Efficient epoxidation of alkenes with sodium periodate catalyzed by manganese porphyrins in ionic liquid: Investigation of catalyst reusability

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ABSTRACT

In the present work, efficient epoxidation of alkenes with sodium periodate catalyzed by tetraphenylpor-phyrinatomanganese(III) chloride, Mn(TPP)Cl, and octabromotetraphenylporphyrinatomanganese(III) chloride, Mn(Br$_8$TPP)Cl, using (1-n-butyl-3-methylimidazolium tetrafluoroborate), [bmim][BF$_4$], as ionic liquid is reported. The effect of substituted bromines on the catalytic activity and reusability of manganese porphyrins was also investigated.

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Ionic liquids (ILs) consist of ions and are liquid at ambient temperature. These compounds have been typically composed of a heterocyclic cation based on substituted imidazole or pyridine and inorganic anions such as [BF$_4$]$^-$ or [PF$_6$]$^-$ [1–4]. Due to the solubility of a wide range of materials including inorganic, organic and even polymeric materials in ionic liquids, excellent chemical and thermal stability, non-flammability, negligible vapor pressure, high polarity, non-volatility, and non-coordinating nature ILs have found in many applications in chemistry [5–7].

Epoxidation of olefins with single oxygen donors catalyzed by metalloporphyrin catalysts, as models for cytochrome P-450 mono-oxygenases enzymes, has been extensively reported [8–17]. Among the metalloporphyrins, manganese porphyrins have been used as good catalysts for epoxidation of alkenes [18–20]. The most important disadvantages associated with homogeneous metalloporphyrins are their instability toward oxidative degradation and difficulty in recovery of these expensive catalysts, which limit the practical applications of metalloporphyrins in both synthetic chemistry and industrial processes. One way to overcome these problems is their immobilization on solid supports. Previously, we have reported the use of supported manganese(III) porphyrins in the oxidation of organic compounds with NaIO$_4$ [21,22]. Another promising alternative to this strategy is immobilization of these catalysts in room temperature ionic liquids (RTILs) [23].

In this paper, efficient epoxidation of alkenes with sodium periodate catalyzed by tetraphenylporphyrinatomanganese(III) chloride, Mn(TPP)Cl, and octabromotetraphenylporphyrinatomanganese (III) chloride, Mn(Br$_8$TPP)Cl, using (1-n-butyl-3-methylimidazolium tetrafluoroborate), [bmim][BF$_4$], as ionic liquid in 1,2-dichloroethane is reported (Scheme 1).

Tetraphenylporphyrin was prepared and metallated according to the literature [24]. Octabromotetraphenylporphyrin was prepared, brominated and metallated as reported previously [25].

First, the effect of various organic solvents on the epoxidation of cyclooctene with NaIO$_4$ catalyzed by Mn(TPP)Cl was investigated. As can be seen in Table 1, the epoxide yield was low in the presence of IL alone (Table 1, entry 1). This may be due to the high viscosity of the ionic liquid and low solubility of NaIO$_4$ in it. In order to completely dissolve the reactants in [bmim]BF$_4$, it was essential to add a solvent to the reaction mixture. The results showed that 1,2-dichloroethane and dichloromethane are the best solvents. In the absence of IL, only small amount of epoxide was observed. Therefore, all reactions were carried out in a mixture of DCE/IL. When [bmim]PF$_6$ was used the yield was lower than [bmim]BF$_4$. It is reported that hydrolysis can occur in IL systems, leading to the decomposition of ILs and formation of HF [26], which poisons the metalloporphyrin catalysts. The
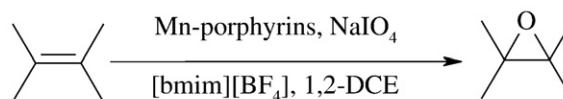
Scheme 1.

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Table 1
Effect of different solvents on the oxidation of cyclooctene with $NaIO_4$ catalyzed by Mn(TPP)Cl[a].

Entry	Solvent	Time (min)	Conversion (%)[b]
1	H_2O/IL	30	30
2	DCE/H_2O/IL	30	100
3	CH_2Cl_2/H_2O/IL	30	98
4	CH_3CN/H_2O/IL	30	76
5	CH_3OH/H_2O/IL	30	70
6	EtOH/H_2O/IL	30	30
7	CCl_4/H_2O/IL	30	10
8	DCE/H_2O/[bmim][PF_6]	30	70
9	DCE/IL(without H_2O)	30	50
10	DCE/H_2O	30	5
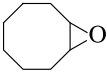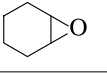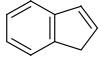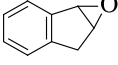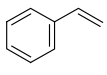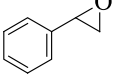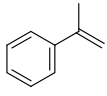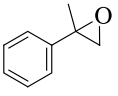
[a] Reaction conditions: cyclooctene (1 mmol), $NaIO_4$ (2 mmol), imidazole (0.1 mmol), catalyst (0.02 mmol).
[b] GC yields.

counter-ion of BF_4^- was preferred in the ILs because of its inertness to hydrolysis compared to PF_6^-. Surprisingly it was found that the presence of water in the catalyst–IL system dramatically enhanced the reaction rate. These results implied that water can accelerate the formation of the active manganese(V)-oxo porphyrin derived from Mn(TPP)Cl in the presence of IL [23,26]. In the case of Mn(Br_8TPP)Cl, similar results were obtained in a 1:5 mixture of [bmim]BF_4/DCE. Under the optimized conditions, different alkenes were epoxidized with $NaIO_4$ in the presence of Mn-porphyrins at room temperature (Table 2) and the corresponding epoxide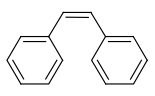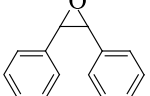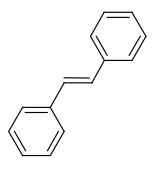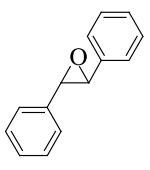s were produced in high yields and excellent selectivities [27]. In the presence of Mn(TPP)Cl, cyclooctene, cyclohexene, indene, styrene and α-methylstyrene were completely converted to their corresponding epoxides with 100% selectivity. Epoxidation of trans-stilbene was preceded in a stereo-specific manner with complete retention of configuration. In contrast, the epoxidation of cis-stilbene was associated with some loss of stereochemistry and affords 88% cis- and 12% trans-stilbene oxides, respectively. Apparently, formation of the thermodynamically more

Table 2
Oxidation of alkenes with a solution of $NaIO_4$ catalyzed by Mn(TPP)Cl (**1**) and Mn(Br_8TPP)Cl (**2**) at room temperature.[a]

Row	Substrate	Product	Time (min)		Conversion[b] (Yield)(%)		TON	
			Mn(TPP)Cl	Mn(Br_8TPP)Cl	Mn(TPP)Cl	Mn(Br_8TPP)Cl	Mn(TPP)Cl	Mn(Br_8TPP)Cl
1			30	30	100 (100)	100 (100)	50	100
2			30	60	100 (100)	98 (83)	50	98
3			30	60	97 (100)	100 (100)	48.5	100
4			30	80	100 (100)	99 (96)	50	99
5			20	60	100 (100)	100 (98)	50	98
6			90	150	100[c](cis-88) (trans-12)	100 (cis-92) (trans-8)	50	100
7			90	180	100[c](100)	100 (100)	50	100

[a]Reaction conditions: alkene (1 mmol), oxidant (2 mmol), imidazole (0.1 mmol), Mn(TPP)Cl (0.02 mmol) or Mn(Br_8TPP)Cl (0.01 mmol), DCE (5 ml), [bmim]BF_4 (1 ml), H_2O (5 ml).
[b]GC yield based on the starting alkene.
[c]Determined by $_1$H NMR spectral data.

Table 3

Comparison of catalytic activity of Mn(TPP)Cl/NaIO$_4$/IL and Mn(Br$_8$TPP)Cl/NaIO$_4$/IL with Mn(TPP)Cl/NaIO$_4$/(n-Bu$_4$NBr) and Mn(TPP)Cl/n-Bu$_4$NIO$_4$.

Alkene	TOF (h^{-1})			
	Mn(Br$_8$TPP)Cl/NaIO$_4$/IL	Mn(TPP)Cl/NaIO$_4$/IL	Mn(TPP)Cl/NaIO$_4$/(n-Bu$_4$NBr)	Mn(TPP)Cl/n-Bu$_4$NIO$_4$
Cyclooctene	200	100	37	14.6
Cyclohexene	98	86.2	26.5	14.5
Styrene	74.43	100	24.4	16.3
α-Methylstyrene	98	151.5	26.3	14.2
trans-Stilbene	33.33	33.3	13	12.5
cis-Stilbene	40	29.3	23.6	13.7
Indene	100	97	26.3	14.6

stable *trans*-stilbene oxide requires a free rotation about the alkene C–C bond at some intermediate steps. Despite of the high catalytic activity of Mn(TPP)Cl in the epoxidation of alkenes at room temperature, the catalyst was not reused even one time. Since, introducing electron-withdrawing substituent on the porphyrin ring increases its robustness toward degradation in the reaction media, therefore, we decided to investigate the catalytic activity of Mn(Br$_8$TPP)Cl epoxidation of alkenes in the presence of [bmim]BF$_4$. The amount of catalyst was optimized in the epoxidation of cyclooctene and the highest yield was obtained with 1 mol% of Mn(Br$_8$TPP)Cl. The results showed that this catalyst has a similar catalytic activity in the epoxidation of alkenes in comparison with Mn(TPP)Cl. The reusability of Mn(Br$_8$TPP)Cl showed that this catalyst retained its catalytic activity during the reaction and was reused three times without significant loss of its catalytic activity.

In order to show the effectiveness of the presented method, the turnover frequencies [28,29] of these two catalytic systems (Mn(TPP)Cl/NaIO$_4$/IL and Mn(Br$_8$TPP)Cl/NaIO$_4$/IL) were compared with our previously reported systems such as Mn(TPP)Cl/NaIO$_4$/(n-Bu$_4$NBr) and Mn(TPP)Cl/n-Bu$_4$NIO$_4$ [30,31]. The results showed that in the presence of [bmim]BF$_4$, the catalytic activity of manganese(III) porphyrins increased (Table 3).

In summary, we have shown an efficient method for the epoxidation of different alkenes with NaIO$_4$ catalyzed by Mn(TPP)Cl and Mn(Br$_8$TPP)Cl in the presence of ionic liquid, [bmim][BF$_4$]. The mild reaction conditions, excellent yield and selectivity of epoxides are the advantages of this method. On the other hand, introducing electron-withdrawing substituents such as bromine increased the catalyst robustness and the catalyst could be recoverable and reusable.

Acknowledgement

References

[1] D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157–189.
[2] T. Welton, Green Chem. 10 (2008) 483.
[3] K. Wilhelm, P. Wasserscheid, Angew. Chem. Int. Ed. 39 (2000) 1772–1789.
[4] M.J. Earle, K.R. Seddon, Pure Appl. Chem. 72 (2000) 1391–1398.
[5] V.I. Parvulescu, C. Hardarcre, Chem. Rev. 107 (2007) 2615–2665.
[6] W.L. Hough, R.D. Rogers, Bull. Chem. Soc. Jpn 12 (2007) 2262–2269.
[7] S. Keskin, D. Kayrak-Talay, U. Akman, O. Hortacsu, J. Supercritical Fluids 43 (2007) 150–180.
[8] J.P. Collman, X. Zhang, V.J. Lee, E.S. Uffelman, J.L. Brauman, Science 261 (1993) 1404–1411.
[9] B. Boitrel, A. Lecas, Z. Renko, E. Rose, New J. Chem. 13 (1989) 73–99.
[10] E. Rose, B. Andrioletti, S. Zrig, M. Quelquejeu-Etheve, Chem. Soc. Rev. 34 (2005) 573–583.
[11] S.E. Creager, S.A. Raybuck, R.W. Murray, J. Am. Chem. Soc. 108 (1986) 4225–4227.
[12] I.G. Denisov, T.M. Makris, S.G. Sligar, I. Schlichting, Chem. Rev. 105 (2005) 2253–2277.
[13] P.D. Goryckit, T.L. Macdonald, Chem. Res. Toxicol. 7 (1994) 745–751.
[14] N.A. Stephenson, A.T. Bell, J. Mol. Catal. A Chem. 275 (2007) 54–62.
[15] B. Meunier, Chem. Rev. 92 (1992) 1411–1456.
[16] J.T. Groves, T.E. Nemo, R.S. Myers, J. Am. Chem. Soc. 101 (1979) 1032–1033.
[17] J.T. Groves, P. Viski, J. Org. Chem. 55 (1990) 3628–3634.
[18] D. Mohajer, Z. Solati, Tetrahedron Lett. 47 (2006) 7007–7010.
[19] M.L. Meriau, S.H. Cho, S.S. Sun, Hupp, Inorg. Chem. 15 (2005) 5523–5529.
[20] A. Kumar, Catal. Commun. 8 (2007) 913–916.
[21] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, A.A. Abbasi-Larki, Appl. Catal. A Gen. 349 (2008) 177–181.
[22] M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, H. Kargar, J. Mol. Catal. A Chem. 288 (2008) 116–124.
[23] Y. Lio, H.J. Zhang, Y. Lu, Y.Q. Cai, X.L. Liu, Green Chem. 9 (2007) 1114–1119.
[24] R.D. Jones, D.A. Summerville, F. Basolo, J. Am. Chem. Soc. 100 (1978) 4416–4424.
[25] P. Bhyrappa, V. Krishnan, Inorg. Chem. 30 (1991) 239–245.
[26] Z. Li, C.G. Xia, J. Mol. Catal. A Chem. 214 (2004) 95–101.
[27] Experimental. All materials were of the commercial reagent grade. Alkenes were obtained from Merck or Fluka. Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. In the GC experiments, n-decane was used as internal standard. ^{1}H-NMR spectra were recorded on a Brucker 400 MHz spectrometer. *General procedure for epoxidation of alkenes* In a 25 mL flask equipped with a magnetic stirring bar, a solution of NaIO$_4$ (2 mmol in 5 ml H$_2$O) was added to a mixture of alkene (1 mmol), Mn(TPP)Cl (0.02 mmol) or Mn(Br$_8$TPP)Cl (0.01 mmol), imidazole (0.1 mmol) and [bmim]BF$_4$ (1 ml) in DCE (5 ml). The mixture was stirred at room temperature. Progress of the reaction was monitored by GC. Since the ionic liquid is immiscible in n-hexane, at the end of the reaction, the organic materials were easily extracted with n-hexane. Evaporation of solvent and chromatography on a short column of silica gel gave the pure product.
[28] J.P. Collman, A. Straumanis, Z. Wang, M. Quelquejeu, E. Rose, J. Am. Chem. Soc. 121 (1999) 460–461.
[29] E. Rose, B. Andrioletti, Q.Z. Ren, Chem. Eur. J. 10 (2004) 224–230.
[30] D. Mohajer, S. Tangestaninejad, Chem. Commun. (1993) 240–241.
[31] D. Mohajer, S. Tangestaninejad, Tetrahedron Lett. 35 (1994) 945–948.