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Comparative study of the catalytic activity of a series of β-brominated Mn–porphyrins in the oxidation of olefins and organic sulfides: Better catalytic performance of the partially brominated ones

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ABSTRACT

The oxidation of olefins and organic sulfides with tetra-*n*-butylammonium periodate (TBAP) in the presence of a Mn(III) complex from a series of partially and fully brominated *meso*-tetraphenylporphyrins, $MnTPPBr_x(OAc)$ ($x = 0$, 2, 4, 6 and 8) has been studied in a comparative manner. With the exception of $MnTPPBr_2(OAc)$, the half-wave potential for the Mn(III)/Mn(II) metal-centered process was gradually shifted to higher values on going from MnTPP(OAc) to $MnTPPBr_8(OAc)$. However, a complex order has been observed for the catalytic activity of the complexes; while the stability of the Mn–porphyrins towards oxidative degradation under the reaction conditions decreases in the order $MnTPPBr_8(OAc) > MnTPP(OAc) > MnTPPBr_6(OAc) > MnTPPBr_2(OAc) > MnTPPBr_4(OAc)$, their catalytic activity has been found to follow the order $MnTPPBr_8(OAc) \ll MnTPP(OAc) \leqslant MnTPPBr_6(OAc) < MnTPPBr_2(OAc) \leqslant MnTPPBr_4(OAc)$. The maximum conversion (42%) was obtained in the case of $MnTPPBr_4(OAc)$ and the minimum conversion (14%) is related to $MnTPPBr_8(OAc)$. Oxidation of methyl phenyl sulfide with TBAP in a 1:1 molar ratio leads to the following pattern of catalytic activity for the used Mn–porphyrins: $MnTPPBr_4(OAc) > MnTPP(OAc) > MnTPPBr_2(OAc) \geqslant MnTPPBr_6(OAc) \gg MnTPPBr_8(OAc)$. The highest methyl phenyl sulfide conversion is 69% at room temperature.

1. Introduction

Biomimetic oxidation of organic compounds in the presence of metalloporphyrins has been studied from different points of view [1]. According to the four-orbital model of Gouterman for metal porphyrins, the electron densities of the HOMOs are largest on the nitrogen and *meso*-carbon atoms for the a_{2u} orbital and on the pyrrole carbon atoms in the case of the a_{1u} orbital (Fig. 1) [2]. The positions with highest electron densities, i.e. the α and *meso* ones, are expected to be involved in the oxidative degradation of metalloporphyrins [3]. One of the most common strategies employed with the aim of reducing the oxidative degradation ofmetalloporphyrins during oxidation reactions is the use of electron-deficient substituents on the aryl groups of *meso*-tetraarylmetalloporphyrins [4,5]. It has been shown previously that electron-donating *meso*-substituents will raise the energy of the a_{2u} orbital by increasing its electron density [6]. Since the *meso*-carbon atoms lie on the nodal planes of the a_{1u} orbital [2], introduction of electron-withdrawing or electron-donating groups at the appropriate positions of the *meso*-aryl substituents seems to have little effect on the energy level of this orbital. In contrast, both the a_{1u} and a_{2u} orbitals are stabilized by the electron-withdrawing effects of a substituent at the β positions [7]. In other words, substitution of electron-withdrawing groups at the β positions may also be used to enhance the oxidative stability of metalloporphyrins. The catalytic activity of partially and fully β-brominated analogs of *meso*-tetrakis(4-carbomethoxyphenyl)porphyrinatomanganese(III) chloride for the hydroxylation of cyclohexane with PhIO and $PhI(OAc)_2$ has been investigated by Idemori and co-workers in a comparative study [8]. We have previously reported the oxidation of olefins and organic sulfides with tetrabutylammonium oxone (TBAO) catalyzed by Mn(III) complexes of partially brominated *meso*-tetraphenylporphyrins [9–13]. Very recently we have studied the catalytic performance of two partially brominated Mn–porphyrins in comparison with that of a range of electron-rich and electron-deficient ones for the oxidation of olefins with tetra-*n*-butylammonium periodate (TBAP) and PhIO. The partially brominated Mn–porphyrins were shown to have higher or lower activities compared to their non-brominated analogs and other electron-rich Mn–porphyrins [14,15]. In the present work, the catalytic activity of a series of *meso*-tetraphenylporphyrins with 0, 2, 4, 6 and 8 bromine atoms at the pyrrole rings in the oxidation of olefins and organic sulfides with TBAP was studied in a comparative manner.

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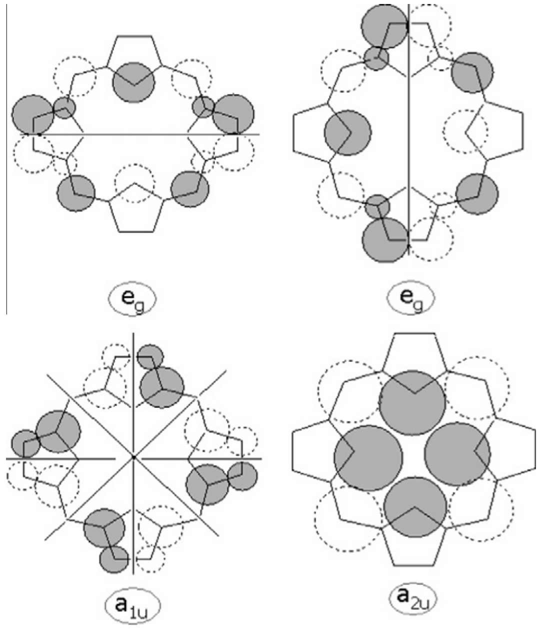

Fig. 1. Gouterman four orbital model.

2. Experimental

2.1. Materials and methods

^1H 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 the calibration of the chemical shift scale. The electronic absorption spectra were recorded on a single beam spectrophotometer (Camspect, UV-M330) in CH_2Cl_2. 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 is 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 °C. Electrochemical measurements were conducted in CH_2Cl_2 solutions containing 0.1 M of tetrabutylammonium perchlorate (TBAPC) and 2×10^{-3} M of manganese porphyrin complexes. Gas chromatographic analyses were performed on a Shimadzu GC-14B flame ionization detector (FID) with a SAB-5 capillary column (phenyl methyl siloxane 30 × 320 × 0.25 mm).

The free base *meso*-tetraphenylporphyrin was prepared and purified as reported previously [16]. Chemicals were purchased from Merck chemical Co. Tetra-*n*-butylammonium periodate (TBAP) was prepared according to the literature [17,18].

2.2. Synthesis

2.2.1. H_2TPPBr_x ($x = 2$ or 4)

β-Di-bromo-*meso*-tetraphenylporphyrin and β-tetra-bromo-*meso*-tetraphenylporphyrin were synthesized independently according to the method reported by Bhyrappa and co-workers, with some modifications [19]. Freshly recrystallized *N*-bromosuccinimide (NBS) (180 mg, 0.98 mmol for H_2TPPBr_2; or 360 mg, 1.96 mmol for H_2TPPBr_4) was added to a solution of H_2TPP (300 mg, 0.49 mmol) in $CHCl_3$ (80 ml) under stirring conditions. The mixture was stirred for 24 h in darkness and then the $CHCl_3$ was evaporated to dryness. The residue was washed with methanol (2 × 20 ml) to remove any soluble succinimide impurities. β-Dibromo-*meso*-tetraphenylporphyrin (H_2TPPBr_2), UV–Vis in CH_2Cl_2, λ_{max} (nm): 423, 520, 595, 650. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.78 (m, 6H, β-pyrrole), 8.20–8.24 (m, 8H, *o*-phenyl), 7.73–7.78 (m, 12H, *m*- and *p*-phenyl), −2.83 (s, 2H, NH). β-Tetra-bromo-*meso*-tetraphenylporphyrin (H_2TPPBr_4), UV–Vis in CH_2Cl_2, λ_{max} (nm): 436, 533, 612, 683. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.69 (m, 4H, β-pyrrole), 8.16–8.19 (m, 8H, *o*-phenyl), 7.70–7.90 (m, 12H, *m*- and *p*-phenyl), −2.82 (s, 2H, NH).

2.2.2. $MnTPPBr_2(OAc)$ and $MnTPPBr_4(OAc)$

$MnTPPBr_2(OAc)$ and $MnTPPBr_4(OAc)$ were prepared as follows [20]. H_2TPPBr_2 or H_2TPPBr_4 (0.13 mmol) was dissolved in a minimum amount of methanol and then 30 ml chloroform was added. $Mn(OAc)_2{\cdot}4H_2O$ (250 mg, 1.04 mmol) was added to the reaction mixture and refluxed for a period of 2 h. $MnTPPBr_2(OAc)$, UV–Vis in CH_2Cl_2, λ_{max} (nm): 375, 475, 583, 619. $MnTPPBr_4(OAc)$, UV–Vis in CH_2Cl_2, λ_{max} (nm): 380, 483, 590.

2.2.3. $MnTPPBr_x(OAc)$ ($x = 6$ or 8)

$MnTPPBr_6(OAc)$ and $MnTPPBr_8(OAc)$ were prepared from H_2TPP by the following four step procedure [21].

2.2.4. NiTPP

H_2TPP (614 mg, 1 mmol) was dissolved in DMF (10 ml). $Ni(OAc)_2{\cdot}4H_2O$ (800 mg, 3 mmol) 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 $Ni(OAc)_2{\cdot}4H_2O$. UV–Vis in DMF, λ_{max} (nm): 414, 527. ^1H 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).

2.2.5. $NiTPPBr_x$ ($x = 6$ or 8)

$NiTPPBr_6$ and $NiTPPBr_8$ were prepared from H_2TPP and freshly recrystallized NBS according to the literature [22] with some modifications. NBS (1.58 g, 9 mmol for $NiTPPBr_6$; or 3.20 g, 18 mmol for $NiTPPBr_8$) 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 440 nm for $NiTPPBr_6$ and to 445 nm in the case of $NiTPPBr_8$). 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. $NiTPPBr_6$, UV–Vis in CH_2Cl_2, λ_{max} (nm): 440, 554. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.3 (m, 2H, β-pyrrole), 7.94 (m, 8H, *o*-phenyl), 7.71–7.72 (m, 12H, *m*- and *p*-phenyl). $NiTPPBr_8$, UV–Vis in CH_2Cl_2, λ_{max} (nm): 445, 555. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.00–8.10 (m, 8H, *o*-phenyl), 7.75–7.90 (m, 12H, *m*- and *p*-phenyl).

2.2.6. H_2TPPBr_x ($x = 6$ or 8)

H_2TPPBr_8 and H_2TPPBr_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 $NiTPPBr_x$ ($x = 6$ 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 dropwise, 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 was over Na_2SO_4. H_2TPPBr_6, UV–Vis in CH_2Cl_2, λ_{max} (nm): 445, 555, 607, 705. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.18–8.51

(m, 2H, β-pyrrole), 8.18 (m, 8H, *o*-phenyl), 7.79–7.92 (m, 12H, *m*- and *p*-phenyl), −2.29 (broad, 2H, NH). H_2TPPBr_8, UV–Vis in CH_2Cl_2, λ_{max} (nm): 368, 469, 569, 625, 745. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.13–8.15 (m, 8H, *o*-phenyl), 7.72–7.75 (m, 12H, *m*- and *p*-phenyl), −1.25 (broad, 2H, NH).

2.2.7. $MnTPPBr_x(OAc)$ (x = 6 or 8)

$MnTPPBr_6(OAc)$ and $MnTPPBr_8(OAc)$ were prepared and purified according to the literature [20]. $MnTPPBr_6(OAc)$, UV–Vis in CH_2Cl_2, λ_{max} (nm): 499, 605, 653. $MnTPPBr_8(OAc)$, UV–Vis in CH_2Cl_2, λ_{max} (nm): 496, 610.

2.3. General oxidation procedure

Stock solutions of the catalyst (0.003 M) and nitrogenous bases (0.5 M) were prepared in CH_2Cl_2. The reagents were added to a test tube in the following order: substrate (0.25 mmol), catalyst (0.003 mmol, 1.0 ml), nitrogenous bases (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 mixture was stirred thoroughly for 4 h at ambient temperature. The reaction solutions were analyzed by GC.

3. Results and discussion

3.1. UV–Vis spectra of H_2TPPBr_x (x = 0, 2, 4, 6 and 8)

The UV–Vis spectra of H_2TPPBr_x (x = 0, 2, 4, 6 and 8) are given in Table 1. The Soret and Q bands of the perhalogenated porphyrins are reportedly red shifted relative to those of the non-brominated analogs [23,24], and this is also observed in this work (Table 1). Large shifts of the Soret and Q (visible) bands of porphyrins have been attributed to the enhanced co-planarity of the phenyl groups with the porphyrin mean plane and/or the out-of-plane deformation of the macro cycle and/or the inductive effects of substituents at *meso* and β-positions [25–27]. According to the X-ray crystallographic studies, substitution of more than 4 bromine atoms at the β positions of *meso*-tetraphenylporphyrins cause the non-planarity of the macrocycle [28]. We have previously attributed the large red shifted bands of β-tetrabrominated-*meso*-tetraphenylporphyrin to the electron-withdrawing effects of the bromine atoms. In the case of H_2TPPBr_6 and H_2TPPBr_8, the out-of-plane deformations of the porphyrin core as well as the electronic effects of the bromine atoms may be used to explain the red shifts of the Soret and the Q(0,0) bands [7].

3.2. ^1H NMR spectra of H_2TPPBr_x (x = 0, 2, 4, 6 and 8)

The ^1H NMR spectral data of H_2TPPBr_x (x = 0, 2, 4, 6 and 8) are summarized in Table 2. The chemical shifts of the phenyl protons were not significantly different from those of H_2TPP (Table 2). The signal of the β-protons of pyrrole rings for H_2TPP appears at δ 8.85. The chemical shifts of the β-protons of H_2TPPBr_2, H_2TPPBr_4 and H_2TPPBr_6 are respectively as follows: 8.78, 8.69 and 8.18–8.51 (Table 2). The upfield shift of the β-protons of the brominated porphyrins may be attributed to the ring current decrease generated by the out-of-plane deformation of the macrocycle [29]. However, due to the planar conformation of the macrocycle in the case of the di- and tetra-brominated porphyrins, the shielding of the β protons cannot be explained according to the ring current effects. The upfield shift of the β protons of H_2TPPBr_2 and H_2TPPBr_4 seems to be due to the shielding of the β protons resulting from the electron-withdrawing effects of the bromine atoms; although the electron-withdrawing effects of the bromine atoms is expected to decrease the total electron density on the porphyrin core, the inductive effects of the bromine atoms seems to increase the electron densities of the π system at the β positions [15]. The ^1H NMR spectra of H_2TPPBr_2 and H_2TPPBr_4 shows upfield shifts of the NH protons relative to that of H_2TPP, which may be due to some weakening of the interamolecular N–H···N hydrogen bonds [30]. Interestingly, the NH resonance of H_2TPPBr_6 and H_2TPPBr_8 is downfield relative to H_2TPP (Table 2). This downfield shift may be attributed to the ring current decrease resulting from the out-of-plane deformation of the porphyrin core, the electron-withdrawing effects of the bromine atoms and the strengthening of N–H···N hydrogen bond in the case of the two porphyrins [31].

Table 1
The Soret and Q(0,0) bands of H_2TPPBr_x (x = 2, 4, 6 and 8) in comparison with the bands of H_2TPP.

Porphyrins	Soret band λ (nm)	Q(0,0) band λ (nm)
H_2TPP	418	646
H_2TPPBr_2	423	651
Δv (cm^{-1})[a]	282	118
H_2TPPBr_4	440	683
Δv (cm^{-1})	1207	838
H_2TPPBr_6	445	705
Δv (cm^{-1})	1415	1295
H_2TPPBr_8	469	745
Δv (cm^{-1})	2601	2057

[a] $\Delta v = 10^7(1/\lambda_1 - 1/\lambda_2)$ relative to the corresponding band of H_2TPP.

3.3. Electrochemical studies

The cyclic voltammograms for MnTPP(OAc), $MnTPPBr_2(OAc)$, $MnTPPBr_4(OAc)$, $MnTPPBr_6(OAc)$ and $MnTPPBr_8(OAc)$ 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 3. The half-wave potentials ($E_{1/2}$) for the first reduction of MnTPP(OAc), $MnTPPBr_2(OAc)$, $MnTPPBr_4(OAc)$, $MnTPPBr_6(OAc)$ and $MnTPPBr_8(OAc)$ corresponding to the Mn^{III}/Mn^{II} couple were located, respectively, at $E_{1/2}$ −342, −380, −161, −141 and −87 mV in CH_2Cl_2. With the exception of $MnTPPBr_2(OAc)$, the potentials were positively shifted (anodic shift) with the progressive increase in the number of bromine atoms. $MnTPPBr_2(OAc)$ exhibited an irreversible voltammogram corresponding to the Mn^{III}/Mn^{II} reduction, while the other complexes showed a quasi-reversible one-electron reduction under the same conditions. The observed anodic shift on going from MnTPP(OAc) to the octabrominated counterpart can be ascribed to the electron-withdrawing and steric effects of the bromine substituents. As reported in the literature [31–38], the electron-withdrawing character and steric effects of the bromine substituents modify the redox properties of the brominated complexes with respect to their precursors due to a decrease in the HOMO–LUMO energy gap, in accordance with the UV–Vis studies.

3.4. Oxidation of olefins

The oxidation of olefins with TBAP has been carried out in the presence of $MnTPPBr_x(OAc)$ (x = 0, 2, 4, 6 and 8). As has been previously reported by Mohajer et al. [40], no reaction was observed in the absence of the catalyst. Different reaction parameters were optimized as follows.

3.4.1. Effect of the TBAP/olefin molar ratio

Different molar ratios of cyclooctene to the oxidant were used (Table 4) and a 1:2 molar ratio has been found to be the optimized one.

Table 2
The ^1H NMR data of H_2TPPBr_x ($x = 0, 2, 4, 6$ and 8).

Porphyrins	β-Pyrrole (ppm)	*o*-Phenyl (ppm)	*m,p*-Phenyl (ppm)	N–H (ppm)
H_2TPP	8.85 (s, 8H)	8.20–8.24 (m, 8H)	7.73–7.77 (m, 12H)	−2.77 (s, 2H)
H_2TPPBr_2	8.78 (s, 6H)	8.20–8.24 (m, 8H)	7.73–7.78 (m, 12H)	−2.83 (s, 2H)
H_2TPPBr_4	8.69 (s, 4H)	8.16–8.19 (m, 8H)	7.70–7.90 (m, 12H)	−2.82 (s, 2H)
H_2TPPBr_6	8.18–8.51 (m, 2H)	8.18 (m, 8H)	7.79–7.92 (m, 12H)	−2.29 (broad, 2H)
H_2TPPBr_8		8.13–8.15 (m, 8H)	7.72–7.75 (m, 12H)	−1.25 (broad, 2H)

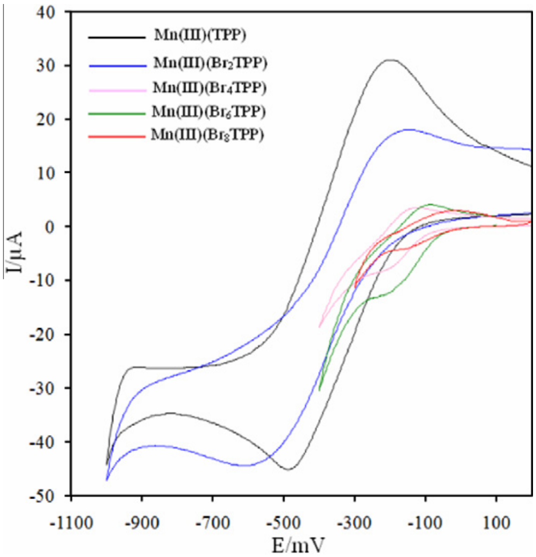

Fig. 2. Cyclic voltammograms of Mn(III)(Br_xTPP) (CH_2Cl_2, MnP = 2×10^{-3} M, TBAP = 0.1 M, scan rate 50 mV s^{-1}).

Table 3
Half-wave potential data for the metal-centered one-electron reduction of Mn(III)–porphyrin complexes.[a]

Mn–porphyrins	E_{pa}	E_{pc}	ΔE_p[b]	$E_{1/2}$
Mn(III)(TPP)	−198	−486	288	−342
Mn(III)(Br_2TPP)	−145	−616	471	−380
Mn(III)(Br_4TPP)	−120	−202	82	−161
Mn(III)(Br_6TPP)	−86	−196	110	−141
Mn(III)(Br_8TPP)	−13	−160	165	−87

[a] Conditions: CH_2Cl_2, MnP = 2.8×10^{-4} M, TBAP = 0.1 M, scan rate 100 mV s^{-1}.
[b] Potential difference ($E_{pa} - E_{pc}$).

Table 4
Effect of various n-Bu_4NIO_4/cyclooctene molar ratios on the cyclooctene epoxidation in the presence of ImH in CH_2Cl_2 at room temperature.[a]

nBuNIO$_4$/ cyclooctene	Conversion %[b]				
	MnTPP	$MnTPPBr_2$	$MnTPPBr_4$	$MnTPPBr_6$	$MnTPPBr_8$
1:2	35	41	38	34	3
1:1	58	55	50	43	14
2:1	90	96	87	51	14

[a] The molar ratios for catalyst:ImH:cyclooctene:oxidant are 1:10:83:x.
[b] For a 4 h reaction time.

Table 5
Effect of various ImH/catalyst molar ratios on the cyclooctene epoxidation rate and selectivity with TBAP in CH_2Cl_2 at room temperature.[a]

ImH/catalyst	Conversion %[b]				
	MnTPP	$MnTPPBr_2$	$MnTPPBr_4$	$MnTPPBr_6$	$MnTPPBr_8$
10	35	41	38	34	3
5	31	41	42	33	6

[a] The molar ratios for catalyst:ImH:cyclooctene:oxidant are 1:x:83:167/4.
[b] For a 4 h reaction time.

3.4.2. The effect of the co-catalyst/catalyst ratio

Effects of different molar ratios of imidazole (ImH) to catalyst on the performance of $MnTPPBr_x$(OAc) ($x = 0, 2, 4, 6$ and 8) are presented in Table 5. The ratio of 5:1 has been used for the oxidation of cyclooctene.

3.4.3. Effect of the number of bromine atoms at the β positions

Oxidation of cyclooctene and cyclohexene with TBAP was carried out in the presence of $MnTPPBr_x$(OAc) ($x = 0, 2, 4, 6$ and 8) (Table 6). According to the data of Table 6, with the exception of $MnTPPBr_8$(OAc), there is no significant meaningful difference between the catalytic activity of the brominated Mn–porphyrins and the non-brominated one. Interestingly, MnTPP(OAc) and the partially brominated counterparts are clearly more efficient than $MnTPPBr_8$(OAc). The stability of the metalloporphyrins towards oxidative degradation under the reaction conditions is one of the main factors influencing their catalytic performance. According to the UV–Vis studies, $MnTPPBr_8$(OAc) is the most stable metalloporphyrin of the series (vide infra) under the reaction conditions. Accordingly, the decreased catalytic performance of the fully β brominated Mn–porphyrin with respect to the partially brominated ones and the non-brominated counterpart cannot be explained on the basis of the stability of the Mn–porphyrins.

3.4.4. Catalyst stability towards the oxidant or the active intermediate

The stability of metalloporphyrins towards oxidative degradation with the active oxidation intermediates or oxidant under the reaction conditions is a major factor influencing their catalytic activity [7,41]. The relative degradation of the used metalloporphyrins has been studied in the presence and the absence of cyclooctene. With the exception of $MnTPPBr_4$(OAc), the stability of the catalysts increased with the increase in number of halogen atoms substituted at the β positions, there is no correlation between the number of bromine atoms and the stability of the brominated Mn–porphyrins relative to MnTPP(OAc); in the case of the di-, tetra and hexa-brominated Mn–porphyrins the catalyst stability decreased relative to the non-brominated one. In contrast, $MnTPPBr_8$(OAc) showed a higher stability compared to MnTPP(OAc). However, $MnTPPBr_8$(OAc) is only slightly more stable than MnTPP(OAc). Apparently, the bromine atoms act as electron donor groups rather than electron acceptors. The enhanced stability of $MnTPPBr_8$(OAc) and $MnTPPBr_6$(OAc) with respect to the di- and tetra-brominated Mn–porphyrins is suggested to be due to the steric effects of the bulky bromine atoms.

3.5. Oxidation of sulfides

Oxidation of methyl phenyl sulfide with TBAP catalyzed by Mn($TPPBr_x$)OAc ($x = 0, 2, 4, 6$ and 8) gave methyl phenyl sulfoxide as the major product. In a search for suitable reaction conditions to achieve the highest selectivity for sulfoxide, the effect of different parameters including solvent, amount of co-catalyst and amount of TBAP were studied in detail. Running the reaction in the absence

Table 6
Oxidation of cyclooctene and cyclohexene with TBAP catalyzed by $MnTPPBr_x(OAc)$ (x = 0, 2, 4, 6 and 8) in the presence of ImH in CH_2Cl_2.[a]

Catalyst	Cyclohexene				Cyclooctene	
	Yield %			Conversion %[b]	Yield %	Conversion %
	Epoxide	1-ol	1-on		Epoxide	
MnTPP(OAc)	32	1	5	38	38	38
$MnTPPBr_2(OAc)$	35	1	5	41	42	42
$MnTPPBr_4(OAc)$	31	2	5	42	38	38
$MnTPPBr_6(OAc)$	28	2	4	34	34	34
$MnTPPBr_8(OAc)$	11	2	1	14	13	13

[a] The molar ratios for catalyst:ImH:alkene:oxidant are 1:5:83:167/4.
[b] For a 4 h reaction time.

Table 8
Effect of various TBAP/sulfide molar ratios on the oxidation of methyl phenyl sulfide in the presence of ImH in CH_2Cl_2 at room temperature.[a]

TBAP/ sulfide	Catalyst	Conversion %[b]	Yield % (sulfoxide)	Yield % (sulfone)	Sulfoxide/ sulfone
1:2	MnTPP	22	19	3	6.3
	$MnTPPBr_2$	21	19	2	9.5
	$MnTPPBr_4$	29	26	3	8.6
	$MnTPPBr_6$	20	18	1	18
	$MnTPPBr_8$	3	3		3
1:1	MnTPP	33	26	7	3.7
	$MnTPPBr_2$	41	30	10	3
	$MnTPPBr_4$	44	33	11	3
	$MnTPPBr_6$	28	23	5	4.6
	$MnTPPBr_8$	4	6	1	6
2:1	MnTPP	56	30	26	1.1
	$MnTPPBr_2$	69	35	34	≈1
	$MnTPPBr_4$	65	41	24	1.7
	$MnTPPBr_6$	46	27	18	1.5
	$MnTPPBr_8$	11	7	3	2.3

[a] The molar ratios for catalyst:ImH:sulfide:oxidant are 1:10:83:*x*.
[b] For a 4 h reaction time.

Table 9
Effect of various ImH/catalyst molar ratios on the oxidation of methyl phenyl sulfide selectivity with TBAP in CH_2Cl_2 at room temperature.[a]

Entry	ImH/ $MnTPPBr_4(OAc)$	Conversion %[b]	Yield % (sulfoxide)	Yield % (sulfone)	Sulfoxide/ sulfone ratio
1	0	6	5	1	5
2	5	24	22	2	11
3	10	29	26	3	8.6

[a] The molar ratios for catalyst:ImH:sulfide:oxidant are 1:*x*:83:167/4.
[b] For a 4 h reaction time.

of metalloporphyrin gives the sulfoxide and sulfone in substantially lower yields (0.64% and 0.87%, respectively).

3.5.1. Solvent effect

In order to obtain the best reaction media, solvents with different dielectric constants [41] have been used (Table 7). According to Table 7, the maximum conversion and highest selectivity for sulfoxide formation was obtained in dichloromethane. Consequently, dichloromethane had the highest ability for sulfoxide formation and was selected for the oxidation of methyl phenyl sulfide.

3.5.2. Effect of the TBAP/sulfide molar ratio

The selective oxidation of sulfides to sulfoxides has been an important challenge in synthetic organic chemistry. While higher ratios of TBAP to the organic sulfide increase the total conversion of the reaction (Table 8), the over-oxidation of sulfoxide to sulfone decreases the chemoselectivity of the reaction. Using different molar ratios of methyl phenyl sulfide to the oxidant (Table 8) shows that the 1:2 molar ratio has been found to be the optimized one to obtain the highest conversion. However, the use of a 2:1 molar ratio leads to the selective oxidation of methyl phenyl sulfide to the corresponding sulfoxide.

3.5.3. Comparison of the Mn–porphyrins

As has been observed in the case of the olefin oxidation, the partially brominated Mn–porphyrins show remarkably higher catalytic activities compared to the fully β brominated one. On the other hand, there is no significant difference between the efficiency of the partially brominated Mn–porphyrins with 2, 4 and 6 bromine atoms at the β positions. Also, the activity of $MnTPPBr_6(OAc)$ is comparable with the non-brominated analog. While high ratios of sulfoxide to sulfone have been observed in the presence of $MnTPPBr_8(OAc)$, the conversion significantly decreased in the reaction catalyzed by $MnTPPBr_8(OAc)$. Interestingly, the catalytic performance of MnTPP(OAc) is much higher than $MnTPPBr_8(OAc)$, but is comparable with $MnTPPBr_6$.

3.5.4. The effect of the co-catalyst/catalyst ratio

The co-catalytic activities of ImH in the presence of $MnTPPBr_4(OAc)$ at various ImH/catalyst ratios are presented in Table 9 and a 10:1 ratio was selected for the oxidation of methyl phenyl sulfide. The effect of ImH concentration on the oxidation of methyl phenyl sulfide has also been studied (Table 9). Addition of ImH up to 5:1 relative to the catalyst led to an increase in the conversion of the reaction with an increase in the ratio of sulfoxide to sulfone. Beyond this ratio, a significant decrease in the ratio of sulfoxide to sulfone was observed.

Whilst the choice of periodate as oxidant, in comparison with oxone used in our previous works [9–13], leads to lower yield of products in the oxidation of olefins and methyl phenyl sulfide, the selectivity towards sulfoxide increased significantly in the oxidation of sulfides. In the case of olefins, using periodate as an oxidant gives some ketone and alcohol in addition to the corresponding epoxide as the major product.

4. Conclusions

In summary, the catalytic activity of the Mn(III) complexes of a series of β brominated *meso*-tetraphenylporphyrins for the oxidation of olefins and organic sulfides with TBAP has been studied and compared. The results show that: (i) there is no correlation between the number of bromine atoms and the stability of the

Table 7
Oxidation of methyl phenyl sulfide with TBAP catalyzed by $MnTPPBr_4(OAc)$ in the presence of ImH in different solvents at room temperature.[a]

Solvent	Dipole moment	Conversion %[b]	Yield % (sulfoxide)	Yield % (sulfone)	Sulfoxide/sulfone
Dichloromethane	1.60	29	26	3	8.6
Tetrahydrofuran	1.63	7	6	1	6

[a] The molar ratios for catalyst:ImH:sulfide:oxidant are 1:10:83:167/4.
[b] For a 4 h reaction time.

Mn–porphyrins relative to the non-brominated one; (ii) the partially brominated Mn–porphyrins are more efficient catalysts compared to MnTPPBr$_8$(OAc); (iii) the catalytic performance of MnTPP(OAc) is comparable with the hexabrominated Mn–porphyrin; (iv) in spite of the higher stability of MnTPPBr$_8$(OAc) with respect to the other Mn–porphyrins, its catalytic activity is significantly lower than that of partially brominated and non-brominated counterparts; (v) with the exception of MnTPPBr$_2$(OAc), the half-wave potential for the Mn(III)/Mn(II) metal-centered process showed anodic shifts on going from MnTPP(OAc) to MnTPPBr$_8$(OAc); (vi) oxidation of cyclohexene and cyclooctene gave the corresponding epoxides as the major product and some alcohol and ketone as the minor products; (vii) cyclooctene and cyclohexene show comparable reactivity towards oxidation with TBAO in the presence of the used catalysts; (viii) in spite of the higher reactivity of methyl phenyl sulfide relative to the olefins in this catalytic system, the low efficiency of this system in the oxidation of the olefins and sulfides seems to be due to the low to moderate oxidizing ability of periodate compared to oxidants such as oxone. However, the selectivity towards sulfoxide increased significantly in the oxidation of sulfides in comparison to Mn–porphyin/oxone catalytic systems.

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