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COMMUNICATION

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A comparative study on the catalytic performance of heme and non-heme catalysts: Metal porphyrins versus metal Schiff bases

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Catalytic activity and oxidative stability of a series of iron and manganese porphyrins with 2-chlorophenyl, phenyl and 4-methoxyphenyl at the meso positions and metallosalens (Mn- and Fe-salens) including N,N′-bis(salicylidene) ethylenediamine, N,N′-bis(5- chlorosalicylidene)ethylenediamine and N,N′-bis (2,4-dihydroxysalicylidene)ethylenediamine for the oxidation of olefins with tetra-n-butylammonium periodate (TBAP) and tetra-n-butyl-ammonium Oxone (TBAO) have been investigated and compared. Although the metalloporphyrins showed an increased catalytic activity relative to the Schiff base complexes, the former provided no significant catalytic advantage over the latter. Also, a comparable or slightly higher oxidative stability was observed for the Schiff base complexes under the reaction conditions. Furthermore, in spite of large difference between the oxidizing ability of TBAO and TBAP, similar patterns were observed for the order of catalytic activity and oxidative stability of the used heme and non-heme catalysts. The introduction of a methyl group at the α position of styrene led to an increase in its reactivity, indicating the dominance of electronic effects over the steric ones in these catalytic systems.

KEYWORDS
iron and manganese complexes, olefins, oxidation, porphyrins, Schiff bases

1 | INTRODUCTION

Porphyrins and Schiff bases are well known ligands which received much attention over the past decades due to their extensive applications in the field of homogeneous and heterogeneous catalysis of organic and inorganic transformations.[1] In 1979, the first article on the use of metalloporphyrins as catalyst for the oxidation of alkanes and olefins was published by Groves *et al.*[1b] However, the first reports on the catalytic activity of Schiff base complexes for the oxidation of hydrocarbons date back to earlier than 1970.[2] The metal complexes of Schiff bases and porphyrins have been extensively utilized to mimic the active site of heme and non-heme enzymes.[3, 1a, 2b] Also, they have found many applications in medicine, synthetic chemistry and industry. The epoxidation of alkenes catalyzed by metalloporphyrins can proceed through the intermediacy of high valent oxo-metal intermediates analogue to the oxoiron(V) species involved in cytochrome P450-mediated oxidations.[1a] On the other hand, high valent manganese and iron oxo species were prepared using their Schiff base complexes.[4] In other words, both metal porphyrins and metal Schiff bases demonstrated ability to form high valent oxo metal species under oxidative conditions. Furthermore, there are some structural and chemical similarities between the Schiff bases and porphyrins metal complexes such as the stability of the aromatic ring, ability to form chelate rings and adopt a planar or approximately planar conformation and the ease of peripheral substitution.[5] The Schiff bases and their metal complexes are usually prepared in higher yields using simple and more efficient procedures and less expensive reactants at lower temperatures in comparison with porphyrins and metalloporphyrins. Furthermore, the former are usually prepared in greener solvent ethanol.[6] Over the past decades, periodate and Oxone were extensively used for the oxidation of organic compounds in the presence of metalloporphyrins and metal Schiff base complexes.[7] However, to date no comparative study was conducted on the two classes of metal complexes. In the present study, the Mn(III) and Fe(III) complexes of *meso*-tetraphenylporphyrin H_2TPP, *meso*-tetrakis(2-chlorophenyl)porphyrin $H_2T(2\text{-}Cl)PP$ and *meso*-tetrakis(4-metoxyphenyl) porphyrin $H_2T(4\text{-}OMe)PP$ (Figure 1) and their similar salen-type ligands *N,N′*-Bis(salicylidene)ethylenediamine H_2L^1, *N,N′*-Bis(5-chlorosalicylidene)ethylenediamine H_2L^2 and *N,N′*-Bis(2,4-dihydroxysalicylidene)ethylenediamine H_2L^3 (Figure 1) were used as catalyst for the oxidation of olefins with tetra-n-butylammonium periodate (TBAP) and tetra-n-butylammonium Oxone (TBAO) as moderate and strong oxidants, respectively. The results of this study show that in the catalytic oxidation of olefins with TBAP and TBAO there is no significant advantage for the metalloporphyrins over the Schiff base complexes and the latter can be successfully used instead of the former.

2 | RESULTS AND DISCUSSION

2.1 | Oxidation of olefins with TBAP

The oxidation of different olefins was conducted with TBAP (Table 1 and Figure 2) and the following orders of catalytic activity were found:

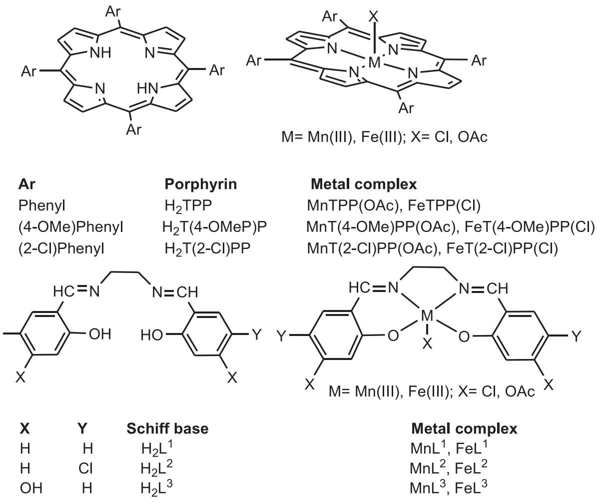

FIGURE 1 Manganese and iron complexes used in this study

TABLE 1 The oxidation of olefins with TBAP in the presence of metal porphyrins and metal salens in acetonitrile at room temperature [a]

Catalyst no.	Catalysts	Conversion (%)[b,c] Styrene	α-Methyl styrene	Indene
1	MnTPP(OAc)	72 [16][d]	73	89
2	$MnL^1(OAc)$	27 [4]	67	73
3	MnT(2-Cl)PP(OAc)	76 [14]	72	79
4	$MnL^2(OAc)$	65 [8]	63	65
5	MnT(4-OMe) PP(OAc)	91 [11]	85	87
6	$MnL^3(OAc)$	44 [100]	57	60
7	FeTPP(Cl)	40 [72]	47	56
8	$FeL^1(Cl)$	57 [11]	63	67
9	FeT(2-Cl)PP(Cl)	70 [6]	75	73
10	$FeL^2(Cl)$	56 [9]	58	72
11	FeT(4-OMe)PP(Cl)	77 [66]	74	86
12	$FeL^3(Cl)$	46 [38]	59	65
-	Average conversion (metalloporphyrins)	71 [31]	71	78
-	Average conversion (Schiff base complexes)	50 [28]	61	67

[a]The molar ratios of metalloporphyrin:ImH:olefin:TBAP are 1:10 (5 for the iron porphyrins):85:170 and molar ratios of metallosalen:olefin:TBAP are 1:50:150.[b] All reactions were repeated three times, analyzed by GC; the average values with an error of ca. 5–10% are reported.[c] Epoxide was formed as the sole product.[d] The data in brackets shows the oxidative stability (%) of the catalyst evaluated on the basis of the absorbance changes (ΔA) at the λ_{max} of the metalloporphyrins or Schiff base complexes (ΔA/A).

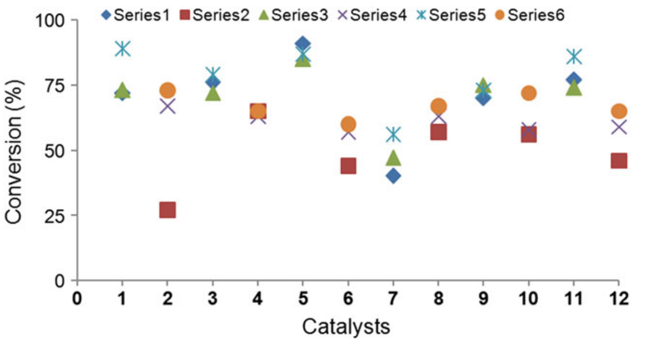

FIGURE 2 The results for the oxidation of styrene, indene and α-methylstyrene with TBAP in the presence of the metalloporphyrins (series **1** [styrene], **3** [α-methylstyrene] and **5** [indene]) and the Schiff base complexes (series **2** [styrene], **4** [α-methylstyrene] and **6** [indene]). See Table 1 for the catalyst numbers

Oxidation of styrene: MnT(4-OMe)PP(OAc) > FeT(4-OMe)PP(Cl) ≈ MnT(2-Cl)PP(OAc) ≥ MnTPP(OAc) ≈ FeT(2-Cl)PP(Cl) ≥ $MnL^2(OAc)$ > $FeL^1(Cl)$ ≈ $FeL^2(Cl)$ >

FeL^{3}(Cl) ≈ MnL^{3}(OAc) ≥ FeTPP(Cl) > MnL^{1}(OAc). Running the oxidation reactions in the presence of the metalloporphyrins and Schiff base complexes led to average conversion values of ca. 70 and 50%, respectively.

Oxidation of α-methylstyrene: MnT(4-OMeP)P(OAc) > FeT(2-ClP)P(Cl) ≈ FeT(4-OMeP)P(Cl) ≈ MnTPP(OAc) ≈ MnT(2-ClP)P(OAc) > MnL^{1}(OAc) ≥ MnL^{2}(OAc) ≈ FeL^{1}(Cl) ≥ FeL^{3}(Cl) > FeL^{2}(Cl) ≈ MnL^{3}(OAc) > FeTPP(Cl). The oxidation products were achieved with average conversion values of ca. 71 and 61% in the presence of the metalloporphyrins and Schiff base complexes, respectively.

Oxidation of indene: MnTPP(OAc) ≈ MnT(4-OMe)PP(OAc) ≈ FeT(4-OMe)PP(Cl) > MnT(2-Cl)PP(OAc) ≥ MnL^{1}(OAc) ≈ FeT(2-Cl)PP(Cl) ≈ FeL^{2}(Cl) > FeL^{1}(Cl) ≈ MnL^{2}(OAc) ≈ FeL^{3}(Cl) > MnL^{3}(OAc) > FeTPP(Cl). Average conversion values of ca. 78 and 67% were obtained in the presence of the metalloporphyrins and Schiff base complexes, respectively.

Although the metalloporphyrins were usually more efficient than the Schiff base complexes, the average conversions achieved in the presence of the former were only 10–20% greater than those observed in the case of the latter.

Also, the oxidative stability of catalysts in the oxidation of styrene with TBAP decreased as MnL^{1}(OAc) ≈ FeT(2-Cl)PP(Cl) ≥ MnL^{2}(OAc) ≥ FeL^{2}(Cl) ≥ FeL^{1}(Cl) ≈ MnT(4-OMe)PP(OAc) ≥ MnT(2-Cl)PP(OAc) ≥ MnTPP(OAc) > FeL^{3}(Cl) >> FeT(4-OMe)PP(Cl) ≥ FeTPP(Cl) > MnL^{3}(OAc). The degree of catalyst degradation was measured on the basis of the absorbance changes (ΔA) at the λ_{max} of the catalysts (Figures 3 and Supporting Information). It is observed that the Schiff base complexes are as stable as the metalloporphyrins in the oxidation reactions performed by periodate that seems to be due to the absence of high valent metal oxo species in these catalytic systems (*vide infra*).

The oxidative degradation of metalloporphyrins occurs through an intermolecular mechanism by the oxidative attack at the carbon atoms with high electron density i.e. the meso, α and β positions.[8] It is noteworthy that according to the four orbital model of porphyrins, the electron density of the a_{1u} and a_{2u} orbitals of porphyrins are largest on the meso, β and α carbons.

The catalytic activity of manganese and iron porphyrins depends on the steroelectronic properties of the meso substituents and nature of the metal centre.[1a, 1b, 1c, 1d, 1e] As was shown in previous studies, electron-rich manganese and iron porphyrins are usually more efficient than the electron-demanding ones. However, the electron-deficient metalloporphyrins are often more stable towards oxidative degradation.[7d, 7i, 7j]

Also, manganese porphyrins usually show higher catalytic activity compared to the iron counterparts. The stronger π-π interaction between the porphyrin core and the iron centre in comparison with the manganese centre was suggested to explain the higher oxidative stability of the iron porphyrins.[7k] The presence of electron-withdrawing substituents at different positions of the meso-substituents makes them more electron-deficient. Furthermore, the introduction of bulky substituents such as chlorine atom at the ortho position may be utilized to increase the electron-deficient character of metalloporphyrins. It should be noted that the latter leads to an increase in the dihedral angle between the meso aryl substituents and porphyrin mean plane and a decrease in the π resonance interactions between their π systems.

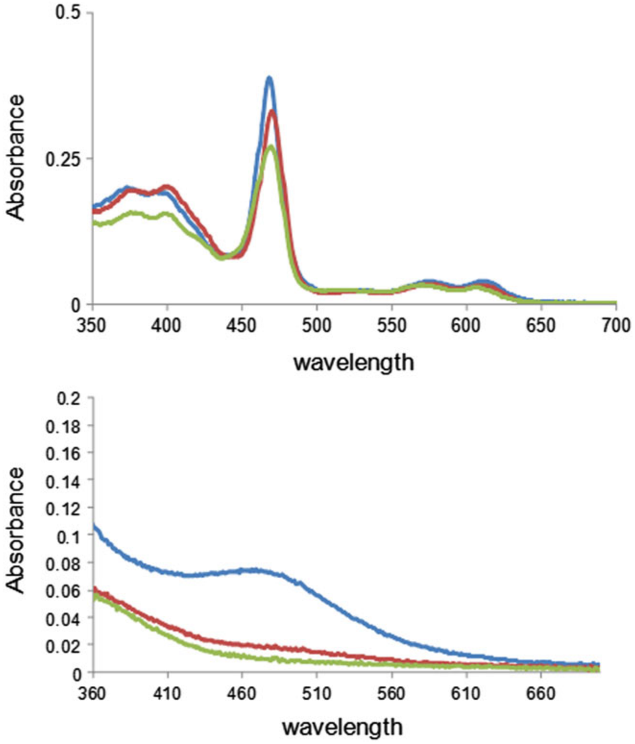

FIGURE 3 (top) the absorbance changes upon the addition of TBAP to a solution containing MnTPP(OAc) and ImH in 1:10 molar ratio (blue curve), immediately after the addition of the oxidant (red curve) and after 4 h (green curve); (down) the changes in the UV–vis spectrum of FeL^{1}(cl) (blue curve), after the addition of TBAP (10 min, red curve and 4 h, green curve)

As was observed, the average catalytic activity of the metalloporphyrins was slightly (10–20%) greater than that of the metal Schiff base complexes. It was previously shown that a periodato six coordinate complex i.e. (ImH)M(Porphyrin)(IO_4) (M = Fe or Mn) is the main active oxidant species in the metalloporphyrin catalyzed oxidation of olefins with periodate[1k,7d,I,j] in combination with a high valent oxo metal species as the minor one. Accordingly, the Mn(III) or Fe(III) species are responsible for the catalytic activity of the two series of the catalyts and therefore no large differences were observed between the catalytic activity of these catalysts. Also, the low oxidizing ability of the dominant active oxidant led to the comparable oxidative stability of the used heme and non-heme catalysts.

Furthermore, the comparison of the reactivity of styrene and α-methylstyrene shows that the steric effects of the methyl group have no effect on the reactivity of styrene. In the case of the Schiff base complexes, the dominance of the electronic effects of the methyl group over its steric effects led to the higher reactivity of α-methylstyrene. On the other hand, higher reactivity of indene compared to styrenes seems to be due to the more reactivity of strained double bond of indene relative to the non-strained terminal double bond of styrene.[1n] However, the nearly planar structure of indene which decreases the steric hindrance about the reaction center may be also involved.

2.2 | Oxidation of olefins with TBAO

The oxidation of olefins was also conducted with TBAO as a strong oxidant and the catalytic activity of the catalysts was found to decrease as follows:

Oxidation of styrene: MnT(2-ClP)P(OAc) ≈ FeT(2-ClP)P(Cl) ≥ MnL^1(OAc) ≈ MnT(4-OMeP)P(OAc) > MnL^2(OAc) > FeTPP(Cl) > FeT(4-OMeP)P(Cl) > FeL^1(Cl) > MnL^3(OAc) ≥ MnTPP(OAc) > FeL^2(Cl) > FeL^3(Cl).

Oxidation of α-methylstyrene: MnT(2-ClP)P(OAc) ≈ MnL^2(OAc) ≈ MnTPP(OAc) ≥ MnT(4-OMeP)P(OAc) ≈ 1MnL^1(OAc) ≈ FeT(2-ClP)P(Cl) > FeTPP(Cl) ≈ FeT(4-OMeP)P(Cl) > FeL^1(Cl) > FeL^2(Cl) > MnL^3(OAc) > FeL^3(Cl).

Oxidation of indene: MnT(2-ClP)P(OAc) ≈ MnL^2(OAc) ≈ MnTPP(OAc) ≥ MnT(4-OMeP)P(OAc) ≈ MnL1(OAc) ≈ FeT(2-ClP)P(Cl) > FeTPP(Cl) ≈ FeT(4-OMeP)P(Cl) > FeL^1(Cl) > FeL^2(Cl) > MnL^3(OAc) > FeL^3(Cl).

Furthermore, the stability of catalysts under the oxidation conditions decreased as MnL^3(OAc) > FeT(2-ClP)P(Cl) > MnT(2-ClP)P(OAc) > FeT(4-OMeP)P(Cl) ≥ FeTPP(Cl) > MnTPP(OAc) ≈ MnT(4-OMeP)P(OAc) ≈ MnL^1(OAc) ≈ MnL2(OAc) ≈ FeL^1(Cl) ≈ FeL^2(Cl) ≈ FeL^3(Cl).

As may be seen from Table 2 and Figure 4, the metalloporphyrins are again more efficient than the Schiff base complexes with average conversion values that are 15–30% greater than those obtained in the case of the Schiff base complexes. However, the former shows an increased (ca. 10%) oxidative stability. As was shown in a previous study [1l, 1m], the oxidation of olefins with strong oxidants such as TBAO and iodosylbenzene in the presence of metalloporphyrins is accompanied with the formation of high-valent metal oxo species as the major active oxidant. As was observed in the case of the oxidation of olefins with periodate, the metalloporphyrins may be considered to be nearly as stable as the Schiff base complexes. In other words, the heme and non-heme complexes used in this study are of similar oxidative stability in the presene of periodate and TBAO as moderate and strong terminal oxidants, respectively. However, the increased oxidative stability of the former seems to be due to the more extended aromatic system of the metalloporphyrins.

TABLE 2 The oxidation of olefins with TBAO in the presence of metal porphyrins and metallosalens in acetonitrile at room temperature[a]

Catalyst no.	Catalysts	Conversion (%) [b,c]		
		Styrene	α-Methyl styrene	Indene
1	MnTPP(OAc)	37 [100][d]	99	96
2	MnL^1(OAc)	96 [100]	99	93
3	MnT(2-Cl)PP(OAc)	100 [49]	98	98
4	MnL^2(OAc)	91 [100]	98	97
5	MnT(4-OMe) PP(OAc)	94 [100]	95	94
6	MnL^3(OAc)	41 [13]	85	58
7	FeTPP(Cl)	84 [88]	93	86
8	FeL^1(Cl)	49 [100]	73	75
9	FeT(2-Cl)PP(Cl)	100 [22]	98	93
10	FeL^2(Cl)	28 [100]	30	71
11	FeT(4-OMe)PP(Cl)	65 [84]	87	84
12	FeL^3(Cl)	16 [100]	59	71
-	Average conversion (metalloporphyrins)	80 [74]	95	92
-	Average conversion (Schiff base complexes)	53 [85]	74	77

[a] See the footnotes of Table 1.

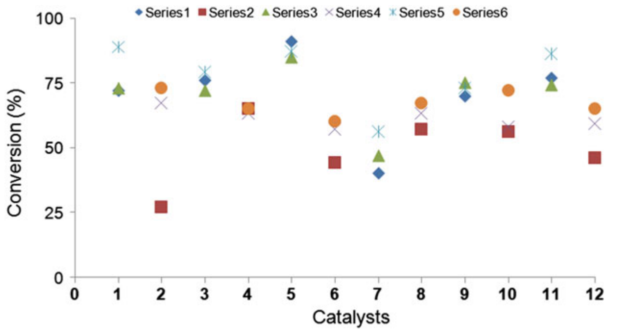

FIGURE 4 The results for the oxidation of styrene, indene and α-methylstyrene with TBAO in the presence of the metalloporphyrins (series **1** [styrene], **3** [α-methylstyrene] and **5** [indene]) and Schiff base complexes (series **2** [styrene], **4** [α-methylstyrene] and **6** [indene]). See Table 2 for the catalyst numbers

Also, the increased reactivity of α-methystyrene compared to that of styrene gave evidence for the dominance of the electronic effects over the steric effects of the methyl group.

A comparison of the data summarized in Tables 1 and 2, shows higher conversion values for the oxidation of olefins performed with TBAO. This observation is in accord with higher oxidizing ability of TBAO compared to that of TBAP. However, comparable or nearly comparable catalytic activity and oxidative stability were found for the used heme and non-heme catalysts in the presence of TBAP and TBAO as moderate and strong terminal oxidants, respectively.

3 | EXPERIMENTAL

3.1 | Preparation of ligands

N,N′-bis(salicylidene)ethylenediamine (H_2L^1), N,N′-bis(5-chlorosalicylidene)ethylenediamine (H_2L^2) and N,N′-bis(2,4-dihydroxysalicylidene)ethylenediamine (H_2L^3) were synthesised according to the literature by the condensation of ethylenediamine and substituted salicylaldehyde in ethanol under reflux conditions;[9] In a typical reaction, 0.2 ml (2 mmol) salicylaldehyde and 67 μl (1 mmol) ethylenediamine were added to a round-bottom flask containing 30 ml ethanol and the mixture was refluxed for 1 h. The yellow precipitates (H_2L^1) obtained after cooling the solution, were washed with cold ethanol and dried under air. Yield (> 90%), mp 129–131 C. $C_{16}H_{16}N_2O_2$ (268.31): Calcd. C 71.62, H 6.016, N 10.44. Found C 70.73, H 6.17, N 10.25%. Selected FT-IR data, ν (cm^{-1}): 3418 (O–H), 2902 (C–H), 1629 (C = N), 1494 (C = C), 1283 (C–O). UV–Vis, λ (nm): 244, 255, 316. ^1H NMR (δ): 3.96 (4H, s, H_2C-CH_2), 6.89–7.34 (8H, m, Ph), 8.38 (2H, s, N = CH), 13.25 (2H, Ph-OH).

The synthesis of H_2L^2 was performed using the same procedure by using 5-chloro-2-hydroxybenzaldehyde. Yield (> 90%), mp 179–181 °C. $C_{16}H_{14}N_2O_2Cl_2$ (337.2): Calc. C 56.99, H 4.18, N 8.31. Found C 56.65, H 3.95, N 8.73%. Selected FT-IR data, ν (cm^{-1}): 3416 (O–H), 2900 (C–H), 1628 (C = N), 1481 (C = C), 1274 (C–O), 825 (C-Cl). UV–Vis, λ (nm): 215, 274, 307. ^1H NMR (δ): 3.98 (4H, s, H_2C-CH_2), 6.91–7.29 (6H, m, Ph), 8.32 (2H, s, N = CH), 13.15 (2H, Ph-OH).

H_2L^3 was prepared by the reaction of 2,4-dihydroxybenzaldehyde and ethylenediamine. Yield (> 90%), $C_{16}H_{16}N_2O_4$ (300.31): Calcd. C 63.99, H 5.37, N 9.33. Found C 63.74, H 4.79, N 9.43%. Selected FT-IR data, ν (cm^{-1}): 3416 (O–H), 2869 (C–H), 1638 (C = N), 1468 (C = C), 1229 (C–O). UV–Vis, λ (nm): 221, 253, 326. ^1H NMR (δ): 3.78 (4H, s, H_2C-CH_2), 6.16–7.18 (6H, m, Ph), 8.36 (2H, s, N = CH), 9.20 (2H, Ph-OH),13.68 (2H, Ph-OH).

Also, meso-tetraphenylporphyrin, H_2TPP, *meso*-tetrakis(4-OCH_3phenyl)porphyrin, H_2T(4-OMe)PP and *meso*-tetrakis(2-Clphenyl)porphyrin, H_2T(2-Cl)PP have been prepared according to the Adler *et al.* method[10] by reaction of pyrrole (5.6 ml, 0.08 mole) and benzaldehyde (8 ml, 0.08 mole) in 300 ml refluxing propionic acid. After 30 min, the mixture was filtered and the filtrate was washed thoroughly with methanol and hot water, respectively. The air dried purple crystals, were chromatographed on a neutral alumina column using chloroform as the eluent. H_2TPP. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: −2.71 (2H, br, s, NH), 7.77–7.83 ($8H_m$ and $4H_p$, m), 8.26–8.28 ($8H_o$, dd), 8.90 ($8H_\beta$, s); UV–Vis in CH_2Cl_2, λ_{max}/nm (logε): 416 (5.79), 513 (4.58), 542 (4.38), 584 (4.30), 644 (4.29); H_2T(4-OMeP)P. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: −2.71 (2H, br, s, NH), 4.13 (4H, s, –OMe), 7.30–7.33 ($8H_m$, d), 8.14–8.16 ($8H_o$, d), 8.89 ($8H_\beta$, s); UV–Vis in CH_2Cl_2, λ_{max}/nm (logε): 421 (5.61), 513 (4.32), 555 (4.22), 585 (4.06), 651 (4.11); H_2T(2-ClP)P. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: −2.62 (2H, s, NH), 7.39–7.87 ($8H_m$, $4H_p$, m), 8.10–8.48 ($4H_o$, m), 8.73 (8 H_β, s); UV–Vis in CH_2Cl_2, λ_{max}/nm (logε): 416 (5.64), 511 (4.47), 542 (4.07), 587 (4.15), 653 (3.96).

3.2 | Preparation of metal complexes

3.2.1 | Manganese complexes

Manganese porphyrins were prepared by refluxing $Mn(OAc)_2.4H_2O$ in DMF according to the procedure of Adler *et al.*[11] The progress of reaction was monitored by UV–vis spectroscopy; MnTPP(OAc). Calcd.: C 76.03, H 4.30, N 7.71. Found C 73.17, H 4.11, N 7.10%. UV–Vis (λ_{max}/nm) in CH_2Cl_2: 470 (Soret band), 575, 612; MnT(4-OMeP)P(OAc). Calcd. C 70.92, H 4.64, N 6.62. Found C 67.54, H 4.62, N 6.33%. UV–Vis (λ_{max}/nm) in CH_2Cl_2: 475 (Soret band), 578, 614; MnT(2-ClP)P(OAc). Calcd.: C 63.91, H 3.15, N 6.48. Found C 62.19, H 3.17, N 6.25%. UV–Vis (λ_{max}/nm) in CH_2Cl_2: 471 (Soret band), 574, 603.

The Mn(III)–Salen complexes were prepared by refluxing an ethanolic solution of ligand and manganese(II) acetate tetrahydrate in 1:1 molar ratio for 1 h[12] The solution was cooled in ice-water, filtered and the residue was washed with cold ethanol to obtain the brown crystalline MnL^1(OAc), MnL^2(OAc) and MnL^3(OAc); MnL^1(OAc). Calcd. C 56.85, H 4.51, N 7.37. Found C 56.51, H 3.70, N 7.47%. FT-IR data, ν (cm^{-1}): 3417 (O–H), 2922 (C–H), 1633 (C = N), 1437 (C = C), 1289 (C–O); UV–Vis (λ_{max}/nm) in acetonitrile: 403; MnL^2(OAc). Calcd. C 48.13, H, 3.37, N 6.24. Found C 48.81, H 3.57, N 6.34%. FT-IR data, ν (cm^{-1}): 3417 (O–

H), 2920 (C–H), 1632 (C = N), 1450 (C = C), 1291 (C–O), 810 (C-Cl); UV–Vis (λ_{max}/nm) in acetonitrile/methanol: 407; $MnL^3(OAc)$. Calcd. C 52.44, H 4.16, N 6.79. Found: C 53.46, H 3.76, N 7.34%. FT-IR data, ν (cm^{-1}): 3413 (O–H), 2923 (C–H), 1594 (C = N), 1478 (C = C), 1232 (C–O); UV–vis (λ_{max}/nm) in acetonitrile/methanol: 482.

3.2.2 | Iron complexes

The iron porphyrins were obtained using $FeCl_2.4H_2O$ according to the procedure of of Kobayashi *et al.*[13] The progress of reaction was monitored by UV–Vis spectroscopy; FeTPP(Cl) Calcd. C 75.06; H 4.01; N 7.96. Found C 70.42, H 4.42, N 7.23%. UV–Vis (λ_{max}/nm) in CH_2Cl_2: 378, 413 (Soret band), 509, 574, 662, 690; FeT(2-ClP) P(Cl) Calcd. C 62.78, H 2.87, N 6.66. Found C 60.59, H 3.15, N 6.01%. UV–Vis (λ_{max}/nm) in CH_2Cl_2: 372, 414 (Soret band), 506, 578, 651, 681; FeT(4-OMeP)P(Cl); Calcd.: C 69.95, H 4.40, N 6.80. Found C 64.01, H 4.81, N 6.13%. UV–Vis (λ_{max}/nm) in $CH_2Cl_{2:}$ 421 (Soret band), 511, 572, 698.

The iron complexes of Schiff bases have been prepared according to the literatur.[14] FeL^1 and FeL^2 were prepared by refluxing the corresponding ligands (1 mmol) with $FeCl_3.6H_2O$ (1 mmol) in ethanol (30 ml) in the presence of 5 drops of triethylamine. At the end of the reaction (30 min), the solution was cooled and the solid product was filtered off and dried in air. In the case of FeL^3, 5 ml acetone was used in addition to 30 ml ethanol and the solution was refluxed for 1 h under argon atomosphere. At the end of the reaction, air was bubbled through the solution for 10 min. $FeL^1(Cl)$. Calcd. C 53.74, H 3.95, N 7.83. Found C 48.77, H 3.57, N 8.38%. FT-IR data, ν (cm^{-1}): 3413 (O–H), 2927 (C–H), 1627 (C = N), 1443 (C = C), 1266 (C–O); UV–Vis (λ_{max}/nm) in acetonitrile: 472; $feL^2(Cl)$. Calcd. C 45.06, H 2.84, N 6.57. Found C 44.55, H 2.56, N 7.02%; FT-IR data, ν (cm^{-1}): 3413 (O–H), 2920 (C–H), 1628 (C = N), 1422 (C = C), 1298 (C–O); UV–Vis (λ_{max}/nm) in acetonitrile/methanol: 508; $feL^3(Cl)$. Calcd. C 49.33, H 3.62, N 7.19. Found C 44.82, H 3.96, N 6.52%. FT-IR data, ν (cm^{-1}): 3414 (O–H), 2849 (C–H), 1590 (C = N), 1479 (C = C), 1245 (C–O); UV–vis (λ_{max}/nm) in acetonitrile/methanol: 475.

3.2.3 | Catalytic oxidation of alkenes

Stock solutions of the metalloporphyrins (0.003 M) and ImH (0.5 M) were prepared in acetonitrile. In a typical reaction, alkene (0.25 mmol), metalloporphyrin (0.003 mmol, 1 ml) and ImH (0.03 mmol, 60 μl) were added into a 10 ml round bottom flask containing 1 ml of CH_3CN. Then, 0.5 mmol (0.217 g) TBAP has been added. The mixture was stirred thoroughly for 4 h at room temperature. The molar ratios of catalyst:ImH:alkene: TBAP were 1:10:85:170 and 1:5:85:170 in the presence of manganese[7d, 7j] and iron[7i] porphyrins, respectively. After the required time, diethyl ether was added to the flask and the reaction mixture was passed through a short silicagel column to remove the unreacted tetra-n-butylammonium periodate and the remaining catalyst. In the oxidations with TBAO, catalyst, ImH, olefin and oxidant were used in 1:20:50:150 molar ratios. Also, at the end of the reaction, sodium bisulfite was added to terminate the reaction.

In the case of the Schiff base complexes, 0.01 mmol of the complex was added to 0.5 mmol of alkene in 3 ml acetonitrile. The reaction was initiated by the addition of 1.5 mmol (0.65 g) TBAP. After the required time (4 h), 3 ml diethyl ether was added to the reaction mixture and the mixture was passed through a short alumina column to eliminate the unreacted oxidant and catalyst. The molar ratios of catalyst:alkene:TBAP are 1:50:150.

3.3 | Degradation of catalysts

Degradation of catalysts was followed by UV–vis spectroscopy at their $\lambda_{max.}$[7i, 7j, 8a] The absorbance at the λ_{max} of the catalysts has been compared with that of the initial one to measure the extent of degradation of the metalloporphyrins.

3.3.1 | Instrumental

A Varian-3800 gas chromatograph equipped with a HP-5 capillary column (phenylmethyl siloxane 30 m × 320 μm × 0.25 μm) or a packed column (Chromosorb WHP 80–100 Mesh, 4 mm × ¼ × 2 m) and a flame-ionization detector was used to analyze the reactions. ^1H NMR spectra were obtained on a Bruker Avance DPX-400 MHz spectrometer. The absorption spectra were recorded on a Pharmacia Biotech Ultrospec 4000 UV–Vis spectro photometer.

4 | CONCLUSION

The oxidation of olefins with TBAP and TBAO in the presence of a series of manganese and iron porphyrins and their similar Schiff bases complexes was conducted in acetonitrile at room temperature and found that: (a) the Schiff base complexes showed their optimum catalytic activity at a concentration approximately equal to that of the metalloporphyrins; (b) the Schiff base ligands and complexes may be prepared under milder conditions. Also, the purification of these compounds was more simple than that of the porphyrins and metalloporphyrins;

(c) while the Schiff base complexes were less soluble compared to the metalloporphyrins, the former showed catalytic activities comparable to those of the metalloporphyrin; (d) the results of this study show that in the catalytic oxidation of olefins with TBAP and TBAO, the metalloporphyrins are to some extent (10–30%) more efficient and more stable (ca. 10%) than the Schiff base complexes. However, there is no preference for the metalloporphyrins over the Schiff base complexes and therefore the latter may be successfully used instead of the former for the catalysis of the oxidation reactions.

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