8.5)	(16.1)	-	-
	Cyclooctanol	15.9 (9.5)	13.5 (3.1)	31.1 (8.1)	23.5 (1.1)
	Cyclooctanone	(4.4)	(3.8)	(3.5)	(3.6)
	Cyclohexanol	10.9 -	15.1 -	29.4 -	19.3 -
	Cyclohexanone	-	-	-	-
	Benzyl alcohol	11.7 -	10.1 -	24.1 -	18.5 -
	Benzaldehyde	-	-	-	-
	Benzophenone	8.6 (1.7)	7.6 (1.1)	18.3 -	11 -

[a]The reactions were all triplicated at room temperature, in CH_2Cl_2 and the average data are reported. GC injections were carried out after 30 min. The molar ratios for {catalyst/axial ligand/substrate/oxidant} are {1/80/83/164}. To analyze the results, external standard method was used.

completely selective [39]. Hydroxylation was performed in the presence of PhIO oxidant, to find out role of the oxidant on the substrate conversion percent and selectivity. The results are shown in Table 2.

Again trends are similar and selectivity for hydroxylation is preserved by pyridine and is lost by imidazole axial ligand. However, conversion percent and yield of hydroxylation are higher for n-Bu_4NHSO_5 than that of PhIO oxidant. *Ortho*-methoxy and fluorine groups on porphyrin periphery can form a hydrogen bonding with appropriate oxidants such as n-Bu_4NHSO_5 (Fig. 3). This ability can facilitate approaching of oxidant to metal center and accelerate the reactions. So n-Bu_4NHSO_5 acts considerably better than PhIO, as seen in Table 1 and 2.

In addition, in our previous works, T(2,3-OMeP)PMnOAc and T(2,3-OHP)PMnOAc complexes showed an efficient catalytic activity in the epoxidation of alkenes that we attributed it to their ability for formation of hydrogen bonding between ortho-methoxy and hydroxy groups on the periphery of porphyrin macrocycle and axial

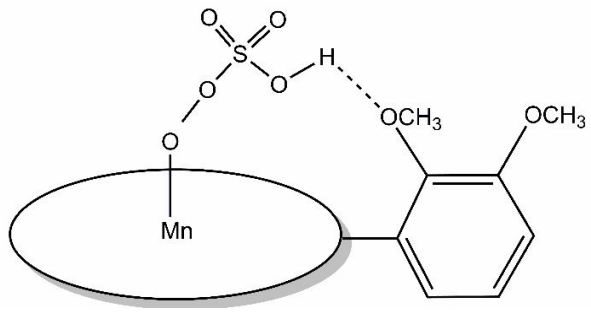


Fig. 3. Presumable hydrogen bonding interaction between oxidant and T(2,3-OMeP)PMnOAc catalyst.

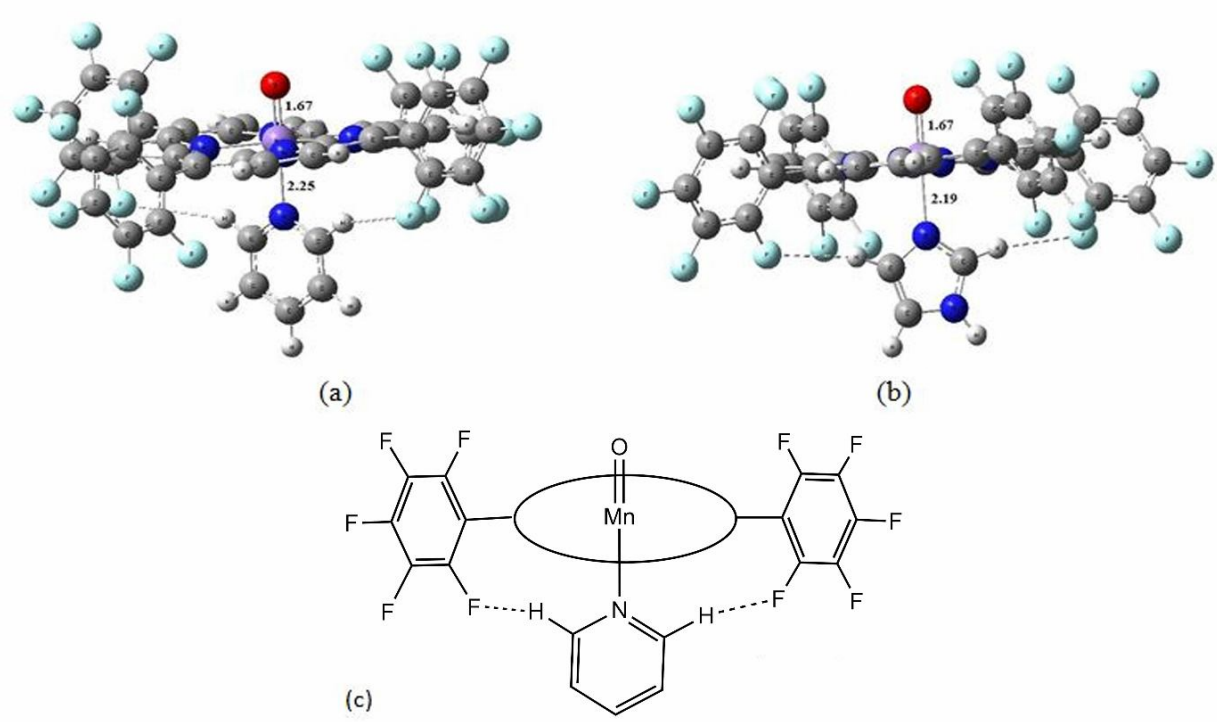


Fig. 4. Investigation of hydrogen bonding between axial ligands and periphery of the porphyrin ring using DFT calculation; (a) $[(TPFPP)Mn^{V}(O)(Py)]^{+}$; (b) $[(TPFPP)Mn^{V}(O)(Im)]^{+}$; (c) Possible hydrogen bonding interaction between pyridine and the ortho-methoxy group of TPFPPMnOAc complex.

bases [30,38]. This claim was further confirmed by our recent work [39] in which catalytic epoxidation of alkenes by T(2,3-OMeP)PMnOAc in the presence of several nitrogenous bases including pyridine and imidazole was investigated. We observed that T(2,3-OMeP)PMnOAc has the most catalytic conversion in the presence of imidazole and pyridine. These observations together with UV-Vis data on catalyst stability provide an indication for our claim on the presence and influence of hydrogen bonding in these systems (Fig. 3). The most interesting result of that study was that the selectivity of the catalyst for epoxidation reactions was 100% in the presence of imidazole while it reduced to 69% in the presence of pyridine. This difference in selectivity together with difference in product distribution led us to conclude that different active oxidizing species and consequently different reaction pathways are involved in

Table 3. Calculated Relative Energies (Kcal mol^{-1}) for Manganese Porphyrin in all Possible Spin States Using OPBE/6-311+G** Method

Entry	Compounds	Singlet	Triplet	Quintet	Mn=O[a]	Mn-N_{axial}[a]
1[b]	$[(TPP)Mn(O)(Py)]^+$	0.00	3.50	4.62	1.51	2.47
2[b]	$[T(2,3\text{-}OMeP)PMn(O)(Py)]^+$	13.40	-	0.00	1.67	2.28
3	$[(TPFPP)Mn(O)(Py)]^+$	8.26	-	0.00	1.67	2.25
4[b]	$[(TPP)Mn(O)(Im)]^+$	0.00	0.89	1.14	1.57	2.42
5[b]	$[T(2,3\text{-}OMeP)PMn(O)(Im)]^+$	7.05	-	0.00	1.65(1.55)[c]	2.21
6	$[(TPFPP)Mn(O)(Im)]^+$	4.64	-	0.00	1.67(1.51)[c]	2.19

[a]Bond length (Å) for most stable spin state. [b]These entries are taken from reference 39 and reported. [c]Number in parenthesis shows bond length (Å) for singlet spin state.

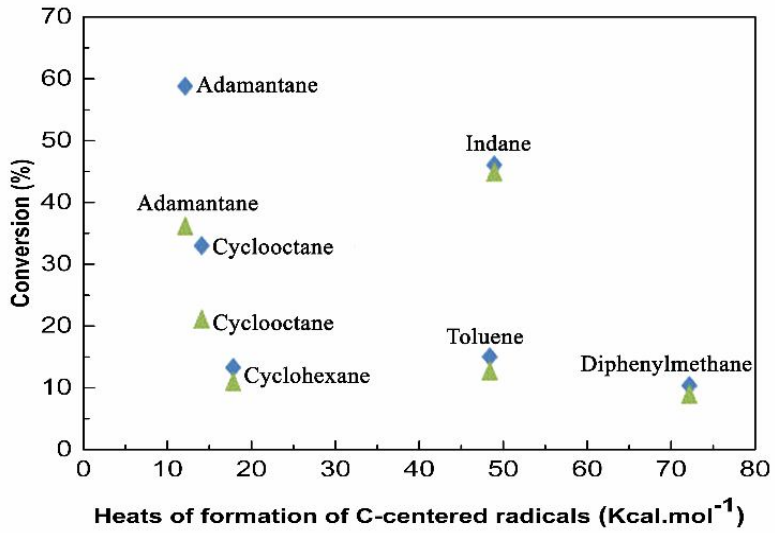


Fig. 5. Plot of hydroxylation conversion percent versus heat of formation of the C-centered radical [46] in the presence of two Mn(Por) for different alkanes. *n*-Bu_4NHSO_5 were used as oxidant.
◇ TPFPPMnOAc used as Catalyst and pyridine as axial base
△ T(2,3-OMeP)PMnOAc used as catalyst and pyridine as axial base

each case. DFT studies confirmed such claim and proposed that active oxidizing intermediates might be a mixture of $^1[(Im)MnV(O)(Por)]^+$, $^5[(Im)MnIV(O)(Por^{\bullet})]^+$ and even [(Im)MnIV(O)(Por)] species in the presence of imidazole. However, in the presence of pyridine axial base and T(2,3-OMeP)PMnOAc/oxidant, highly reactive compound 1 type active species $^5[(Py)MnIV(O)(Por^{\bullet})]^+$ is formed.

Further studies in this work shows the effect of hydrogen bonding of axial ligands with periphery of the porphyrin ring. Mn-N axial bond distance reflects the

Table 4. The Comparison of Catalytic Performance of the Present Work with some other Previos Reported Catalysts

Entry	Catalyst	Substrate	Conversion	Oxidizing agent	Ref.	Present work (Conversion)
1	Mn(TPFPP)OAc	Indane	18	*n*-Bu_4NIO_4	[47]	45.9
2	MnTPPS-PMP	Cycloocatane	19	$NaIO_4$	[48]	33.0
3	$MnTPPBr_2OAc$	Cycloocatane	34	*n*-Bu_4NHSO_5	[49]	33.0
4	$MnTPPBr_2OAc$	Adamantane	45	*n*-Bu_4NHSO_5	[49]	58.7
5	*Cis*-[$MnBr_{12}$DAPDPP]Cl	Adamantane	31	PhIO	[50]	58.7
6	MnTPyP-CMP	Adamantane	35	$NaIO_4$	[51]	58.7

strength of hydrogen bonding. Strong hydrogen bonding caused shorter Mn-N axial bond distance (Entries 1 and 4 compared to others). Figure 4 represent such effect, and Table 3 summarizes the result obtained by DFT calculation.

As it is evident from Table 3 and Fig. 4, strong interaction of axial base with manganese center in the presence of the hydrogen bonding results in longer Mn=O bond distance and this caused stabilization of ^{5}[(Por$^{\bullet}$) MnIV(O$^{\bullet}$)(X)]$^+$ over ^{1}[(Por) MnV(O)(X)] species; where X is pyridine or imidazole axial base. Longer Mn=O accompanied by radical nature of former active oxidant (with similar nature of compound 1) result in very active catalyst for hydrogen abstraction mechanism presented in Fig. 1.

For the TPPMn(O)(Py) the singlet state which is representative of MnV(Por) oxidation state is 4.62 Kcal.mol^{-1} more stable than MnIV(Por)$^{\bullet}$+ and very short manganese oxygen bond is formulated as triple bond Mn≡O. However, changing the periphery of the porphyrin from phenyl to 2,3-OMe phenyl in entry 2 caused stabilization of quintet state by 13.40 Kcal mol^{-1} and increased manganese and oxygen bond to 1.67 Å which is representative of Mn=O.

Furthermore, [(TPP)Mn(O)(Im)]$^+$ has very close singlet, triplet and quintet spin states relative to that of [(TPP)Mn(O)(Py)]$^+$, that result to further reactivity of [(TPP)Mn(O)(Im)]$^+$ to that of [(TPP)Mn(O)(Py)]$^+$, especially for alkene epoxidation. This trend changed when T(2,3-OMeP)PorMnOAc is used, in which singlet state is 7.05 Kcal mol^{-1} more stable than quintet. However, the Mn=O bond distance for imidazole counterpart is 0.07 angstrom shorter to that of pyridine reflecting lower activity of [T(2,3-OMeP)PMn(O)(Im)]$^+$ to [T(2,3-OMeP)PMn(O)(Py)]$^+$.

Plot of hydroxylation conversion percent versus heat of formation ($\Delta_fH°$) of the C-centered corresponding radicals of the substrates is drawn in Fig. 5 [46]. As can be seen, conversion percent for adamantane by TPFPPMnOAc is considerably higher than that of T(2,3-OMeP)PMnOAc (58.7 to 36.1). This difference in conversion percent may arise from steric crowdedness resulted by ortho methoxy substitution and adamantane. The trend of conversions is in agreement with heat of formation of C-centered radical reported in the literature [46] except for indane. However heat of formation of indane (secondary radical formation) and toluene (primary radical formation) was reported the same, although one expects lower number for indane to that of toluene.

Thus the trends confirm the conclusion that C-H activation in these systems involves a hydrogen abstraction and recombination as mechanism of hydroxylation (Fig. 1). So, ^{5}[(py)MnIV(O)(Por$^{\bullet}$)]$^+$ is considered as almost only intermediate in the presence of pyridine and a mixture of ^{5}[(Im)MnIV(O)(Por$^{\bullet}$)]$^+$ and ^{1}[(Im)MnV(O)(Por)]$^+$ are

considered as intermediates in the presence of imidazole.

Finally, in order to evaluate the activity of the synthesized catalysts with the other ones, a comparison was made between our prepared catalysts and the other catalysts in which various porphyrins was used in the oxidation of saturated C-H bonds and the results are summarized in Table 4. According to the results, the prepared catalysts is more officious and show better catalytic activity compared to the other catalysts.

CONCLUSIONS

This study presents a confirmation for our previous idea that the ability of the axial base to form a hydrogen bonding with appropriate groups on porphyrin periphery can control the nature of active oxidizing intermediate in biomimetic model reactions. Also, it is an indication of that hydrogen bonding interactions plays a key role in action of cytochrome

REFERENCES

[1] T. Gensch, M.N. Hopkinson, F. Glorius, J. wencel-Delord, Chem. Soc. Rev. 45 (2016) 2900.
[2] G.M. Ucoski, V.H. Araujo Pinto, G.D. Freitas-Silva, J.S. Reboucas, R.M. Silva Jr, I. Mazzaro, F.S. Nunes, S. Nakagaki, Micropor. Mesopor. Mater. 256 (2018) 84.
[3] R. Fu, W.A. Goddard, M.J. Cheng, R.J. Nielsen, ACS Catal. 7 (2018) 356.
[4] A.C. Lindhorst, S. Haslinger, F.E. Kuhn, Chem. Commun. 51 (2015) 17193.
[5] J.M. Mayer, I.B. Meunier, Biomimetic Oxidations Catalyzed by Transition Metal Complexes, Imperial College Press, London, 2000.
[6] M. Costas, Coord. Chem. Rev. 255 (2011) 2912.
[7] K. Godula, D. Sames, Science (2006) 67.
[8] A.B. McQuarters, M.W. Wolf, A.P. Hunt, N. Lehnert, Angew. Chem., Int. Ed. 53 (2014) 4750.
[9] H. Lu, X.P. Zhang, Chem. Soc. Rev. 40 (2011) 1899.
[10] W. Nam, Acc. Chem. Res. 40 (2007) 522.
[11] V.S. Silva, Y.M. Idemori, G. Freitas-Silva, Appl. Catal., A 498 (2015) 54.
[12] E. Tabor, J. Poltowicz, K. Pamin, S. Basag, W. Kubiak, Polyhedron 119 (2016) 342.
[13] K.A. Castro, S. silva, P.M.R. Pereira, M.M.Q Simoes, M.G. neves, J.A. Cavaleiro, F. Wypych, J.P. Tome, S. Nakagaki, Inorg. Chem. 54 (2015) 4382.
[14] V.S. Silva, W.C. Santos Vieira, A.M. Meireles, G.M. Ucoski, S. Nakagaki, Y.M. Idemori, G. Freitas-Silva, New. J. Chem. 41 (2017) 997.
[15] M.G. Araujo Torres, V.S. Silva, Y.M. Idemori, G. freitas-Silva, Arab. J. Chem. (2017).
[16] A. Wang, Y. She, H. Fu, H. Li, Catal. Today 264 (2016) 185.
[17] K.A. Castro, F.H. Lima, M.M. Simoes, M.G. Neves, F.A. Almeida Paz, R.F. Mendes, S. Nakagaki, J.A. Cavaleiro, Inorg. Chim. Acta 455 (2017) 575.
[18] Z. Feng, Y. Xie, F. Hao, P. Liu, H. Luo, J. Mol. Catal. A: Chem. 410 (2015) 221.
[19] J.T. Groves, T.E. Nemo, J. Am. Chem. Soc. 105 (1983) 6243.
[20] J.T. Groves, T.E. Nemo, R.S. Myers, J. Am. Chem. Soc. 101 (1979) 1032.
[21] N. Safari, F. Bahadoran, J. Mol. Catal. A: Chem. 171 (2001) 115.
[22] H.R. Khavasi, S.S. Hosseiny Davarani, N. Safari, J. Mol. Catal. A: Chem. 188 (2002) 115.
[23] H.R. Khavasi, N. Safari, J. Mol. Catal. A: Chem. 220 (2004) 127.
[24] A.K. Mandal, V. Khanna, J. Iqbal, Tetrahedron Lett. 37 (1996) 3769.
[25] M.A. Schiavon, Y. Iamamoto, O.R. Nascimento, M.d.D. Assis, J. Mol. Catal. A: Chem. 174 (2001) 213.
[26] W. Nam, Y.M. Goh, Y.J. Lee, M.H. Lim, C. Kim, Inorg. Chem. 38 (1999) 3238.
[27] C.-C. Guo, J.-X. Song, X.-B. Chen, G.-F. Jiang, J. Mol. Catal. A: Chem. 157 (2000) 31.
[28] H.R. Khavasi, N. Safari, J. Porphyrins Phthalocyanines 09 (2005) 75.
[29] T.G. Traylor, A.R. Miksztal, J. Am. Chem. Soc. 111 (1989) 7443.
[30] A. Aghabali, N. Safari, J. Porphyrins Phthalocyanines. 14 (2010) 335.
[31] N. Safari, F. Bahadoran, M.R. Hoseinzadeh, R. Ghiasi, J. Porphyrins Phthalocyanines 04 (2000) 285.
[32] H. Fujii, J. Am. Chem. Soc. 115 (1993) 4641.

[33] D. Mohajer, L. Sadeghian, J. Mol. Catal. A: Chem. 272 (2007) 191.
[34] K.W. Kwong, D. Patel, J. Malone, N.F. Lee, B. Kash, R. Zhang, New. J. Chem. 41 (2017) 14334.
[35] Y. Kang, H. Chen, Y.J. Jeong, W. Lai, E.H. Bae, S. Shaik, W. Nam, Chem. A.: Eur. J. 15 (2009) 10039.
[36] N. Jin, D.E. Lahaye, J.T. Groves, Inorg. Chem. 49 (2010) 11516.
[37] M.T. Green, J. Am. Chem. Soc. 122 (2000) 9495.
[38] T. Alemohammad, N. Safari, S. Osati, J. Porphyrins Phthalocyanines 15 (2011) 181.
[39] E. Mesbahi, N. Safari, M. Gheidi, J. Porphyrins Phthalocyanines 18 (2014) 354.
[40] J.S. Lindsey, H.C. Hsu, I.C. Schreiman, Tetrahedron Lett. 27 (1986) 4969.
[41] A.D. Adler, F.R. Longo, F. Kampas, J. Kim, J. Inorg. Nucl. Chem. 32 (1970) 2443.
[42] K.M. Kadish, B.C. Han, M.M. Franzen, C. Araullo-McAdams, J. Am. Chem. Soc. 112 (1990) 8364.
[43] Benjamin R. Travis, Benjamin P. Ciaramitaro, B. Borhan, Eur. J. Org. Chem. 2002 (2002) 3429.
[44] K.H. Pausacker, J. Chem. Soc. (Resumed), (1953) 107.
[45] P.E.M. Siegbahn, Faraday Discuss. 124 (2003) 289.
[46] Y.-R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, 2002.
[47] D. Mohajer, M. Bagherzadeh, J. Chem. Res. (1998) 556.
[48] S. Tangestaninejad, M.H. Habib, V. Mirkhani, M. Moghadam, J. Chem. Res. 10 (2001) 444.
[49] S. Rayati, S. Zakavi, V. Noroozi, S.H. Motlagh, Catal. Commun. 10 (2008) 221.
[50] V.S. da Silva, Y.M. Idemori, G. DeFreitas-Silva, Appl. Catal., A 498 (2015) 54.
[51] S. Tangestaninejad, M. Moghadam, V. Mirkhani, H. Kargar, Ultrason. Sonochem. 13 (2006) 32.