Mn-porphyrin Catalyzed Epoxidation of Alkenes with Polyvinylpyrrolidone-Supported H_2O_2

Saeed Zakavi,[*] Azam Abasi, Ali Reza Pourali, and Saeed Rayati[†]

Department of Chemistry, Damghan University of Basic Sciences, Damghan 36716-41167, Iran. [*]E-mail: zakavi@dubs.ac.ir
[†]Department of Chemistry, Faculty of Science, Zanjan University, Zanjan 45195-313, Iran

Received November 5, 2007

Key Words : Epoxidation, Polyvinylpyrrolidone-supported H_2O_2, Mn-porphyrins, Hydrogen bond

In combination with metal catalysts, hydrogen peroxide has been used as a selective oxidant for liquid phase oxidation of organic compounds.[1] In order to avoid the hazards connected with the use of concentrated solution of H_2O_2 and also in the permanent quest for cheap, clean, selective and efficient reagents for the epoxidation of alkenes, two complexes of H_2O_2 with urea (UHP) and DABCO-di-N-oxide have been reported.[2]

The mild oxidizing action of hydrogen peroxide is considerably enhanced in the presence of certain metal oxides, metal Schiff base and metal-porphyrin catalysts. The best known of these reagents is Fenton's reagent, which consists of ferrous and H_2O_2. But the yields of the oxidized substrate are often low, which severely limits the synthetic utility of Fenton's reagent.[3]

Very recently, the efficacy of polyvinylpyrrolidone-supported H_2O_2 (PVP-H_2O_2) in the epoxidation of α,β-enones has been reported. PVP-H_2O_2 is very stable at room temperature and easy to handle. However, the reagent has been shown to have relatively low activity towards electron rich and simple alkenes.[4,5]

In the present work, very mild conditions for the efficient epoxidation of a wide range of acyclic and cyclic alkenes including electron-rich, electron deficient and simple ones with PVP-H_2O_2 in the presence of manganese(III) *meso*-tetraphenylporphyrin, Mn(tpp)X (X = SCN, OCN, Cl, OAc) (Fig. 1) is reported.

The reaction of cyclohexene with PVP-H_2O_2 in the presence of Mn(tpp)SCN in dioxane at room temperature immediately and quantitatively gives cyclohexene oxide as the sole product (Table 1, entry 1). In the absence of Mn(tpp)SCN it has taken up to 24 hrs to reach maximum conversion of 30% under reflux condition.[4]

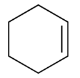
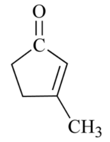
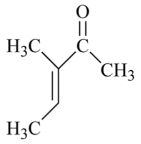
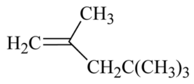
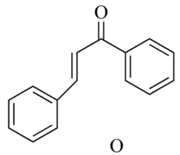
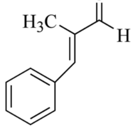
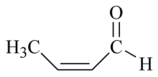
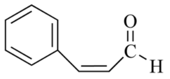
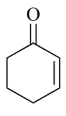
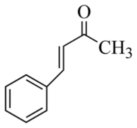
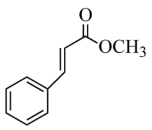
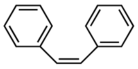
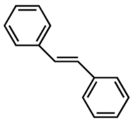
The change of counter-ion from SCN^- to OCN^-, OAc^- and Cl^- had a dramatic effect on the catalytic activity of metalloporphyrin, showing the importance of counter-ion in the course of the reaction. Although Mn(tpp)SCN shows excellent catalytic activity towards the selective epoxidation of cyclohexene, Mn(tpp)Cl and Mn(tpp)OAc exhibit very little or no catalytic activity. Mn(tpp)OCN, on the other hand, demonstrates good catalytic activity towards alkenes epoxidation, giving a conversion of 50% and a selectivity of 100% in 5 minutes. However, replacement of SCN by OCN leads to a substantial decrease in the epoxide yield.

The reaction is also very sensitive to the solvent and the best one for this reaction was found to be dioxane. The addition of imidazole and pyridine to the reaction mixture up to 20 : 1 ratio of nitrogen donor to metalloporphyrin has no observable effect on the reaction rate even in the case of relatively slow reactions (see below).

The Mn(tpp)SCN/PVP-H_2O_2 catalytic system is very efficient for epoxidation of cyclohexene (Table 1). The comparison of cyclohexene (entry 1) and 2-cyclohexen-1-one (entry 9) clearly demonstrates that electron-rich alkenes are more reactive and react more readily with the active oxidant, *i.e.* π-electron withdrawing effects of carbonyl groups probably cause the less reactivity of the latter with respect to the former. Although, the oxygen atom is a σ-acceptor but π-resonance will increase the electron density on reaction center through the oxygen lone pairs. Accordingly, the presence of a methoxy group in methyl cinnamate (entry 11) probably causes the enhanced reactivity of this alkene with respect to benzylideneacetone (entry 10). The decreased reactivity of 2,4,4-trimethyl-1-pentene (entry 4) seems to be due to the steric bulk of *tert*-butyl substituents of the alkene. The comparison of entries 3 and 4 may indicate the dominance of steric factors in epoxidation of compound 4. Interestingly, less hindered alkenes such as 3-methyl-3-pentene-2-one has almost the same reactivity as cyclohexene which again shows the importance of steric factors. The high reactivity of *cis*-crotonaldehyde (entry 7) and cinnamaldehyde (entry 8), in spite of the electron withdrawing effects of carbonyl group, may be due to the *cis* orientation of the substituents in the two compounds which facilitates the approach of the alkene to the active oxidant (also compare *cis*- and *trans*-stilbene). In general, since the alkenes act as nucleophiles attacking the peroxide (or the active oxidant) bond, for structurally simple olefins the rate of epoxidation is enhanced by increasing alkyl substitution. Thus, the scene seems to be entirely dominated by the electron-donating properties of the substituents, while the steric effects of the substituents are not important.

It should be noted that the base-catalyzed epoxidation of alkenes with PVP-H_2O_2 prefers electron-deficient alkenes, *i. e.* α,β-unsaturated carbonyl compounds, to the electron-rich ones, because the rate determining step seems to be the nucleophilic addition of the deprotonated H_2O_2 to the C,C-double bond.[4]

Table 1. Epoxidation of alkenes with H_2O_2-PVP in the presence of Mn(tpp)SCN at room temperature[a]

Entry	alkenes	epoxide Yield (%)[b]	Selectivity (%)	time (min)
1		100	100	5
2		98	100	5
3		100	100	5
4		75	100	5
5		50	100	5
6		70	100	5
7		90	100	5
8		70	100	5
9		60	100	5
10		50	100	5
11		70	100	5
12		80	100	5
13		50	100	5

[a] The molar ratios for Mn(tpp)SCN: substrate: oxidant are 0.02:1:2. [b] The physical properties and the spectra were in agreement with those of authentic samples prepared according to literature procedures.

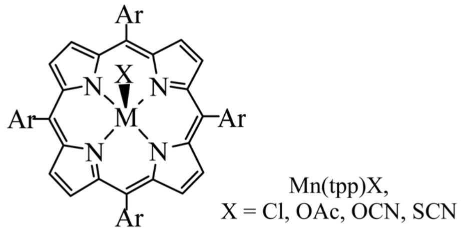


Figure 1. Mn-porphyrin used in this study.

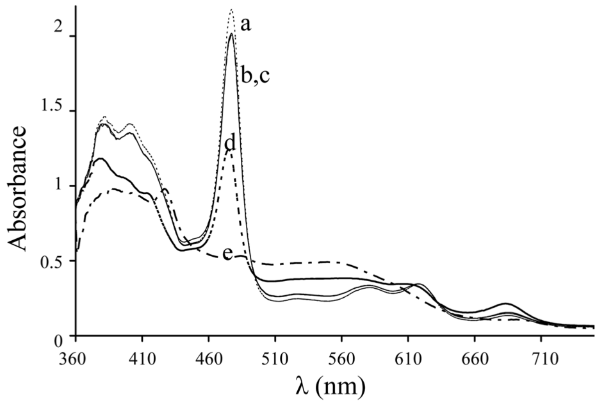


Figure 2. UV-vis spectra of a solution of Mn(tpp)SCN in dioxane (curve a) in the presence of PVP-H_2O_2 at room temperature after 30 minutes (curve b), 1 h (curve c, essentially superimposed to curve b), 3 h (curve d) and 4 h (curve e).

It has been shown that catalyst stability is a major factor contributing to apparent catalyst ability.[6] Figure 2 demonstrates the UV-vis spectra of a solution of Mn(tpp)SCN in dioxane in the presence of PVP-H_2O_2 at different time intervals. It is observed that the metalloporphyrin is quite stable up to *ca*. 60 minutes at room temperature.

It is proposed that in H_2O_2-PVP, hydrogen peroxide is hydrogen bonded to the polymer through the carbonyl groups of PVP and to less extent through the lone pair of sp^2 nitrogen atom and the CH bond adjacent to the nitrogen atom (Figure 3). Similar structure have been proposed for urea-hydrogen bonded complex of H_2O_2, known as UHP.[7]

According to the covalent model of hydrogen bond,[8] formation of strong $\text{-O-H}\cdots\text{O}=\text{C}$ hydrogen bond is associated with the weakening of OH bond due to the shift of electron densities from the oxygen atoms of carbonyl group to the σ^* orbital of OH bond. Also, the formation of $O^{\delta-}$-$H^{\delta+}$ $\cdots O^{\delta-}$ bond causes the proton to be drawn away from the electrons in O-H bond by the electric field of O.[9] This in turn increases the electron densities on oxygen atoms of OO bond and leads to the weakening of the bond and the activation of hydrogen peroxide.

The nature of the active oxidant in this system is not well defined and needs further study but, due to the crucial role played by the nature of counter-ion in this catalytic system it is reasonable to think that the sixth coordination site of manganese atom is occupied by the counter ion in the active oxidant. Consistent with this observation, the addition of imidazole up to 20:1 ratio of imidazole to Mn(tpp)SCN has detectable effect on the reaction rate even in the case of relatively slow reactions. It should be noted that the em-

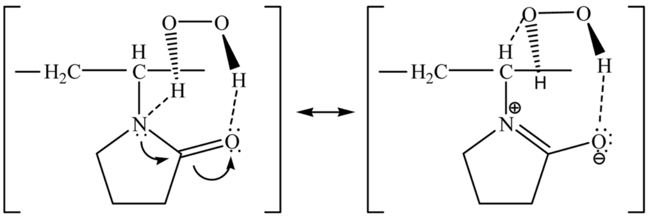


Figure 3. PVP-H_2O_2 complex.

ployment of such nitrogen donors as imidazole and pyridine in metalloporphyrin systems for mimicking the oxygenation function of cytochromes P-450 has led to marked improvements in yields, selectivities and turnover rates in the epoxidation of alkenes.[10] The formation of a five-coordinate metalloporphyrin with a free axial coordination site available for the oxygen atom of oxidant is very common in metalloporphyrin-catalyzed epoxidation of alkenes with different oxidants.[10] However, nitrogen donors showed little or no co-catalytic activity in Mn(tpp)SCN/PVP-H_2O_2 catalytic system which demonstrates that imidazole (or pyridine) has no contribution to the active oxidant *i.e.*, it is not directly attached to the metal centre.

However, the firm attachment of hydrogen peroxide onto the surface of polymer makes it less likely that the epoxidation proceeds through a concerted mechanism, *i.e.* a one-step attachment of the substrate to Mn-porphyrin and the oxygen atom of PVP-supported hydrogen peroxide, instead it is more possible that a Mn-oxo moiety forms prior to the epoxidation reaction. A further study to define the nature of active oxidant is in progress.

Experimental Section

The free base porphyrin and Mn(tpp)X were prepared according to the literature.[11,12] General procedure for the preparation of PVP supported hydrogen peroxide were as described before.[4] Dioxane were dried according to the literature.[13] The progress of reaction was monitored by thin-layer chromatography on commercial Merck precoated TLC plates (silica gel 60 F254) or by GLC on a Plus 6890 A. The capacity of the reagent was determined to be 7.5 mmol of H_2O_2 per gram of the solid reagent. The reagent could be stored in the refrigerator for several months without loss of its weight or activity.

In a typical reaction, PVP-H_2O_2 (0.3 g, equivalent to *ca*. 2 mmol H_2O_2) was added to a solution containing cyclohexene (1 mmol), dry dioxane (5 mL) and Mn(tpp)SCN (0.02 mmol) in a 25 mL round bottom flask. The reaction mixture was stirred at room temperature and the progress of reaction was monitored by TLC and GC.

Acknowledgements. This work was supported by the Damghan University of Basic Sciences and Zanjan University Research Councils.

References

1. Elliott, M. C. *J. Chem. Soc*., *Perkin Trans. 1* **2000**, 1291.
2. Heaney, H. In *Novel Organic Peroxygen Reagents for Use in Organic Synthesis*; Top. Curr. Chem. Series 164: Organic Peroxygen Chemistry; W. A. Herrmann, Ed.; Springer-Verlag: Berlin, **1993**.
3. Sheldon, R.; Kochi, K In *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: NY, 1981.
4. Pourali, A. R.; Ghanei, M. *Bull. Korean Chem. Soc*. **2006**, *27*, 1674.
5. Zolfigol, M. A.; Chehardoli, G.; Shiri, M. *React. Funct. Polym*. **2007**, *67*, 723.
6. Cunningham, I. D.; Danks, T. N.; Hay, J. N.; Hamerton, I.; Gunathilagan, S.; Janczak, C. *J. Mol. Catal. A*: *Chem*. **2002**, *185*, 25.
7. Jones, C. W. In *Applications of Hydrogen Peroxide and Derivatives*; The Royal Society of Chemistry: Cambridge, U.K. 1999.
8. Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, 1977; p 190.
9. Eisenberg, D.; Kauzmann, W. In *The Structure and Properties of Water*; Oxford University Press: Oxford, 1969; p 194.
10. (a) Mohajer, D.; Sadeghian, L. *Journal of Molecular Catalysis A: Chemical* **2007**, *272*, 191. (b) Mohajer, D.; Karimipour, G.; Bagherzadeh, M. *New J. Chem.* **2004**, *28*, 740. (c) Mohajer, D.; Rezaeifard, A. *Tetrahedron Lett.* **2002**, *43*, 1881. (d) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Hampton, P. D.; Naruta, Y.; Michida, T. *Bull. Chem. Soc. Jpn.* **1998**, *61*, 47. (e) Gross, Z.; Ini, S. *J. Org. Chem.* **1997**, *62*, 5514. (f) Naruta, Y.; Maruyama, K. *Tetrahedron Lett.* **1987**, *28*, 4553.
11. Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem*. **1967**, *32*, 476.
12. Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem*. **1970**, *32*, 2443.
13. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. In *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Elmsford, NY, 1980.