A Very Efficient System for Alkene Epoxidation by Hydrogen Peroxide: Catalysis by Manganese-Porphyrins in the Presence of Imidazole

Jean-Paul Renaud, Pierrette Battioni, Jean François Bartoli, and Daniel Mansuy

Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UA 400, Université René Descartes, 45 rue des Saints-Pères, 75270 Paris Cedex 06, France

In the presence of imidazole, Mn- (or Fe-) porphyrins catalyse the epoxidation of various alkenes including alk-1-enes by H_2O_2; with chloromanganese(tetra-2,6-dichlorophenylporphyrin) as a catalyst, alkene conversion by a few equivalents of H_2O_2 is complete within less than 1 h at 20 °C and epoxide yields are very high (90—99%).

Epoxidation of alkenes has been performed by using the single oxygen atom donors iodosylbenzene[1] and hypochlorite[2] as oxidizing agents and simple metalloporphyrins as biomimetic catalysts. However, simple Fe^{III}- or Mn^{III}-porphyrins were found to be unable to catalyse epoxidation of alkenes by alkyl hydroperoxides[3] presumably because they lead to a 'Fenton-like' homolytic cleavage of the alkylhydroperoxide O–O bond[3,4] and not a heterolytic cleavage of this bond which would lead to the epoxidizing $Fe^V=O$ or $Mn^V=O$ species. It was recently reported[5] that, in the presence of catalytic amounts of imidazole, Fe^{III}- or Mn^{III}-(TPP)(Cl) (TPP = tetraphenylporphyrin) catalysed the epoxidation of styrene, cyclohexene, 2-methylhept-2-ene, and stilbene by cumyl hydroperoxide with yields between 20 and 40%. As far as hydrogen peroxide is concerned, there has so far been no report on epoxidizing systems using it as an oxidizing agent and Fe- or Mn-porphyrins as catalysts. Moreover, only a few efficient systems for alkene epoxidation by H_2O_2 catalysed by transition metal complexes have been described so far and, in several cases, the H_2O produced by the reaction inhibits the epoxidation.[6]

We report here that, in the presence of imidazole, Mn- (or Fe-) porphyrins catalyse the epoxidation of alkenes by H_2O_2 and that, by a suitable choice of the Mn-porphyrin and of the reaction conditions, even electron-poor monosubstituted alkenes are epoxidized with almost quantitative conversion of the alkene and very high yields under mild conditions.

Upon slow addition of a mixture of H_2O_2 (30% in H_2O; 5 equiv.) and imidazole (0.5 equiv.) in MeCN within 1 h to a solution of styrene (0.25 M) in MeCN–CH_2Cl_2 (2:1) containing Mn(TPP)(Cl) (6.25 mM) and imidazole (25 mM), 58% conversion of the alkene takes place with the formation of styrene epoxide (45%), benzaldehyde (8%), and 2-phenyl-ethanal (1%) (Table 1) within less than 1.5 h at 20 °C. The Mn-catalyst is completely destroyed at the end of the reaction as shown by the disappearance of the porphyrin peak at

476 nm. Under identical conditions, but with Mn(TMP)(Cl) (TMP = tetramesitylporphyrin) as catalyst, the conversion and yield of styrene epoxide are respectively 83 and 80%. Only traces of benzaldehyde are formed and the Mn-porphyrin is only half-destroyed. By using an Mn-porphyrin more resistant toward oxidation,[7] Mn(TDCPP)(Cl) (TDCPP = tetra-2,6-dichlorophenylporphyrin), styrene conversion is quantitative and high yields (93%) of epoxide are obtained. This Mn-catalyst is unchanged at the end of the reaction and addition of fresh styrene and H_2O_2 to the solution leads to almost identical yields of epoxide. The particular interest of Mn(TDCPP)(Cl) in the catalysis of alkene epoxidation by single oxygen atom donors, PhIO[7a] or ClO^-,[7b] was recently stressed.

It is noteworthy that both the Mn-porphyrin and imidazole are required for efficient epoxidation of styrene. Under identical conditions but in the absence of either, only traces of styrene epoxide are formed (Table 1). Satisfactory epoxide yields are still obtained in the presence of lower amounts of imidazole. For instance, under identical conditions but with 10% imidazole relative to styrene instead of 60%, styrene epoxide is formed in 50% yield.

Similar results are obtained for epoxidation of cyclo-octene by H_2O_2 with the Mn-porphyrin–imidazole system (molar ratios relative to the alkene: 0.025—0.6), the best catalyst again being Mn(TDCPP)(Cl). Upon progressive addition of H_2O_2, almost quantitative conversion of the alkene takes place with 3 equiv. of H_2O_2, the yield of cyclo-octene epoxide being 90% (Table 2). Under similar conditions, the trisubstituted alkene 2-methylhept-2-ene is converted quantitatively into the corresponding epoxide. With 5 equiv. of H_2O_2, cyclohexene is converted in 91% yield into cyclohexene epoxide, allylic oxidation products being formed in very low amounts. In this respect it is remarkable that these H_2O_2-dependent oxidations can be performed with almost identical results in the presence or absence of dioxygen. This is true for

---

Table 1. Epoxidation of styrene by H_2O_2 in the presence of imidazole and various Mn-porphyrins.[a]

Mn-catalyst	Styrene conversion (%)[b]	Styrene epoxide yield (%)[b]	Other products	Final state of Mn-catalyst[c]
Mn(TPP)(Cl)	58	45	PhCHO, 8%; PhCH$_2$CHO, 1%	Destroyed
Mn(TMP)(Cl)	83	80	PhCHO, 1%; PhCH$_2$CHO, 1%	50% Destroyed
Mn(TDCPP)(Cl)	100	93	PhCHO, 1%; PhCH$_2$CHO, 1%	Intact
Mn(TMP)(Cl)[d]	N.d.[f]	1	N.d.	Intact
Mn(TDCPP)(Cl)[d]	N.d.	2.5	N.d.	Intact
None[e]	N.d.	1	N.d.	—

[a] Conditions as given in the text. [b] Based on starting styrene. [c] At the end of the reaction. [d] Identical conditions but without imidazole. [e] Identical conditions but without Mn-porphyrin catalyst. [f] N.d. = not determined.

Table 2. Epoxidation of alkenes by H_2O_2 catalysed by Mn(TDCPP)(Cl) in the presence of imidazole.[a]

Alkene	2-Methylhept-2-ene	Cyclo-octene[b]	Cyclohexene	Styrene	Non-1-ene
Alkene conversion (%)	100	100	100	100	100
Epoxide yield (%)	99	90	91	93	90

[a] Conditions as in Table 1 but with Mn(TDCPP)(Cl) as the only Mn-catalyst. The catalyst was intact at the end of the reaction in all cases.
[b] Conditions as in the text except the use of 3 equiv. of H_2O_2 instead of 5.

all the alkenes indicated in Table 2 but particularly remarkable for cyclohexene which is prone to undergo allylic oxidation by autoxidation in the presence of metalloporphyrins.[8]

The great efficiency of the Mn(TDCPP)(Cl)–imidazole–H_2O_2 system is well illustrated by its ability to epoxidize even the less electron-rich monosubstituted alkenes. With 2 equiv. of H_2O_2, 78% conversion of non-1-ene is obtained with a 74% yield of nonene epoxide. With 5 equiv. of H_2O_2, the conversion of non-1-ene is complete and nonene epoxide is formed in 90% yield within 1 h at 20 °C (Table 2). For all reactions indicated in Table 2, the presence of both Mn(TDCPP)(Cl) and imidazole is required for efficient epoxidation and the Mn-catalyst is unchanged at the end of the reaction. The presence of MeCN as a cosolvent is not necessary since, under identical conditions except for replacement of MeCN by H_2O (two-phase system) or MeOH (single-phase system), good yields of epoxides are also obtained (91 and 85% respectively for 2-methylhept-2-ene and cyclo-octene in MeOH instead of 99 and 90% for these two alkenes in MeCN).

Under identical conditions, Fe(TDCPP)(Cl) also catalyses alkene epoxidation but is less efficient than Mn(TDCPP)(Cl). For instance, the yields of cyclo-octene epoxide upon addition of 3 equiv. of H_2O_2 are 16% with the former and 90% with the latter.

The aforementioned results lead to a very simple system using catalytic amounts of Mn(TDCPP)(Cl) in the presence of imidazole which performs the epoxidation of various alkenes, including monosubstituted ones, by dilute solutions of H_2O_2. With a few equivalents of H_2O_2, the alkene conversion is complete within less than 1 h at room temperature and very good yields of epoxide (90—99%) are obtained. One of the main interests of this epoxidizing system is the formation of H_2O as the only product derived from the oxidizing agent which is thus easily separated from the expected epoxide. Moreover, it does not seem that H_2O has any inhibitory effect toward the epoxidation in that system contrary to what has been reported for other H_2O_2–transition metal complex systems.[6]

References

1 (a) J. T. Groves and T. E. Nemo, J. Am. Chem. Soc., 1983, 105, 5786; (b) J. R. Lindsay Smith and P. R. Sleath, J. Chem. Soc., Perkin Trans. 2, 1982, 1009.
2 B. Meunier, E. Guilmet, M. E. De Carvalho, and R. Poilblanc, J. Am. Chem. Soc., 1984, 106, 6668.
3 D. Mansuy, J. F. Bartoli, and M. Momenteau, Tetrahedron Lett., 1982, 23, 2781.
4 W. A. Lee and T. Bruice, J. Am. Chem. Soc., 1985, 107, 513.
5 D. Mansuy, P. Battioni, and J. P. Renaud, J. Chem. Soc., Chem. Commun., 1984, 1255.
6 R. A. Sheldon and J. K. Kochi, in 'Metal-catalysed Oxidations of Organic Compounds,' Academic Press, New York, 1981, pp. 275—288.
7 (a) P. S. Traylor, D. Dolphin, and T. G. Traylor, J. Chem. Soc., Chem. Commun., 1984, 279; (b) B. de Poorter and B. Meunier, Tetrahedron Lett., 1984, 25, 1895.
8 D. R. Paulson, R. Ullman, and R. B. Sloan, J. Chem. Soc., Chem. Commun., 1974, 186.