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Substitution effects on the catalytic activity of Mn(III)-porphyrins in epoxidation of alkenes with iodosylbenzene: A comparison between the electron-rich and electron-deficient porphyrins

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ABSTRACT

Oxidation of different olefins with iodosylbenzene in the presence of Mn(III) complexes of *meso*-tetra(*para*-tolyl)porphyrin, *meso*-tetra(*ortho*-tolyl)porphyrin, *meso*-tetra(thien-2-yl)porphyrin and β -hexaboromo-*meso*-tetra(thien-2-yl)porphyrin as catalyst has been studied. Oxidation of *cis*- and *trans*-stilbene in a competitive reaction strongly suggests the involvement of a high valent (porphyrin)Mn=O as the active oxidant intermediate, in the case of each catalyst. Clear observation of the band relevant to a (porphyrin)Mn(IV)=O species in the presence of excess amounts of styrene shows the stability of this moiety towards reaction with olefins. Although, the stability of metalloporphyrins towards oxidative degradation decreases in the order MnT(*o*-tolyl)P(OAc) > MnT(thien-2-yl)PBr₆(OAc) > MnT(*p*-tolyl)-P(OAc) \geq MnT(thien-2-yl)P(OAc), a complex pattern of catalytic activity and product (epoxide) selectivity has been found for the Mn-porphyrins in oxidation of various alkenes.

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1. Introduction

Peripheral substitution of the porphyrin macrocycle with the aim of preparing more stable "second- and third-generation" porphyrins with halogen, nitro or sulfone substituents has been used as an effective strategy to increase the stability of metalloporphyrins towards oxidative degradation and develop new porphyrin-based catalysts with enhanced catalytic activity for oxidation reactions [1]. The stabilization of HOMO level of the so called electron-deficient porphyrins, causes the improved activity as well as the stability of the corresponding metalloporphyrins under reaction conditions [2–4]. On the other hand, resonance interactions between the *meso*-aryl substituents and the porphyrin π system lead to the destabilization of the a_{2u} orbital [5]. Large dihedral angles between the porphyrin mean plane and the aryl groups induced by introduction of bulky substituents at ortho positions of aryl groups hinder the effective resonance interactions [6,7]. [Mntmp]OAc (tmp = meso-tetramesitylporphyrin) has been found to show higher catalytic activity relative to Mn(tpp)OAc in the oxidation of sterically unhindered cycloalkanes and aryalkanes with periodate as oxidant [8]. In a recent work, similar catalytic activities for Ru(IV)(tmp)Cl₂ and Ru(IV)(tdcpp)Cl₂ (tdcpp = mesotetra(2,6-dichlorophenyl)porphyrin) have been reported [9].

Although it is generally accepted that the presence of electronwithdrawing substituents on the macrocycle enhances the stability as well as the catalytic activity of the corresponding metalloporphyrins in oxidative conditions, there are many reports that show comparable or higher catalytic activity of electron-rich metalloporphyrins relative to the electron-deficient ones in oxidation of hydrocarbons with periodate, iodosylbenzene or *meta*-chloroperbenzoic acid (*m*-CPBA) as oxidant [8,10–14].

In the present work, catalytic activity of a series of electron-rich and electron-deficient Mn(III)-porphyrins with five and six membered rings at *meso*-positions and H or Br atoms at β -positions in oxidation of alkenes with iodosylbenzene (PhIO) has been studied in a comparative manner. Also, attempts have been made to elucidate the nature of the active intermediates of the oxidation reaction in the presence of the title Mn-porphyrins. It should be noted that using excess amounts of organic substrate relative to oxidant is among the main strategies have been utilized to overcome the problems associated with the stability of metalloporphyrins [15–17]. In the present work, the molar ratio of alkene to PhIO is *ca.* 17:1 which enables us to compare the catalytic activity of different metalloporphyrins in a systematic study.

2. Experimental

2.1. Preparation of porphyrins

$$\label{eq:meso-tetra} \begin{split} Meso-tetra(para-tolyl) porphyrin, \ H_2T(p-tolyl)P \ [18], \ meso-tetra(ortho-tolyl) porphyrin, \ H_2T(o-tolyl)P \ [18], \ meso-tetra(thien-2-yl) porphyrin, \ H_2T(thien-2-yl)P \ [19] \ (Fig. 1) \ were \ synthesized, \ characterized \ and \ purified \ according \ to \ the \ literature \ methods. \end{split}$$



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Fig. 1. Porphyrin used in this study.

Bromination of H₂T(thien-2-yl)P with excess amounts of N-bromosuccinimide (freshly recrystallized from hot water and dried at 80 °C under vacuum) [20] leads to the formation of β-hexaboromo-*meso*-tetra(thien-2-yl)porphyrin, H_2T (thien-2-yl)PBr₆; H₂T(thien-2-yl)P (0.5 mmol) was dissolved in CHCl₃ (80 ml). N-bromosuccinimide (918 mg, 5.0 mmol) was added and the solution was stirred for 24 h at room temperature. Evaporation of the solvent gave a solid which was washed with methanol to remove any soluble succinimide impurities. The product, H₂T(thien-2-vl)PBr₆ was recrystallized from $CHCl_3/n$ -hexane (3:1, v/v) and dried under vacuum. The degree of bromination of porphyrin has been determined by ¹H NMR spectrometry based on the ratio of the intensities of the signals corresponding to the protons from H_{β} and meso-substituents (H_{β}/H_{3} ratio). $H_{2}T$ (thien-2-yl)PBr₆: ¹H NMR (δ ppm) (CDCl₃, 250 MHz): -2.62 (2H, br, s, NH); 7.52-7.53 (4H, m); 7.68–7.70 (4H, m); 7.90 (4H, m); 8.99 (8H, s, β); UV–Vis (λ/nm) in CH₂Cl₂: 458 (Soret), 553, 612, 711.

2.2. Metallation of porphyrins

Metallation of the porphyrins with $Mn(OAc)_2 \cdot 4H_2O$ was carried out following the literature methods [21]. The λ_{max} of MnT(thien-2-yl)P(OAc), MnT(*p*-tolyl)P(OAc), MnT(*o*-tolyl)P(OAc) and MnT(thien-2-yl)PBr₆(OAc) appears at 478, 479, 479 and 503 nm, respectively.

2.3. Preparation of PhIO

PhIO has been prepared and purified according to the method developed by Sharefkin et al. [22].

2.4. General oxidation procedure

Stock solutions of the metalloporphyrins (0.003 M) were prepared in dichloromethane. In a typical reaction, alkene (1.15 mmol) and metalloporphyrin (0.0005 mmol) were added into a 5 ml round bottom flask containing 3 ml of dichloromethane. Reaction was conducted by adding PhIO (0.068 mmol) to the solution. The molar ratios for catalyst:alkene:PhIO were 1:2300:136. The mixture was stirred thoroughly for 3 h at ambient temperature. The progress of reaction was followed using TLC and GC analysis. After the required time, the reaction was quenched by adding sodium bisulfite. The dichloromethane phase was separated and dried over anhydrous magnesium sulfate. The resulting solution was analyzed by GLC using *n*-octane as internal standard. It should be noted that in a non-stoichiometric reaction, the limiting reagent (here, PhIO) should be used *to calculate* the expected yields and conversions. Accordingly, the molar ratio of PhIO to the olefin i.e. $136/2300 \times 100\% = 5.91$ mol% is corresponding to a conversion of 100% based on the starting oxidant. Other values are calculated considering the value of 5.91% for the 100% conversion. In the case of *cis*- and *trans*-stilbene, the products were analyzed by ¹H NMR. All reactions were repeated at least three times.

2.5. Degradation of metalloporphyrins

General procedure and the molar ratios are as mentioned in Section 2.4. After the required time, sodium bisulfite has been added to quench the reaction. The dichloromethane phase was separated and dried over anhydrous magnesium sulfate. The absorbance of the final solution has been compared with that of the initial one at the λ_{max} of the metalloporphyrin to measure the extent of degradation of initial metalloporphyrin.

2.6. Instrumentation

¹H spectra were obtained in CDCl₃ solutions with a Bruker Avance DPX 250 MHz spectrometer. The absorption spectra were recorded on a Pharmacia Biotech Ultrospec 4000 UV–Vis spectrophotometer. The reaction products of oxidation were analyzed by a Varian-3800 gas chromatograph equipped with a HP-5 capillary



Fig. 2. Spectral changes upon addition of PhIO to a solution of (a) MnT (o-tolyl)P(OAc) in dichloromethane in the absence of alkene (b) after 1 min, (c) after 3 min and (d) after the addition of sodium bisulfite. The molar ratio for MnT (o-tolyl)P(OAc):PhIO are 1:136.



Fig. 3. The absorbance change at the λ_{max} of (1) MnT(thien-2-yl)P(OAc) (478 nm), (2) MnT(*p*-tolyl)P(OAc) (479 nm), (3) MnT(thien-2-yl)PBr₆(OAc) (503 nm) and (4) MnT(*o*-tolyl)P(OAc) (479 nm) relative to the initial absorbance (see the text).

Table 1

Competitive oxidation of *cis*- and *trans*-stilbene in the presence of different Mnporphyrins at room temperature.^a

Catalyst	Cis-epoxide	Trans-epoxide	<i>Cis/trans</i>
	(%) ^b	(%) ^b	ratio
MnT(thien-2-yl)P(OAc)	19.6	12.8	1.53
MnT(p-tolyl)P(OAc)	26.4	25.5	1.03
MnT(thien-2-yl)PBr ₆ (OAc)	5.5	5	1.1
MnT(o-tolyl)P(OAc)	16.5	16.3	1.01

^a The molar ratios for catalyst:alkene:PhIO are 1:(500:500):167.

^b Based on the starting PhIO for 3 h reaction time.

column (phenylmethyl siloxane $30\,m\times320\,\mu m\times0.25\,\mu m)$ and flame-ionization detector.

3. Results and discussion

Mn(III) complexes of the porphyrins (Fig. 1) have been used as catalyst in oxidation of alkenes with PhIO. Cyclic and acyclic olefins with hindered and unhindered double bonds have been used to study the comparative catalytic activity of different metalloporphyrins.

3.1. Stability of metalloporphyrins

Stability of the metalloporphyrins towards oxidative degradation in the presence and the absence of alkene (styrene) have been studied. Addition of PhIO to the solution of MnT(*o*-tolyl)P(OAc) in dichloromethane in the absence of styrene led to the appearance of a band at 430 nm and gradual disappearance of the band at the λ_{max} of MnT(*o*-tolyl)P(OAc) (Fig. 2).

A similar spectral pattern was observed in the presence of styrene, but the rate of disappearance of the band at λ_{max} decreased. Upon the addition of sodium bisulfite to the reaction mixture, the band at 430 nm disappeared and the band due to the metalloporphyrin has been observed (Fig. 2, curve d). Using other metalloporphyrins led to the appearance of an absorption band at 432 nm. 440 nm and 459 nm for MnT(p-tolyl)P(OAc), MnT(thien-2-yl)P(OAc) and MnT(thien-2-yl)PBr₆(OAc), respectively. Although the competitive oxidation of *cis*- and *trans*-stilbene strongly suggests the involvement of a high valent manganese oxo intermediate in the catalytic cycle (vide infra), the absorption bands at 430-459 nm can not be attributed to the formation of a Mn(V)oxo species; The band due to a Mn(V)-oxo species appears at ca. 410 nm in dichloromethane/alcohol mixed solvent and disappears rapidly in the presence of alkenes [19,23]. However, in the present work, the band at 430-459 nm (for different Mn-porphyrins) has been observed as a strong band in the presence as well as the absence of styrene which is probably due to the formation of stable Mn(IV)-oxo species [24].

The stability of metalloporphyrins (Fig. 3) decreases in the order $MnT(o-tolyl)P(OAc) > MnT(thien-2-yl)PBr_6(OAc) > MnT(p-tolyl)-P(OAc) > MnT(thien-2-yl)P(OAc).$

The observed pattern of stability may be explained by electronic and steric effects of substituents. The substitution of *meso*-tetraphenylporphyrins with methyl groups in *ortho* positions gives porphyrins with increased dihedral angles between the *meso*substituted aryls and the porphyrin mean plane [6]. This in turn, hinders the effective resonance interactions between the aryl groups and the porphyrin core and leads to a decrease in the electron donation from the aryl groups to the porphyrin core [6,7]. On the other hand, introduction of bulky substituents on the aryl groups, especially at the site adjacent to the *meso* positions, has been used as a strategy to reduce intermolecular catalyst interactions and so prevent oxidation of resting catalyst by the active intermediate [1,25].

Higher oxidative stability of MnT(o-tolyl)P(OAc) relative to $MnT(thien-2-yl)PBr_6(OAc)$, seems to be due to the smaller size of





the five membered thienyl ring with respect to phenyl one which allows for increased coplanarity between thienyl groups and porphyrin mean plane leading to better electron donation to the porphyrin core [26]. Also, the less hindered *meso*-positions of MnT(thien-2-yl)PBr₆(OAc) relative to those of MnT(*o*-tolyl)P(OAc) should be taken into consideration.

Oxidation of styrene with PhIO in the presence of imidazole (ImH) and the catalyst has been achieved. Interestingly, no absorption band relevant to a Mn(IV)–oxo species has been observed in UV–Vis spectra. It should be noted that in the absence of ImH the band due to the high valent Mn(IV)–oxo was observed clearly during the course of reaction which disappeared after the addition



Fig. 5. Results of oxidation of indene (see the caption of Fig. 4).



Fig. 6. Results of oxidation of styrene (see the caption of Fig. 4).



Fig. 7. Results of oxidation of α -methylstyrene (see the caption of Fig. 4).



Fig. 8. Results of oxidation of 3-chloro-2-methyl-1-propene (see the caption of Fig. 4).



Fig. 9. Results of oxidation of cis-stilbene (see the caption of Fig. 4, cis-epoxide selectivity:blank column; trans-epoxide selectivity:black column).

of sodium bisulfite. Furthermore, addition of ImH to the reaction mixture (up to 1:20 M ratio of catalyst/ImH) has little effect on the catalytic activity of the metalloporphyrins.

3.2. Oxidation of olefins

3.2.1. Competitive oxidation of cis- and trans-stilbene

Oxidation of *cis*- and *trans*-stilbene, in a competitive reaction, has been shown to be a useful probe to elucidate indirectly the nature of active oxidant in the metalloporphyrin catalyzed epoxidation of olefins in the absence of nonbulky *ortho*-substituents on the phenyl groups of *meso*-tetraphenylporphyrins [11,27]. The results of competitive epoxidation of the two compounds with PhIO in the presence of different Mn-porphyrins have been summarized in Table 1. The observed ratios strongly suggest the involvement of a high valent Mn-oxo species as the sole active oxidant in the presence of the used Mn-porphyrins.

3.2.2. Comparative catalytic activity of the Mn-porphyrins

The results of oxidation of different olefins with PhIO catalyzed by the four Mn-porphyrins were summarized in Tables S1–S8.

Fig. 4 shows the efficiency of different catalysts in oxidation of cyclohexene as a sterically unhindered alkene [28,29]. Conversion decreased in the order MnT(p-tolyl)P(OAc) > MnT(thien-2-yl)P(OAc) > MnT(o-tolyl)P(OAc) >> MnT(thien-2-yl)PBr₆(OAc). Although, the maximum yield of epoxide has been obtained in the presence of MnT(o-tolyl)P(OAc), but there is no significant difference between

the first three complexes. However, the best selectivity for cyclohexene oxide was obtained with MnT(o-tolyl)P(OAc). Interestingly, $MnT(thien-2-yl)PBr_6(OAc)$ is the least efficient catalyst of the four. Also, MnT(o-tolyl)P(OAc) which is more stable than the other Mn-porphyrins in the order of stability, shows less activity relative to MnT(p-tolyl)P(OAc) and MnT(thien-2-yl)P(OAc). The results of oxidation of other olefins have been shown in Figs. 5–11.

In oxidation of indene (Fig. 5), comparable epoxide selectivity is observed for the four catalysts but, the best conversion and yield of epoxide are obtained in the presence of MnT(thien-2-yl)P(OAc) and $MnT(thien-2-yl)PBr_6(OAc)$.



Fig. 10. Cis to trans isomerization in oxidation of cis-stilbene.



Fig. 11. Results of oxidation of trans-stilbene (trans-epoxide selectivity:blank column, see the caption of Fig. 4).



Fig. 12. Results of oxidation of 1-hexene (see the caption of Fig. 4).

Oxidation of styrene (Fig. 6) and sterically more hindered α methylstyrene (Fig. 7) was carried out with similar efficiency and selectivity in the presence of the four Mn-porphyrins.

Catalytic efficiencies of MnT(p-tolyl)P(OAc), MnT(thien-2-yl)-P(OAc) and MnT(o-tolyl)P(OAc) in epoxidation of 3-chloro-2-methyl-1-propene are comparable (Fig. 8). In the case of $MnT(thien-2-yl)PBr_6(OAc)$, the selectivity to epoxide is remarkably lower than the other catalysts.

Catalytic activity of the Mn-porphyrins in selective oxidation of cis-stilbene (Fig. 9) to the epoxide product decreases in the order $MnT(thien-2-yl)PBr_6(OAc) >> MnT(o-tolyl)P(OAc) > MnT(p-tolyl)-$ P(OAc) > MnT(thien-2-yl)P(OAc). Epoxidation of *cis*-stilbene with different oxidant is usually accompanied with the cis to trans isomerization [11,27]. Interestingly, the isomerization significantly increased in the presence of MnT(o-tolyl)P(OAc) as catalysts. It is notable that due to the steric hindrance caused by the methyl groups in the position ortho to the meso-carbons, which prevent the free rotation about the C-C bond in the common intermediate, lower extent of isomerization would be expected [11]. However, this observation shows the significant cleavage of the C=C double bond in the intermediate. Apparently, the increased electrophilicity of the Mn(V)=O moiety of O=Mn(V)T(o-tolyl)P(OAc) (see Section 3.2.2) relative to that of the other Mn-porphyrins led to the enhanced electron donation from the double bond to the Mn(V)=O species and significant cleavage of the double bond (Fig. 10).

Oxidation of sterically demanding *trans*-stilbene [11] gives *trans*-stilbene oxide as the sole product. The order of catalytic activity of the Mn-porphyrins (Fig. 11) correlates well with the relative stability of the catalysts towards the active oxidant (see Section 3.1).

MnT(thien-2-yl)PBr₆(OAc) shows poor catalytic activity and product (epoxide) selectivity compared with the other catalysts in the oxidation of 1-hexene (Fig. 12). The efficiency of the other Mn-porphyrins is nearly the same.

4. Conclusions

In summary, the competitive oxidation of *cis*- and *trans*-stilbene in the presence of the Mn-porphyrins strongly suggests that a high valent manganese oxo complex is involved as the reactive intermediate responsible for oxygen atom transfer. A complex order of catalytic activity for the Mn-porphyrins has been observed in the oxidation of various alkenes with PhIO, so that the electron rich Mn-porphyrins showed higher catalytic efficiencies than the electron-deficient ones in oxidation of most of the used alkenes. Different orders of catalytic performance of the used Mn-porphyrins in the oxidation of alkenes of various types can not be simply explained by the steric and electronic effects of the substituents attached to the double bond as well as the oxidative stability of the Mn-porphyrins.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.04.015.

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