J. Chem. Research (S), 1998, 242–243†

Alkene Epoxidation and Alkane Hydroxylation with Periodate Catalysed by Manganese(III) Porphyrin Supported on Poly(4-vinylpyridine)†

Shahram Tangestaninejad* and **Majid Moghadam**

Department of Chemistry, Esfahan University, Esfahan 81744, Iran

Sulfonated manganese(III) tetraphenylporphyrin supported on poly(4-vinylpyridine), Mn(tpps)–PVP, can act as an efficient heterogeneous catalyst for alkene epoxidation and alkane hydroxylation by sodium periodate.

So far a great variety of metalloporphyrin-based systems for the catalytic oxidation of hydrocarbons using various single-oxygen-atom donors, such as PhIO,[1,2] ClO^-[3,4] and IO_4^-[5,6] have been described. The attachment of metalloporphyrin catalysts to insoluble polymer supports appears to be a good way to render them more practicable and improve their catalytic activity and selectivity.[7–9] In this report we describe a new periodate-heterogenized metalloporphyrin system for alkene epoxidation and alkane hydroxylation.

In the absence of imidazole, the Mn(tpps)–PVP/$NaIO_4$ system is less efficient for oxidation of hydrocarbons [H_2tpps = 5,10,15,20-tetra(sulfonato)phenylporphyrin, PVP = poly(4-vinylpyridine)]. Reactions were performed at room temperature under air in CH_3CN/H_2O medium containing the alkene, oxidant, imidazole and Mn(tpps)–PVP in 1:2:0.2:0.0145 ratio, respectively. This catalytic system led to the epoxidation of various alkenes (Table 1) with good yields (40–95%). In the case of stilbenes, *trans*-stillbene is converted only into the *trans*-epoxide and *cis*-stilbene into a 70:2 mixture of *cis* and *trans*-epoxide. The regioselectivity observed for epoxidation of (*R*)-(+)-limonene with the Mn(tpps)–PVP/$NaIO_4$ system is comparable to that on moderately hindered Mn(tmpp)Cl and Mn(tdcpp)Cl with NaOCl and PhIO or H_2O_2.[10,11] In this case the ratio of 8,9-epoxide to 1,2-epoxide was 0.8:1 in epoxidation on Mn(tpps)–PVP by $NaIO_4$ in the presence of imidazole.

Alkanes were oxidized with $NaIO_4$ by Mn(tpps)–PVP to the corresponding alcohols and ketones only in the presence of imidazole (Table 2). In the absence of the supported metalloporphyrin catalyst, cyclooctene and cyclooctane remained almost unchanged by $NaIO_4$ in CH_3CN/H_2O after 24 h.

Table 1 Epoxidation of alkenes with $NaIO_4$ catalysed by Mn(tpps)–PVP in the presence of imidazole

Alkene	Conversion (%)[a]	Epoxide yield (%)[a]	Reaction time/h
Cyclooctene	100	95	4
Cyclohexene	100	93	4
Styrene	96	75	4
α-Methylstyrene	90	85	4
(+)-Camphene	60	60	4
Oct-1-lene	55	40	8
trans-Stilbene	40	40 (*trans*)	8
cis-Stilbene	72	70 (*cis*)[b] 2 (*trans*)	8
(*R*)-(+)-Limonene	45	25 (1,2-epoxide)[b] 20 (8,9-Epoxide)	3.5

[a]GLC yield based on the starting olefin. [b]Both ^1H NMR and GLC data confirmed the reported yields.

Table 2 Hydroxylation of alkanes with $NaIO_4$ catalysed by Mn(tpps)–PVP in the presence of imidazole; reaction time 8 h

Alkane	Ketone (%)[a]	Alcohol (%)[a]
Cyclooctane	20	36
Ethylbenzene	60	–
Fluorene	25	–
Diphenylmethane	18	–

[a]GLC yield based on the starting alkane.

In conclusion, the Mn(tpps)–PVP/$NaIO_4$ system seems to have some advantages in comparison to the homogeneous Mn(tppcl)/$NaIO_4$ system.[5] The manganese prophyrin remains stable and strongly bonded to poly(4-vinylpyridine) during the reaction and is easily recovered by simple filtration at the end of the reactions. This supported catalyst can be used in other solvents such as acetone–water. The heterogenized metalloporphyrin system has shown a considerable selectivity in oxidation reactions.

Experimental

The porphyrin H_2tpps, was prepared and metallated according to the literature procedures.[12,13] The Mn(tpps) immobilized on cross-linked poly(4-vinylpyridine) (Fluka) was prepared according to the reported procedure[14] [100 mg of Mn(tpps) were immobilized on 500 mg of the resin].

Typical Reaction Procedure.—A 25 cm^3 flask was charged with alkene or alkane (1 mmol), Mn(tpps)–PVP (158 mg), imidazole (0.2 mmol) and CH_3CN (10 cm^3). After addition of sodium periodate solution (2 mmol in 10 cm^3 H_2O), the mixture was stirred by a magnetic stirrer at room temperature for 3.5–8 h. The progress of the reaction was monitored by GLC. The reaction mixture was diluted with CH_2Cl_2 (20 cm^3) and filtered. The resin was thoroughly washed with CH_2Cl_2 and the combined washings and filtrates were purified on silica gel plates or a silica gel column. The identities of the products were confirmed by IR and ^1H NMR spectral data.

Partial support of this work by the Esfahan University Research Council is gratefully acknowledged.

Received, 11th November 1997; Accepted, 18th December 1997
Paper E/7/08106E

References

1 J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 5786.
2 A. J. Appleton, S. Evans and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1996, 281.
3 O. Bortolini and B. Meunier, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1967.
4 B. Meunier, E. Guilmet, M. E. De Carvalho and R. Poilblane, *J. Am. Chem. Soc.*, 1984, **106**, 6668.
5 D. Mohajer and S. Tangestaninejad, *J. Chem. Soc., Chem. Commun.*, 1993, 240.
6 D. Mohajer and S. Tangestaninejad, *Tetrahedron Lett.*, 1994, **35**, 945.

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

7 D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1991, 25.

8 T. Mori, T. Santa and M. Hirobe, *Tetrahedron Lett*., 1985, **26**, 5555.

9 D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1917.

10 N. Mizuno, M. Tateshi, T. O. Hirose and M. Iwamoto, *Chem. Lett*., 1993, 1985.

11 P. Battioni, J. P. Renaud, J. F. Bartoli, M. Reina-Artiles, M. Fort and D. Mansuy, *J. Am. Chem. Soc*., 1988, **110**, 8462.

12 C. A. Busby, R. K. DiNello and D. Dolphin, *Can. J. Chem*., 1975, **53**, 1554.

13 A. Harriman and G. Porter, *J. Chem. Soc., Faraday 2*, 1979, **75**, 1532.

14 S. Campestrini and B. Meunier, *Inorg. Chem*., 1992, **31**, 1999.