

# ROLE OF Mn(TPP)Cl IN THE EPOXIDATION WITH SINGLET OXYGEN

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## Abstract

Mn(TPP)Cl catalyzes cooxidation of olefin in the singlet oxygenation of sulfid. Mn(TPP)Cl is able to transfer an oxygen atom from a peroxidic intermediate generated in singlet oxygenation of sulfide to a metal ion affording metal oxo species which is responsible for epoxidation. This system leads to alkenes epoxidation such as styrene and cyclooctene. Epoxidation of cyclohexene produces cyclohexenol, cyclohexenone and cyclohexene oxide.

## Introduction

The photoxygenation of sulfides is responsible for the loss of activity of several important enzymes which are damaged in photodynamic action [1]. Much attention has been devoted to the structures and reactivities of initially formed reactive intermediates such as persulfoxide, diradical and thiadioxirane intermediates in singlet oxygenation of sulfides [2-13]. To our knowledge, no interaction between a sulfide- oxygen adduct and a metal ion is yet known. Meanwhile, a high valency iron oxo species as an active oxidant in the cytochrome p-450 mediated monooxygenases is thought to be involved in the model systems employing Manganese (III) porphyrin and chemical oxidants such as iodosylarenes [14-16], hypochlorite [17-27], tertiary amine oxides [28-38], and hydroperoxides or percarboxylic acids [31-41].

We report here an example of an oxygen atom transfer from a peroxidic intermediate generated in singlet oxygenation of sulfide to a metal ion affording metal oxo species, which is responsible for epoxidation. However, the Co-oxidation of olefin in the singlet oxygenation of sulfide catalyzed by Fe ( TPEP ) Cl, was reported by Wataru et. al. for the first time [42].

**Keywords :** Singlet oxygenation ; Cooxidation ; Photooxidation ; Porphyrin

## Experimental Section

### Materials

Dichloromethane was distilled from calcium hydride, oxidation substrates (styrene, cyclohexene, cis-cyclooctene, diethyl sulfide) were purchased from Merk Chemical Co.

All substrates were passed through a short column with activity I neutral alumina just prior to use to remove trace oxide contaminates and in the case of styrene to remove inhibitor, H<sub>2</sub>, TPP, Mn (TPP) Cl were prepared by published methods [44-4 ].

### Instrumentation

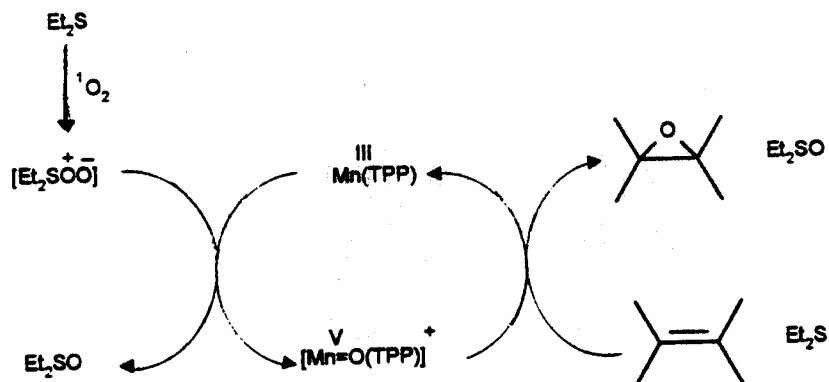
Oxidation products were analyzed on a Perkin Elmer model 8700 GC. Dodecane was used as the internal standard for calculating yields. Product identification was performed by GC-mass spectral analysis.

### Photochemical Reactions

The light source was two 500-w tungsten-halogen lamps. Irradiation was carried out in a pyrex tube in an ice-water bath while oxygen was passed through.

## Results and Discussion

In a typical experiment, a dichloromethane solution of diethyl sulfide ( $8.3 \times 10^{-2}$  M) and cyclohexene (2.3M)



was photoirradiated at 20°C for 8 hours with tetraphenylporphine (TPP,  $5.8 \times 10^{-4}$  M) as a sensitizer under an oxygen flow by employing a small amount of (tetraphenylporphinato)Manganese(III) chloride (Mn(TPP)Cl) as a catalyst. The resulting mixture was subjected to analytical GLC and GC-MS (Table 1). The products were cyclohexene oxide, cyclohexenol, cyclohexenone, diethyl sulfone and diethyl sulfoxide.

Nitrogen Bases effected as cocatalysts, as mentioned above (Table 1), in the presence of imidazole, the yields of products do not increase. We propose that this effect was due to stabilization persulfoxide intermediate

generated in singlet oxygenation of sulfide by hydrogen bonding with imidazole. Its roles as an axial Mn ligand and as a base catalyst are not significant in the formation of  $Mn^V=O$  intermediate. Very similar results were also obtained with cis-cyclooctene and styrene. Since less nucleophilic olefins such as styrene were scarcely (Table 1), the active oxidizing reagent in the epoxidation reaction seems to have an electronic nature. We expect that, like the Mn (porphyrin) /  $H_2O_2$  system [36], the capacity of the Mn catalyst to transfer an oxygen atom to the double bond increased in the following order:

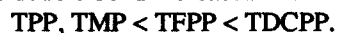


Table 1. Cooxidation of olefin in the potoxidation of Diethyl sulfide in the presence of Mn (TPP) Cl

| time | olefin :Sulfide:porphyrin                   | olefin          | product  | yield,%          | Et <sub>2</sub> S <sup>a</sup> conv, % | catalys <sup>b</sup> turnover |
|------|---|-----------------|--|------------------|--|-------------------------------|
| 8h   | 4603: 162: 1                                | cyclohexenone   | cyclohexene oxide<br>cyclohexenol<br>cyclohexenone | 0.32<br>14<br>18 | 55                                     | 0.3<br>11<br>15               |
| 8h   | 250: 130: 1                                 | cyclohexene     | cyclohexene oxide<br>cyclohexenol<br>cyclohexenone | 0.5<br>37<br>9   | 7.5                                    | 0.4<br>30<br>7                |
| 8h   | 1250: 130: 1;<br>Imidazol: Mn (TPP)<br>1: 1 | cyclohexene     | cyclohexene oxide<br>cyclohexenol<br>cyclohexenone | 0.5<br>34<br>11  | 14.5                                   | 0.4<br>28<br>9                |
| 8h   | 1338: 127: 1                                | cis-cyclooctene | —  | —                | —                                      | —                             |
| 12h  | 285: 11: 1                                  | cis-cyclooctene | cyclooctene oxide                                  | 15               | 28                                     | 17                            |
| 12h  | 298: 11: 1                                  | styrene         | styrene oxide                                      | 0.9              | 39                                     | 0.9                           |

<sup>a</sup>In each case, Et<sub>2</sub>SO and Et<sub>2</sub>SO<sub>2</sub> were also obtained.

<sup>b</sup>Epoxide produced / porphyrin used.

Consequently the primary persulfoxide intermediate is likely to transfer an outer oxygen atom to Mn(TPP) to afford Mn<sup>v</sup> =O (TPP)<sup>+</sup>, which can oxidize olefin and sulfide to epoxide and sulfoxide (Scheme 1).

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