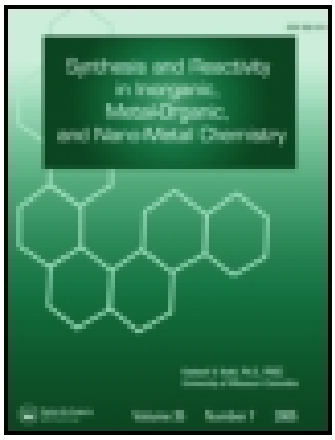




Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt20

# Partial and Full β-Chlorination of meso-Tetraphenylporphyrin: Effects on the Catalytic Activity of the Manganese Complexes for Oxidation of Organic Compounds with Periodate

Saeed Rayati[a], Elaheh Bohloulbandi[a], Saeed Zakavi[b], Majid Jafarian[a] & Mehdi Rashvand avei[a]

[a] Department of Chemistry, K.N. Toosi University of Technology, P.O. Box 16315-1618, Tehran 15418, Iran

[b] Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, Iran

Accepted author version posted online: 31 Dec 2014.

To cite this article: Saeed Rayati, Elaheh Bohloulbandi, Saeed Zakavi, Majid Jafarian & Mehdi Rashvand avei (2014): Partial and Full β-Chlorination of meso-Tetraphenylporphyrin: Effects on the Catalytic Activity of the Manganese Complexes for Oxidation of Organic Compounds with Periodate, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, DOI: 10.1080/15533174.2013.862660

To link to this article: http://dx.doi.org/10.1080/15533174.2013.862660

# Partial and Full β-Chlorination of *meso*-Tetraphenylporphyrin: Effects on the Catalytic Activity of the Manganese Complexes for Oxidation of Organic Compounds with Periodate

Saeed Rayati[a,*], Elaheh Bohloulbandi[a], Saeed Zakavi[b,*], Majid Jafarian[a], Mehdi Rashvand avei[a]

[a] *Department of Chemistry, K.N. Toosi University of Technology, P.O. Box 16315-1618, Tehran 15418, Iran*

[b] *Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, Iran*

* Corresponding author. *E-mail address*: rayati@kntu.ac.ir



**Abstract**

A series of β-chlorinated *meso*-tetraphenylporphyrins, $H_2TPPCl_x$ (x = 2, 4, 6 or 8) have been prepared and the catalytic activity of their manganese(III) complexes in oxidation of cyclooctene, cyclohexene and methyl phenyl sulfide with tetra-n-butylammonium periodate was studied. The catalytic activity of the manganese porphyrins in oxidation of cylohexene and cyclooctene decreased in the order $MnTPPCl_6(OAc) \geq MnTPP(OAc) \sim MnTPPCl_2(OAc) > MnTPPCl_4(OAc) >> MnTPPCl_8(OAc)$. The oxidative stability of the manganese porphyrins decreased as $MnTPP(OAc) > MnTPPCl_6(OAc) > MnTPPCl_8(OAc) > MnTPPCl_4(OAc) > MnTPPCl_2(OAc)$. Oxidation of methyl phenyl sulfide gave the following order: $MnTPP(OAc) \sim MnTPPCl_6(OAc) > MnTPPCl_4(OAc) \sim MnTPPCl_2(OAc) > MnTPPCl_8(OAc)$.

**Keywords** β-Chlorinated manganese porphyrins, Oxidation, Olefins, Organosulfur; tetra-n-Butylammonium periodate

## INTRODUCTION

Many studies on metalloporphyrin-catalyzed oxygenation of organic compounds since the late 1980s have been devoted to the modeling of the catalytic cycle of cytochrome P-450. [1] In this regard, a wide range of metalloporphyrins, terminal oxidants and co-catalysts were used to mimic P450 enzymes. [1-7] Coordination of terminal oxidants to the metal centre is usually essential for a metal-catalysed transformation to take place. [2] In other words, in the absence of steric hindrance, an increase in the Lewis acidity of the metal centre would facilitate the coordination of oxidant as donor molecule to the metal centre as acceptor one. Also, the formation of high-valent metal-oxo porphyrin species is accompanied with the metal and/or porphyrin centered oxidation of the metalloporphyrins. [7] On the other hand, the Lewis acidity and redox potentials of metal center as well as the oxidative stability of metalloporphyrins depend on the electronic properties of the substituents at the porphyrin periphery [8,9]. Although electron-deficient metalloporphyrins have been found to be more efficient catalysts than the electron-rich ones, [10-11] there are many reports which show comparable or higher catalytic activity of the latter in comparison with the former. [12-17] The effect of degree of β-bromination of *meso*-tetrakis(4-carbomethoxyphenyl)porphyrinato-manganese(III) chloride on its catalytic efficiency for hydroxylation of cyclohexane with iodosylbenzene and iodobenzene diacetate was studied by Idemori and co-workers. [18] Also, in a recent work, [19] we have compared the catalytic performance of a series of Mn(III) β-brominated *meso*- tetraphenylporphyrins for oxidation of organosulfurs and olefins with tetra-n-butylammonium periodate (TBAP); a partially brominated Mn-porphyrin, $MnTPPBr_4(OAc)$ and MnTPP(OAc) shown higher catalytic activity compared to the other analogues. Herein, we report the comparative study of catalytic

activity of a series of β-chlorinated *meso*- tetraphenylporphyrins in oxidation of some olefins and methyl phenyl sulfide with TBAP. Also, the half-wave potentials ($E_{1/2}$) for the metal-centered one electron reduction of the complexes were used to study the influence of chlorine atoms on the distribution of electron density at the manganese atom. [9] Due to the higher electronegativity of chlorine substituent with respect to bromine atom, [20] the introduction of bromine atoms at the β positions expected to create more electron deficient character on the porphyrin macrocycle and consequently on the corresponding manganese porphyrin.



## EXPERIMENTAL

### Materials and Methods

$^1$H NMR spectra were obtained in $CDCl_3$ solutions with a Bruker FT-NMR 300 (300 MHz) spectrometer. The residual $CHCl_3$ in conventional 99.8 atom% $CDCl_3$ gives a signal at $\delta$ = 7.26 ppm, which was used for calibration of the chemical shift scale. The electronic absorption spectra were recorded on a single beam spectrophotometer (Camspect, UV-M 330) in $CH_2Cl_2$. Gas chromatographic analyses were performed on a Shimadzu GC-14B flame ionization detector (FID) with a SAB-5 capillary column (phenyl methyl siloxane 30 m × 320 mm × 0.25 mm). Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of an EG&G model 273A potentiostat/galvanostat. The system was run by a PC through M270 commercial software via a GPIB interface. A coiled platinum wire served as an auxiliary electrode and an Ag wire conventional reference electrode was employed. All measurements were carried out at the ambient temperature of 25 ± 2 $^{\circ}$C.

Electrochemical measurements were conducted in $CH_2Cl_2$ solutions containing 0.1 M of Tetra-n-butylammonim perchlorate (TBAPC) and $2 \times 10^{-3}$ M of manganese porphyrin complexes.

The free base *meso*-tetraphenylporphyrin was prepared and purified as reported previously. [21] Chemicals were purchased from Merck chemical Co. Tetra-n-butylammonium periodate (TBAP) was prepared according to the literature. [22,23]

**Synthesis of the chlorinated porphyrins**

**$H_2TPPCl_x$ (x = 2, 4, 6 or 8)**

$MnTPPCl_2(OAc)$, $MnTPPCl_4(OAc)$, $MnTPPCl_6(OAc)$ and $MnTPPCl_8(OAc)$ (Fig. 1) were prepared from $H_2TPP$ by the following four step procedure. [24]

**NiTPP**

$H_2TPP$ (614 mg, 1mmol) was dissolved in DMF (10 ml). $Ni(OAc)_2.4H_2O$ (800 mg, 3mmol) was added to the reaction mixture and refluxed for 4 h. At the end of reaction, the solvent was evaporated under reduced pressure and the product was washed twice with distilled water to remove the excess of $Ni(OAc)_2.4H_2O$. UV-Vis in DMF, $\lambda_{max}$ (nm): 414, 527. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.74 (s, 8H, β-pyrrole), 8.13-8.20 (m, 8H, *o*-phenyl), 7.68 (broad, 12H, *m*- and *p*- phenyl).

**$NiTPPCl_x$ (x = 2, 4, 6 or 8)**

$NiTPPCl_2$ , $NiTPPCl_4$ , $NiTPPCl_6$ and $NiTPPCl_8$ were prepared from NiTPP and NCS according to the literature [25] with some modification. NCS (0.40g, 3mmol for $NiTPPCl_2$; 0.80g,

6mmol for $NiTPPCl_4$; 1.20 g, 9 mmol for $NiTPPCl_6$; or 2.40 g, 18mmol for $NiTPPCl_8$) was added with stirring to a solution of NiTPP (1.0 g, 1.5 mmol) in 1,2-dichlorobenzene (60 mL). The solution was brought to reflux for 2-3 h, and the reaction was monitored using UV-Vis spectroscopy (the soret band shifted from 414 to 419 nm for $NiTPPCl_2$, to 424 nm for $NiTPPCl_4$, to 430 nm for $NiTPPCl_6$ and to 439 nm in the case of $NiTPPCl_8$). After the end of reaction, the solvent was evaporated under reduced pressure and the crude residue was washed using a mixture of solvents, 30 mL of $CH_2Cl_2$/MeOH (1:10 v/v) to remove any soluble succinimide impurities. $NiTPPCl_2$, UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 419, 530. $^1$H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.61-8.74 (m, 6H, β-pyrrole), 7.83-8.05 (m, 8H, *o*-phenyl), 7.55-7.71 (m, 12H, *m*- and *p*-phenyl). $NiTPPCl_4$, UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 424, 542. $^1$H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.65-8.85 (m, 4H, β-pyrrole), 8.05-8.20 (m, 8H, *o*-phenyl), 7.75-8.00 (m, 12H, *m*- and *p*-phenyl). $NiTPPCl_6$, UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 430, 542. $^1$H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.65-8.73 (m, 2H, β-pyrrole), 7.83-7.96 (m, 8H, *o*-phenyl), 7.63-7.70 (m, 12H, *m*- and *p*-phenyl). $NiTPPCl_8$, UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 439, 550. $^1$H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.90-8.00 (m, 8H, *o*-phenyl), 7.65-7.80 (m, 12H, *m*- and *p*- phenyl).

**$H_2TPPCl_x$ (x = 2, 4, 6 or 8)**

$H_2TPPCl_2$, $H_2TPPCl_4$, $H_2TPPCl_6$ and $H_2TPPCl_8$ were prepared by demetallation of the Ni(II) complexes with $H_2SO_4$ and $NH_3$ in $CH_2Cl_2$. About 400 mg of $NiTPPCl_x$ (x = 2, 4, 6 or 8) was suspended in 100 ml of $CH_2Cl_2$, and 30 ml of $H_2SO_4$ (98%) was added. The mixture was rigorously stirred for 3-4 h at room temperature. The progress of the reaction was followed by UV-Vis spectroscopy. At the end of the reaction, the flask was transferred to an

ice bath, and $NH_3$ solution (25%) was added drop wise, with great precaution, to avoid overheating and violent boiling/evaporation of the organic solvent. The mixture was extracted several times with $H_2O$ and washed with a saturated solution of $NaHCO_3$ until the pH reached a value of 7.0. The organic phase dried for 45 min on $Na_2SO_4$. $H_2TPPCl_2$, UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 420, 515, 548, 595, 651. $^1$H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.67-8.91 (m, 6H, β-pyrrole), 8.08-8.24 (m, 8H, o- phenyl), 7.72-7.82 (m, 12H, m- and p-phenyl), -2.83 (d, 2H, NH). $H_2TPPCl_4$, UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 426, 523, 599, 667. $^1$H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.65-8.75 (m, 4H, β-pyrrole), 8.00-8.10 (m, 8H, o-phenyl), 7.60-7.80 (m, 12H, m- and p- phenyl), -2.80 (d, 2H, NH). $H_2TPPCl_6$, UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 433, 529, 572, 613, 675. $^1$H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.30-8.70 (m, 2H, β-pyrrole), 8.20-7.92 (m, 8H, *o*- phenyl), 7.77 (m, 12H, *m*- and *p*- phenyl), -2.40 (d, 2H, NH). $H_2TPPCl_8$, UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 355, 453, 551, 601, 719. $^1$H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.10-8.15 (m, 8H, *o*- phenyl), 7.70-7.80 (m, 12H, *m*- and *p*-phenyl), -1.55 (broad, 2H, NH).

**$MnTPPCl_x(OAc)$ (x = 2, 4, 6 or 8)**

MnTPP(OAc) ,$MnTPPCl_2$(OAc), $MnTPPCl_4$(OAc), $MnTPPCl_6$(OAc) and $MnTPPCl_8$(OAc) were prepared and purified according to the literature. [18,26] $MnTPPCl_2$(OAc), UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 472, 590, 615. $MnTPPCl_4$(OAc), UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 484, 589, 627. $MnTPPCl_6$(OAc), UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 490, 598, 638. $MnTPPCl_8$(OAc), UV-Vis in $CH_2Cl_2$, $\lambda_{max}$ (nm): 495, 607, 652.

**General oxidation procedure**

Stock solution of the catalyst (0.003 M) and imidazole (ImH, 0.5 M) were prepared in $CH_2Cl_2$. In a test tube, the reagents were added in the following order: substrate (0.25 mmol), catalyst (0.003 mmol, 1.0 ml), ImH (0.03 mmol, 60 μl), chlorobenzene (1 mmol) as an internal standard. TBAP (167 mmol) was then added to the reaction solution at 25 °C. The reaction solutions were analyzed by GC after stirring for 4 h.



**RESULS AND DISCUSSION**

**Electrochemical studies**

The cyclic voltammograms for MnTPP(OAc), $MnTPPCl_4(OAc)$, $MnTPPCl_6(OAc)$ and $MnTPPCl_8(OAc)$ in $CH_2Cl_2$ (0.1 M TBAP) are presented in Fig. 2, and the redox potential data for the one-electron process associated with the Mn(III)/Mn(II) couple are summarized in Table 1. The half-wave potentials ($E_{1/2}$) for the first reduction of MnTPP(OAc), $MnTPPCl_4(OAc)$, $MnTPPCl_6(OAc)$ and $MnTPPCl_8(OAc)$ corresponding to the $Mn^{III}/Mn^{II}$ couple were located, respectively, at $E_{1/2}$ = -319, -242, -124, -121.005 and -102 mV in $CH_2Cl_2$. The potentials were positively shifted (anodic shift) with successive increase in the number of chlorine atoms. These complexes showed a quasi-reversible one-electron reduction under the same conditions. The observed anodic shift on going from MnTPP(OAc) to $MnTPPCl_8(OAc)$ can be attributed to the steric as well as the electron-withdrawing effects of chlorine atoms. The electron-withdrawing effects of the chlorine atoms modify the redox properties of the halogenated complexes with respect to their non-halogenated counterparts due to tuning of the HOMO-LUMO energy gap, as was evident by UV-Vis spectroscopy. [27-34]

**Oxidation of olefins**

Oxidation reactions catalyzed by $MnTPPCl_x(OAc)$ (x = 0, 2, 4, 6 and 8) using TBAP as oxidant were investigated in order to verify the effect of the β-chlorination and the influence of the $Mn^{(III)}/Mn^{(II)}$ reduction potential on the catalytic properties of the Mn-porphyrin series. In a search for suitable reaction conditions to achieve the maximum conversion and product selectivity, different reaction parameters were optimized as follows.



**Effect of the TBAP/olefine molar ratio**

The reaction was performed using different molar ratios of cyclooctene to the oxidant (Table 2) and a 1:2 molar ratio has been found to be the optimized one.

**The effect of the co-catalyst/catalyst ratio**

The co-catalytic activity of ImH in the presence of $MnTPPCl_x(OAc)$ (x = 0, 2, 4, 6 and 8) at various ImH/catalyst ratios are presented in Table 3 and a 5:1 molar ratio was selected for the oxidation of cyclooctene. According to data of Table 3, the 1:5 molar ratio of ImH to catalyst has been the best one for the oxidation of olefins with TBAP and the use of ImH in molar ratios higher than this ratio, leads to a decrease in the efficiency of the catalysts, possibly due the partial formation of an inactive $Mn(Porphyrin)(ImH)_2$ species.

**Effect of the number of chlorine atoms at the β position**

Oxidation of cyclooctene and cyclohexene with TBAP was carried out in the presence of $MnTPPCl_x(OAc)$ (x = 0, 2, 4, 6 and 8) (Table 4).

**Stability of the catalyst against the degradation with oxidant**

Stability of metalloporphyrins toward oxidative degradation by the active oxidation intermediates or terminal oxidant under the reaction conditions is a major factor influencing their catalytic activity. [35] The oxidative degradation of the used metalloporphyrins has been studied in the presence of cyclooctene by UV-Vis spectroscopy at their $\lambda_{max}$ and the following order of stability was observed: MnTPP (OAc) > $MnTPPCl_6$(OAc) > $MnTPPCl_8$(OAc) > $MnTPPCl_4$(OAc) > $MnTPPCl_2$(OAc). In comparison of the chlorinated Mn-porphyrins, the oxidative stability increased with increase in number of chlorine atoms substituted at the β positions, but $MnTPPCl_6$(OAc) was found to be more stable than the other ones. Interstingly, MnTPP(OAc) demonstrated higher stability than the β-chlorinated Mn-porphyrins. Also, $MnTPPCl_8$(OAc) showed lower degree of oxidative stability compared to $MnTPPCl_6$(OAc).

**Comparison of the manganese porphyrins**

The catalytic activity of the manganese porphyrins (Table 4) in oxidation of cylohexene and cyclooctene with TBAP in the presence of ImH decreased in the order $MnTPPCl_6$(OAc) ≥ MnTPP(OAc) ~ $MnTPPCl_2$(OAc) > $MnTPPCl_4$(OAc) >> $MnTPPCl_8$(OAc). No correlation is observed between the catalytic efficiency of the complexes and their relative oxidative stability. Also, the partially chlorinated manganese porphyrin i.e. $MnTPPCl_6$(OAc) and MnTPP(OAc) with no chlorine substituents showed the highest catalytic activity. Interestingly, the catalytic activity of $MnTPPCl_8$(OAc) is unusually lower than that of the other complexes. We have observed such a complex order of catalytic activity for oxidation of different olefins with TBAP

in the case of manganese and iron porphyrins. [15-17,19] Apparently, the order of electron donor ability of substituents at the β and meso positions of metalloporphyrins can be completely different from that found in many organic reactions and transformations especially in the electrophilic substitution of aromatic compounds. [16] The observed complex order of catalyst stability for the manganese porphyrins seems to be due to the involvement of different active oxidants in the catalytic cycle of the complexes.



**Comparison with the brominated analogues**

In a previous work [19], the catalytic activity of the β-brominated manganese *meso*-tetraphenylporphyrins with 2, 4, 6 and 8 bromine atoms in the oxidation of olefins and sulphides with TBAP has been studied and compared with that of the non-brominated manganese porphyrin. While in the oxidation of olefins, the stability of the catalysts decreased in the order $MnTPPBr_8(OAc)$ > $MnTPP(OAc)$> $MnTPPBr_6(OAc)$> $MnTPPBr_2(OAc)$ > $MnTPPBr_4(OAc)$, in the case of the chlorinated complexes the following order has been observed: $MnTPP(OAc)$> $MnTPPCl_6(OAc)$> $MnTPPCl_8(OAc)$ > $MnTPPCl_4(OAc)$ > $MnTPPCl_2(OAc)$. Also, the order of catalytic activity of the complexes is as $MnTPPBr_4(OAc)$ ≥ $MnTPPBr_2(OAc)$> $MnTPPBr_6(OAc)$≥ $MnTPP(OAc)$>> $MnTPPBr_8(OAc)$ and $MnTPPCl_6(OAc)$≥ $MnTPP(OAc)$≈ $MnTPPCl_2(OAc)$> $MnTPPCl_4(OAc)$ >> $MnTPPCl_8(OAc)$ for the brominated and chlorinated catalysts, respectively. The results show different order of oxidative stability and catalytic activity for the series of chlorinated and brominated manganese complexes. However, in both series, the octa-halogenated complex has been found to be the least effective catalyst of the

series. Also, in the oxidation of sulfides, with the exception of the octa-halogenated complexes, different order of catalytic activity was found for the catalysts of the two series.

**Oxidation of methyl phenyl sulfide**

Oxidation of methyl phenyl sulfide with TBAP in the presence of catalytic amounts of $MnTPPCl_x(OAc)$ (x = 0, 2, 4, 6 and 8) in dichloromethane at room temperature led to the selective sulfoxidation of the substrate. In a search for suitable reaction conditions to achieve the highest selectivity for sulfoxide, the effect of varying a number of reaction parameters has been studied. In the absence of metalloporphyrin, the reaction gives the sulfoxide and sulfone in substantially lower yields (0.64 and 0.87%, respectively).

**Effect of TBAP /sulfide molar ratio**

In synthetic organic chemistry, the selective oxidation of sulfides to sulfoxides has been an important challenge. The reaction was performed using various equivalents of oxidant for oxidation of methyl phenyl sulfide (Table 5, Fig. 3). It shows that the highest conversion was achieved with the 1:2 molar ratio of methyl phenyl sulfide to TBAP .

**The effect of the co-catalyst/catalyst ratio**

Oxidation of methyl phenyl sulfide in the presence of various ratios of imidazole to catalyst changes the ratio of sulfoxide to sulfone in the products rather than the total conversion. The effect of ImH concentration on the oxidation of methyl phenyl sulfide has also been studied (Fig. 4). Addition of ImH up to 5:1 relative to the catalyst led to an increase in the conversion of

reaction with increase the ratio of sulfoxide to sulfone. The addition of ImH beyond this ratio led to a decrease in the ratio of sulfoxide to sulfone.

**Comparison of the catalysts**

Oxidation of methyl phenyl sulfide with TBAP in the presence of the manganese porphyrins gave the corresponding sulfoxide and sulfone as the products (Table 5). The catalytic activity of the manganese porphyrins was found to decrease as MnTPP(OAc) ~ $MnTPPCl_6$(OAc) > $MnTPPCl_4$(OAc) ~ $MnTPPCl_2$(OAc) > $MnTPPCl_8$(OAc). However, in the case of using the sulfide and TBAP in 1:1 or 2:1 molar ratios, nearly no catalytic activity was observed for $MnTPPCl_8$(OAc) in comparison with the other manganese porphyrins. Also, the former gave methyl phenyl sulfide sulfoxide as the major product.

**CONCLUSIONS**

In this study, effect of partial and full chlorination of *meso*-tetraphenylporphyrinatomanganese(III) acetate at the β positions on the catalytic activity of this manganese porphyrin for the oxidation of cyclohexene, cyclooctene and methyl phenyl sulfide with TBAP has been studied. The catalytic activity of the manganese porphyrins in the oxidation of olefins and methyl phenyl sulfide was found to decrease as $MnTPPCl_6$(OAc) ≥ MnTPP(OAc) ~ $MnTPPCl_2$(OAc) > $MnTPPCl_4$(OAc) >> $MnTPPCl_8$(OAc) and MnTPP(OAc) ~ $MnTPPCl_6$(OAc) > $MnTPPCl_4$(OAc) ~ $MnTPPCl_2$(OAc) > $MnTPPCl_8$(OAc), respectively. No clear correlation was found between the catalytic activity of the complexes and their relative oxidation stability in the reaction condition. Interestingly, $MnTPPCl_8$(OAc) showed an unusually low catalytic activity compared to the other manganese porphyrins of the series. In combination with the results of previous studies concerning the relative catalytic activity and stability of the β

halogenated manganese porphyrins, the electronic effects of halogen atoms substituted at the β positions of metalloporphyrins as aromatic compounds, seem to be completely different from that found in many organic reactions and transformations especially in the electrophilic substitution of aromatic compounds. In other words, there is no correlation between the number of halogen atoms introduced at the β positions and the catalytic activity as well as the stability of the manganese porphyrins in oxidation conditions.

**ACNOWLEDGEMENTS**

The financial support of this work by K.N. Toosi University of Technology research council is acknowledged.



**REFERENCES**

1. Meunier, B. *Chem. Rev.* **1992**, 1411.

2. Sheldon, R. A.; Kochi, J. K. Eds. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, **1981,** Chapt. 6 and 8.

3. Lee, K. A.; Nam, W. *J. Am. Chem. Soc.* **1997**, *119*, 1916.

4. Meunier, B. *Biomimetic Oxidations Mediated by Metal Complexes,* Imperial College Press, London, **2000,** Chapt. 3 and 4.

5. Nam, W. *Acc. Chem. Res.* **2007**, 40, 522.

6. Wang, B.; Li, C.; Cho, K.-B.; Nam, W.; Shaik, S. *J. Chem. Theory Comput*. In press.

7. Yang, X.-L.; Xie, M.-H.; Zou, C.; He, Y.; Chen, B.; O'Keeffe, M.; Wu, C.-D. *J. Am. Chem. Soc.* **2012**, 134, 10638.

8. Kadish, K. M.; Caemelbecke, E. A. *J. Solid State Electrochem.* **2003**, 7, 254-258.

9. Friedermann, G. R.; Halma, M.; de F. Castro, K. A. D.; Benedito, F. L.; Doro, F. G.; S. Drechsel, M.; Mangrich, A. S.; Assis, M. D.; Nakagaki, S. *Appl. Catal. A: Gen.* **2006**, *308*, 172.

10. Mansuy, D. *Pure Appl. Chem.* **1994**, *66*, 737.

11. Nam, W.; Choi, H. J.; Han, H. J.; Cho, S. H.; Lee, H. J.; Han, S. Y. *Chem. Commun.* **1999**, 387.

12. Chen, J.; Che, C. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4950.

13. Mohajer, D.; Karimipour, G.; Bagherzadeh, M. *New J. Chem*. **2004**, 28, 740.

14. Zakavi, S.; Ebrahimi, L. *Polyhedron* **2011**, *30*, 1732.

15. Zakavi, S.; Heidarizadi, F.; Rayati, S. *Inorg. Chem. Commun*. **2011**, *14*, 1010.

16. Zakavi, S.; Mojarrad, A. G.; Rayati, S. *J. Mol. Catal. A: Chem.* **2012**, *363-364*, 153.

17. Zakavi, S.; Mokary yazdeli, T. *J. Mol. Catal. A: Chem.* **2013**, *367*, 108.

18. da Silva, D. C.; DeFreitas-Silva, G.; do Nascimento, E.; Rebouças, J. S.; Barbeira, P. J. S.; de Carvalho, M. E. M. D.; Idemori, Y. M. *J. Inorg. Biochem.* **2008**, *102*, 1932.

19. Rayati, S.; Zakavi, S.; Bohloulbandi, E.; Jafarian, M.; Rashvand avei, M. *Polyhedron* **2012**, *34*, 102.

20. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th, HarperCollins College Publishers, New York, **1993**, pp. 187.

21. Adler, D.; Longo, F. R.; Finarelli, J. D.; Golldmacher, J.; Assour, J.; Korsakof, L. *J. Org. Chem.* **1976**, *32*, 476.

22. Mohajer, D.; Abbasi, M. *Eur. J. Inorg. Chem*. **2008**, *20*, 3218.

23. Santaniello, E.; Manzocchi, A.; Farachi, C. *Synthesis* **1980**, 563.

24. Spyroulias, G. A.; Despotopoulos, A. P.; Rapotopoulous, C. P.; Terzis, A.; de Montauzon, D.; Poilblanc, R.; Coutsolelos, A. G. *Inorg. Chem*. **2002**, *41*, 2648.

25. Bhyrappa, P.; Krishnan, V. *Inorg. Chem.* **1991**, *30*, 239.

26. Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J.; *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

27. Batinic-Haberle, I.; Liochev, S. I.; Spasojevic, I.; Fridovich, I.; *Arch. Biochem. Biophys.* 1997, 343, 225.

28. Spasojevic, I.; Batinic-Haberle, I. *Inorg. Chim. Acta* **2001**, *317*, 230.

29. Reboucas, J. S.; de Carvalho, M. E. M. D. Idemori, Y. M. *J. Por. Phthal.* **2002**, *6*, 50.

30. Kadish, K. M.; D'Souza, F.; Villard, A.; Autret, M.; van Caemelbecke, E.; Bianco, P.; Antonini, A.; Tagliatesta, P. *Inorg. Chem.* **1994**, *33*, 5169.

31. Parusel, A. B. J.; Wondimagegn, T.; Ghosh, A. *J. Am. Chem. Soc.* **2000**, *122*, 6371.

32. Woller, E. K.; Dimango, S. G. *J. Org. Chem.* **1997**, *62*, 1588.

33. Kadish, K. M.; Autrey, M.; Ou, Z.; Tagliatesta, P.; Boschi, T.; Fares, V.; *Inorg. Chem.* 1997, 36, 204.

34. Gassman, P. G.; Ghosh, A.; Almlof, J. *J. Am. Chem. Soc.* 1992, 114, 9990.

35. Fuji, H. *Coord. Chem. Rev.* 2002, 226, 51.



**Table 1**

Half-wave potential data for the metal-centered one-electron reduction of the Mn(III) complexes.[a]

| Mn-porohyrins | $E_{ox}$ (mV) | $E_{red}$ (mV) | $\Delta E_p$[b] (mV) | $E_{1/2}$ (mV) |
|---|---|---|---|---|
| Mn(III)(TPP) | -246 | -392 | 146 | -319 |
| Mn(III)($Cl_2$TPP) | -150 | -334 | 184 | -242 |
| Mn(III)($Cl_4$TPP) | -20 | -228 | 208 | -124 |
| Mn(III)($Cl_6$TPP) | -50 | -192 | 142 | -121 |
| Mn(III)($Cl_8$TPP) | -40 | -164 | 124 | -102 |

[a] Conditions: $CH_2Cl_2$, MnP = $2 \times 10^{-3}$ M, TBAP = 0.1 M, scan rate 50 $mV.s^{-1}$. Versus Ag/AgCl.

[b] Potential difference ($E_{ox}$-$E_{red}$).

**Table 2**

Effect of various TBAP/cyclooctene molar ratios on the cyclooctene epoxidation in the presence of ImH in dichloromethane.[a]

| TBAP/ cyclooctene | Conversion %[b] | | | | |
|---|---|---|---|---|---|
| | MnTPP | $MnTPPCl_2$ | $MnTPPCl_4$ | $MnTPPCl_6$ | $MnTPPCl_8$ |
| 1:2 | 35 | 28 | 26 | 32 | 3 |
| 1:1 | 58 | 43 | 42 | 46 | 3 |
| 2:1 | 90 | 59 | 56 | 62 | 4 |

[a]The molar ratios for catalyst:ImH:cyclooctene:oxidant are 1:10:83:x .

[b] All reactions were run at room temperature for 4 h.

**Table 3**

Effect of various ImH/Catalyst molar ratios on the cyclooctene epoxidation rate and selectivity with TBAP in dichloromethane[a]

| ImH/Catalyst | Conversion %[b] | | | | |
|---|---|---|---|---|---|
| | MnTPP | $MnTPPCl_2$ | $MnTPPCl_4$ | $MnTPPCl_6$ | $MnTPPCl_8$ |
| 10 | 35 | 28 | 26 | 32 | 3 |
| 5 | 36 | 35 | 28 | 44 | 6 |

[a] The molar ratios for catalyst:ImH: cyclooctene: oxidant are 1:x:83:167 .

[b] All reactions were run at room temperature for 4 h.



**Table 4**

Oxidation of cyclooctene and cyclohexene with TBAP catalyzed by $MnTPPCl_x(OAc)$ (x = 0, 2, 4, 6 and 8) in the presence of ImH in dichloromethane. [a]

| Catalyst | Cyclooctene | | Cyclohexene | | | |
|---|---|---|---|---|---|---|
| | Yield % (Epoxide) | Conversion % | Yield % | | | Conversion %[b] |
| | | | Epoxide | 1-ol | 1-on | |
| MnTPP(OAc) | 36 | 36 | 26 | 1 | 4 | 31 |
| $MnTPPCl_2(OAc)$ | 35 | 35 | 21 | 1 | 2 | 24 |
| $MnTPPCl_4(OAc)$ | 28 | 28 | 8 | 1 | 1 | 10 |
| $MnTPPCl_6(OAc)$ | 44 | 44 | 21 | 1 | 3 | 25 |
| $MnTPPCl_8(OAc)$ | 6 | 6 | 7 | 1 | 1 | 9 |

[a] The molar ratios for catalyst:ImH:alkene:oxidant are 1:5:83:167 .

[b] All reactions were run at room temperature for 4 h.

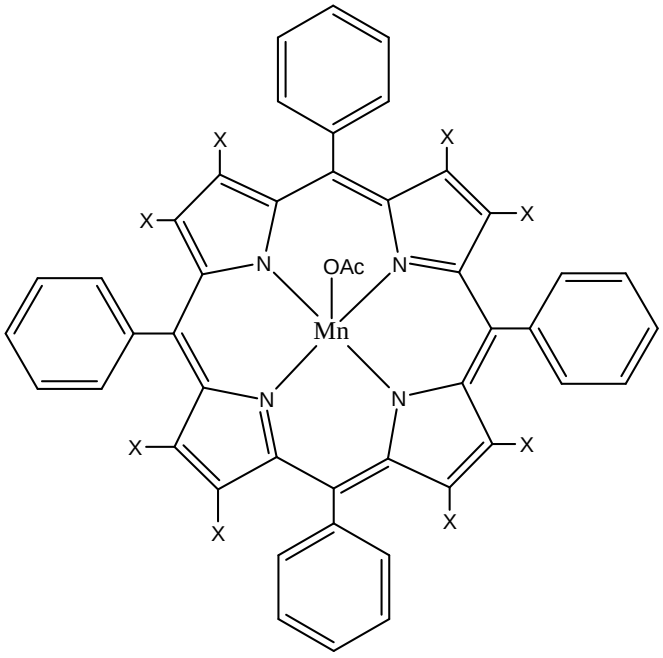
**Table 5**

Effect of various TBAP/sulfide molar ratios on the oxidation of methyl phenyl sulfide in the presence of ImH in dichloromethane .[a]

| TBAP/ Sulfide | Catalyst | Conversion %[b] | Yield % (sulfoxide) | Yield % (sulfone) | Sulfoxide/sulfone |
|---|---|---|---|---|---|
| 1:2 | MnTPP | 22 | 19 | 3 | 6.3 |
| | $MnTPPCl_2$ | 18 | 17 | 1 | 17 |
| | $MnTPPCl_4$ | 16 | 14 | 2 | 7 |
| | $MnTPPCl_6$ | 21 | 20 | 1 | 20 |
| | $MnTPPCl_8$ | 2 | 2 | 0 | - |
| 1:1 | MnTPP | 49 | 35 | 14 | 2.5 |
| | $MnTPPCl_2$ | 37 | 29 | 8 | 3.6 |
| | $MnTPPCl_4$ | 39 | 30 | 9 | 3.3 |
| | $MnTPPCl_6$ | 48 | 38 | 10 | 3.8 |
| | $MnTPPCl_8$ | 3 | 3 | 0 | - |
| 2:1 | MnTPP | 58 | 26 | 32 | 0.8 |
| | $MnTPPCl_2$ | 40 | 22 | 18 | 1.2 |
| | $MnTPPCl_4$ | 41 | 25 | 16 | 1.5 |
| | $MnTPPCl_6$ | 57 | 31 | 26 | 1.1 |
| | $MnTPPCl_8$ | 18 | 9 | 9 | 1 |

[a] The molar ratios for catalyst:ImH:sulfide:oxidant are 1:10:83:x.

[b] All reactions were run at room temperature for 4 h.




X = 0 MnTPP(OAc)
X = 2Cl $MnTPPCl_2(OAc)$
X = 4Cl $MnTPPCl_4(OAc)$
X = 6Cl $MnTPPCl_6(OAc)$
X = 8Cl $MnTPPCl_8(OAc)$

**Fig. 1.** The used metalloporphyrin in this study

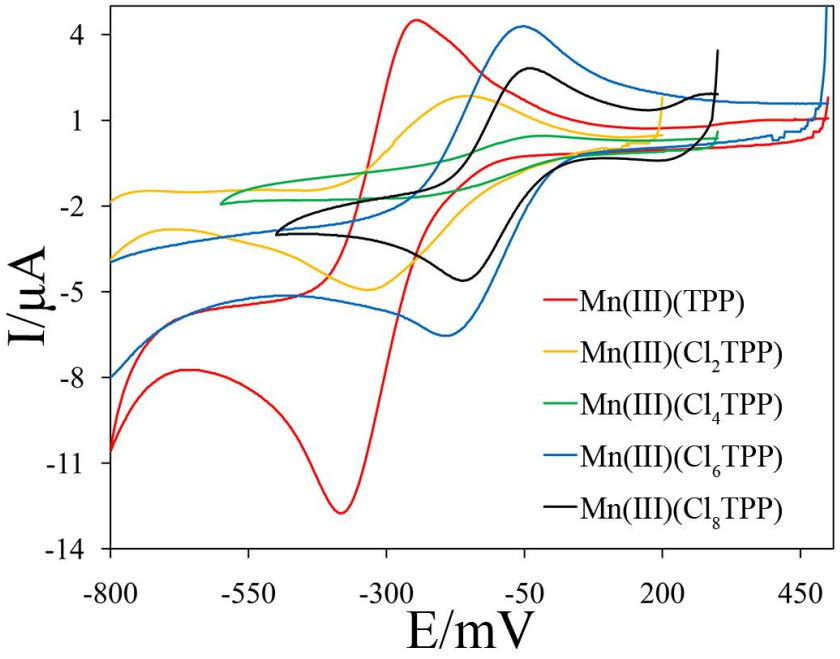



**Fig. 2.** Cyclic voltammograms of Mn(III)($Cl_x$TPP) ($CH_2Cl_2$, MnP = $2 \times 10^{-3}$ M, TBAP = 0.1 M, scan rate 50 mV $s^{-1}$).

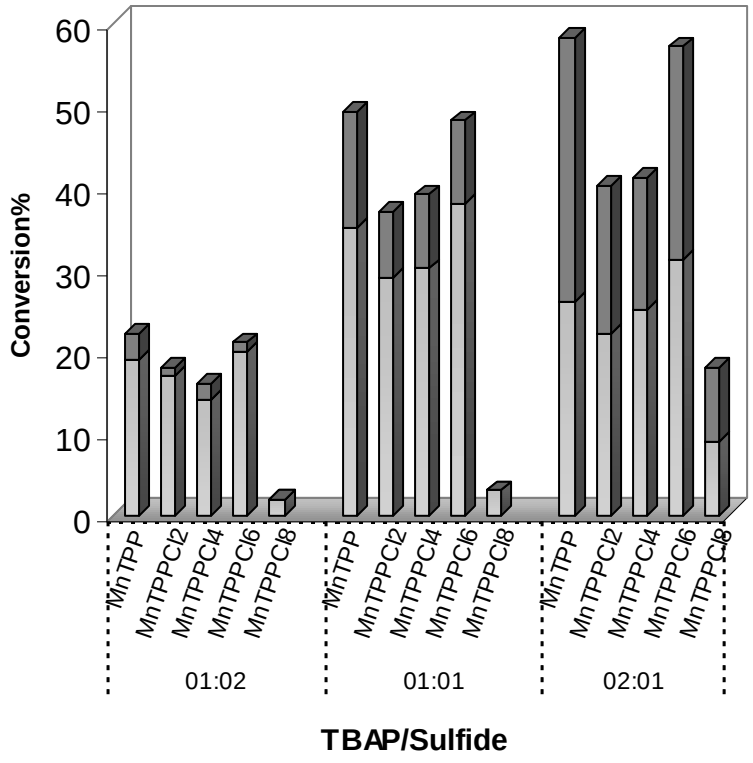



**Fig**. 3. Effect of various TBAP/sulfide molar ratios on the oxidation of methyl phenyl sulfide in the presence of ImH in dichloromethane. Light color: yield of sulfoxide, dark color: yield of sulfone.

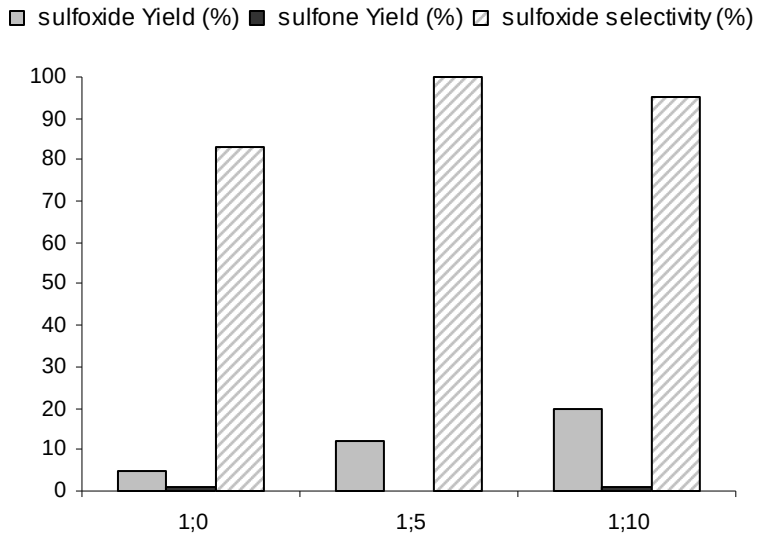



**Fig. 4.** Effect of ImH/$MnTPPCl_6(OAc)$ molar ratios on the oxidation of methyl phenyl sulfide with TBAP in dichloromethane at room temperature. The molar ratios for catalyst:ImH:sulfide:oxidant are 1:x:83:167.