

# Polynuclear manganese complexes catalyzed epoxidation of olefins with molecular oxygen

R. Krishnan, S. Vancheesan\*

*Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India*

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## Abstract

Catalytic epoxidation of olefins with molecular oxygen was studied in the presence of a sacrificial aldehyde using polynuclear manganese complexes of ligands, 2,5-dihydroxyterephthalaldehyde ( $[\text{Mn}^{\text{II}}(\text{dhter})]_n$ ) and its Schiff bases ( $[\text{Mn}_n^{\text{II}}(\text{Pdhteren})]$ ,  $[\text{Mn}_n^{\text{III}}(\text{Pdhteren})(\text{OAc})_n]$  and  $[\text{Mn}_n^{\text{III}}(\text{Pdhterpn})(\text{OAc})_n]$ ) under different reaction conditions. Cyclohexene, cyclooctene, styrene, 1-hexene and 1-pentene were used as substrates for epoxidation. The influence of reaction medium, structure of aldehyde and nature of the ligand environment around catalytic metal center on epoxidation reaction was studied. The manganese(II)–Schiff base complex with nitrogen coordinating environment is more stable and effective epoxidation catalyst than the oxygen bound complex,  $[\text{Mn}^{\text{II}}(\text{dhter})]_n$ . The catalytic system was used under heterogenized homogeneous condition using environmental friendly molecular oxygen as an oxidant. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Schiff base; Polynuclear manganese complexes; Epoxidation; Oxygen; Catalyst

## 1. Introduction

Oxidative functionalization of hydrocarbons into useful organic compounds is of immense interest in the era of transition metal complexes mediated reactions [1,2]. Epoxidation of olefins is a useful reaction that has numerous applications in organic synthesis [3,4].

Over the past three decades transition metal complexes of a variety of ligand systems like porphyrins, Schiff bases, diketones, cyclic amines, bipyridine, etc. have been reported as active catalysts for the catalytic oxygen transfer reactions in the oxidation of hydrocarbons [5–11]. Catalytic oxidation of hydrocarbons have been carried out using a variety of

oxidants such as  $\text{PhIO}$ ,  $\text{NaOCl}$ ,  $\text{H}_2\text{O}_2$ , alkyl hydroperoxides, percarboxylic acids, magnesium monoperoxophthalate and molecular oxygen [12–15]. Among these oxygen donors molecular oxygen is becoming increasingly important oxidant both in industry and academic research. Molecular oxygen as a cheap, environmentally clean and readily available oxidant has received much attention in recent years [16,17]. The increasing interest on using molecular oxygen as oxidant is largely due to the fact that at present time the economical and the environmental impact of chemical productions is under severe scrutiny and chemical companies are facing increasing restrictions to reduce environmental pollution [18].

It is generally recognized that manganese and iron complexes are environmentally less damaging than other transition-metal complexes and such complexes have received considerable attention as biomimetic

\* Corresponding author. Tel.: +91-44-58248;  
fax: +91-44-235-0509.  
E-mail address: vancheesan@hotmail.com (S. Vancheesan).

oxidation catalysts [19,20]. In spite of the great emphasis given to the study of homogeneous catalysts, its heterogenization using organic or inorganic matrices has received much attention. Homogeneous catalysts are often more difficult to handle than heterogeneous catalysts. Industrial processes utilizing soluble transition metal catalysts encounter the problem of recovery of the catalysts from the products. One way of overcoming this problem while retaining the advantages of the transition metal complex catalysts is to anchor the catalyst to an inert organic or inorganic solid supports [21–25]. However, in the polymer-supported catalytic systems, the number of active metal sites usually less, which often limits their catalytic behavior. This limitation could be minimized by the use of suitable polynuclear metal complexes with large number of active metal centers [26,27]. There is much interest in the preparation and characterization of multinuclear manganese complexes as models for the structural and functional properties of the biological enzymes [28–30].

Herein we report the epoxidation of olefins with environmentally friendly and cheap molecular oxygen catalyzed by polynuclear manganese catalysts derived from 2,5-dihydroxyterephthalaldehyde and its Schiff base polymers under mild conditions.

## 2. Experimental

All the solvents were obtained in reagent grade and purified according to the standard literature procedure. The 2,5-dihydroxyterephthalaldehyde (dhterH<sub>2</sub>, L), and its Schiff base polymeric ligands, PdhterenH<sub>2</sub> (PL<sub>1</sub>) and PdhterpnH<sub>2</sub> (PL<sub>2</sub>), respectively, obtained from ethylene diamine (en) and propylene diamine (pn), were prepared as reported procedures [31,32]. The manganese complexes [Mn<sup>III</sup>(Pdhteren)(OAc)<sub>n</sub>] (Mn<sup>III</sup>PL<sub>1</sub>), [Mn<sup>III</sup>(Pdhterpn)(OAc)<sub>n</sub>] (Mn<sup>III</sup>PL<sub>2</sub>), [Mn<sup>II</sup>(Pdhteren)] (Mn<sup>II</sup>PL<sub>1</sub>) and [Mn<sup>II</sup>(dhter)]<sub>n</sub> (Mn<sup>II</sup>L) were prepared as reported earlier [33,34]. Cyclohexene, cyclooctene, styrene, 1-hexene and 1-pentene were distilled before use under N<sub>2</sub> atmosphere. The reaction products were analyzed on a Nucon model 5765 gas chromatograph using dodecane as an internal standard. OV 17 column was employed with a flame ionization detector. WinAcids 5.0 software was used for data processing.

### 2.1. Measurement of oxygen uptake

The uptake of molecular oxygen gas was measured in a gas burette connected to the Schlenk lined reaction system. The oxygen absorptions were measured by determining the volume of gaseous dioxygen taken up by the catalyst (20 mg) in dichloroethane (5 ml) in the presence of cyclohexene (10 mmol) and butyraldehyde (10 mmol).

### 2.2. Epoxidation of olefins

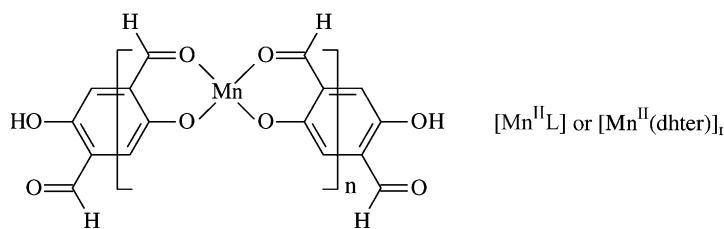
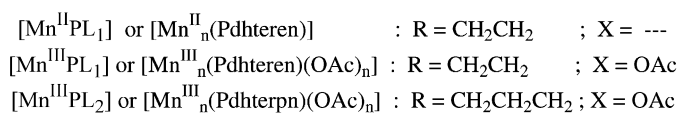
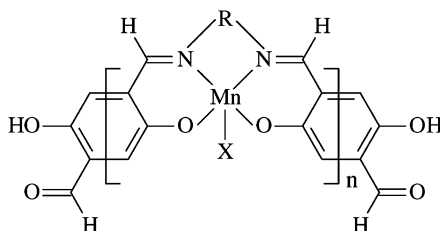
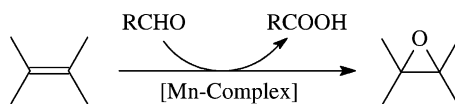
The epoxidation reactions were carried out as follows: oxygen gas was bubbled into a reaction mixture containing olefin (10 mmol), aldehyde (20 mmol) and the catalyst (30 mg) in an organic solvent (10 ml). The reactions were carried out for 12 h at room temperature. The products were filtered and analyzed by using GC.

## 3. Results and discussion

Epoxidation of olefins with molecular oxygen catalyzed by polynuclear manganese complexes were studied in the presence of an aldehyde under heterogenized homogeneous condition. The manganese complexes used as catalysts are given in Scheme 1.

### 3.1. Oxygen uptake

A systematic preliminary study was carried out to evaluate the activity of polynuclear manganese complexes towards the activation of molecular oxygen by monitoring the oxygen absorption by manganese catalysts in the presence of cyclohexene (10 mmol) and butyraldehyde (10 mmol) in dichloroethane (DCE). Fig. 1 depicts the time course of oxygen uptake by manganese complexes, [Mn<sup>III</sup>PL<sub>1</sub>], [Mn<sup>III</sup>PL<sub>2</sub>], [Mn<sup>II</sup>PL<sub>1</sub>] and [Mn<sup>II</sup>L]. The manganese(III)–Schiff base complexes [Mn<sup>III</sup>PL<sub>1</sub>] and [Mn<sup>III</sup>PL<sub>2</sub>], respectively, absorbed 8.3 and 7.5 ml of molecular oxygen gas in 12 h. Thus, the manganese(III)-complex, [Mn<sup>III</sup>PL<sub>1</sub>], which was derived from ethylene diamine bridged Schiff base ligand is more active than the corresponding propylene diamine bridged



Scheme 1.

Schiff base complex,  $[\text{Mn}^{\text{III}}\text{PL}_2]$ . The  $[\text{Mn}^{\text{II}}\text{PL}_1]$  absorbed 18.4 ml of oxygen in 12 h. The activity of the manganese(II)–Schiff base complex is higher than the analogous manganese(III)-complex. The higher activity of manganese(II)-complex than the corresponding manganese(III)-complex is most possibly due to the availability of the vacant coordination site for oxygen activation. The oxidative addition of activated oxygen in the presence of aldehyde at the metal center could also be the reason for greater activity of the manganese(II)-complex,  $[\text{Mn}^{\text{II}}\text{PL}_1]$  than manganese(III)-complex,  $[\text{Mn}^{\text{III}}\text{PL}_1]$  under identical Schiff base ligand environment [35,36]. Under identical reaction conditions the complex  $[\text{Mn}^{\text{II}}\text{L}]$  absorbed 13.6 ml of oxygen. Thus, manganese(II)-complex derived from Schiff base polymer ligand is more active than that derived from oxygen coordinating bridging ligand.

### 3.2. Effect of manganese complexes on epoxidation of cyclohexene

Epoxidation of cyclohexene was studied in the presence of various manganese complexes. Table 1 shows the results obtained for epoxidation of cyclohexene with molecular oxygen catalyzed by various

Table 1  
Cyclohexene epoxidation with molecular oxygen catalyzed by manganese complexes in the presence of butyraldehyde<sup>a</sup>

Run	Catalyst	Conversion (%)	Selectivity (%)
1	$[\text{Mn}^{\text{III}}\text{PL}_1]$	50	88
2	$[\text{Mn}^{\text{III}}\text{PL}_2]$	46	90
3	$[\text{Mn}^{\text{II}}\text{PL}_1]$	63	91
4	$[\text{Mn}^{\text{II}}\text{L}]$	64	90

<sup>a</sup> Cyclohexene (10 mmol), butyraldehyde (20 mmol), catalyst (30 mg) in dichloroethane (10 ml) under oxygen atmosphere for 12 h.

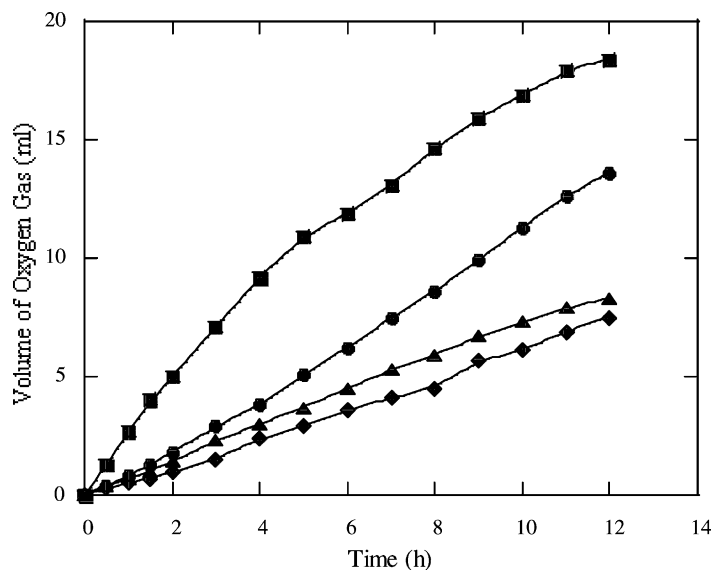


Fig. 1. Time course of oxygen uptaken by cyclohexene (10 mmol), butyraldehyde (10 mmol) in dichloroethane catalyzed by (●), [Mn<sup>II</sup>L]; (■), [Mn<sup>II</sup>PL<sub>1</sub>]; (▲), [Mn<sup>III</sup>PL<sub>1</sub>] and (◆), [Mn<sup>III</sup>PL<sub>2</sub>] at 25 °C.

polynuclear manganese complexes in the presence of butyraldehyde. The reactions were carried out as follows: oxygen gas was bubbled into a reaction mixture containing cyclohexene (10 mmol), butyraldehyde (20 mmol) and catalyst (30 mg) in 10 ml of DCE at room temperature for 12 h. The manganese(III)–Schiff base complexes, [Mn<sup>III</sup>PL<sub>1</sub>] and [Mn<sup>III</sup>PL<sub>2</sub>] gave 50 and 46% of cyclohexene conversions with 88 and 90% of epoxide selectivity, respectively, in 12 h. Under identical reaction conditions manganese(II)–Schiff base complex [Mn<sup>II</sup>PL<sub>1</sub>] gave 63% of cyclohexene conversion with 91% selectivity towards epoxidation product. Thus, manganese(II)-complex is better catalyst for epoxidation of olefins than the corresponding manganese(III)-complex under these reaction conditions. The oxygen coordinated manganese complex, [Mn<sup>II</sup>L], which was derived from 2,5-dihydroxyterephthalaldehyde bridging ligand gave 64% conversions of cyclohexene with 90% selectivity towards cyclohexene epoxidation. However, the catalyst was unstable under this reaction condition and the activity of catalyst, [Mn<sup>II</sup>L] was lost after a single run. Therefore, manganese(II)–Schiff base complex, [Mn<sup>II</sup>PL<sub>1</sub>] was used for further studies due to its higher activity than the other manganese catalysts prepared.

### 3.3. Solvent effect

Cyclohexene epoxidation with O<sub>2</sub> catalyzed by manganese complex, [Mn<sup>II</sup>PL<sub>1</sub>] in the presence of butyraldehyde was taken as a model system to study the influence of the solvent on catalytic activity. Epoxidation was carried out in different solvents. The results are shown in Table 2. Oxidation of cyclohexene in coordinating solvents such as methanol and acetonitrile gave 49 and 52% conversions, respectively, with 89 and 90% of epoxide selectivity in 12 h. The catalytic activity was found to increase when epoxidation reactions were performed in non-coordinating solvents. Reactions in CH<sub>2</sub>Cl<sub>2</sub> and dichloroethane gave, respectively, 56 and 63% of cyclohexene conversion

Table 2  
Effect of solvent on epoxidation of cyclohexene with O<sub>2</sub> catalyzed by [Mn<sup>II</sup>PL<sub>1</sub>] in the presence of butyraldehyde<sup>a</sup>

Run	Solvent	Conversion (%)	Selectivity (%)
1	CH <sub>2</sub> Cl <sub>2</sub>	56	85
2	CH <sub>3</sub> OH	49	89
3	CH <sub>3</sub> CN	52	90
4	CICH <sub>2</sub> CH <sub>2</sub> Cl	63	91

<sup>a</sup> Cyclohexene (10 mmol), butyraldehyde (20 mmol), catalyst (30 mg) in solvent (10 ml) under oxygen atmosphere for 12 h.

Table 3  
Effect of aldehyde structure on epoxidation of cyclohexene with O<sub>2</sub> in dichloroethane catalyzed by [Mn<sup>II</sup>PL<sub>1</sub>]<sup>a</sup>

Run	Aldehyde	Conversion (%)	Selectivity (%)
1	Acetaldehyde	40	83
2	Propanaldehyde	58	85
3	Butyraldehyde	63	91
4	<i>iso</i> -Butyraldehyde	69	93
5	Pivalaldehyde	74	95

<sup>a</sup> Cyclohexene (10 mmol), aldehyde (20 mmol), catalyst (30 mg) in dichloroethane (10 ml) under oxygen atmosphere for 12 h.

with selectivity of 85 and 91% towards epoxidation reaction. The lower activity and epoxidation selectivity in dichloromethane than in dichloroethane suggests the radical nature of the molecular oxygen activation [37].

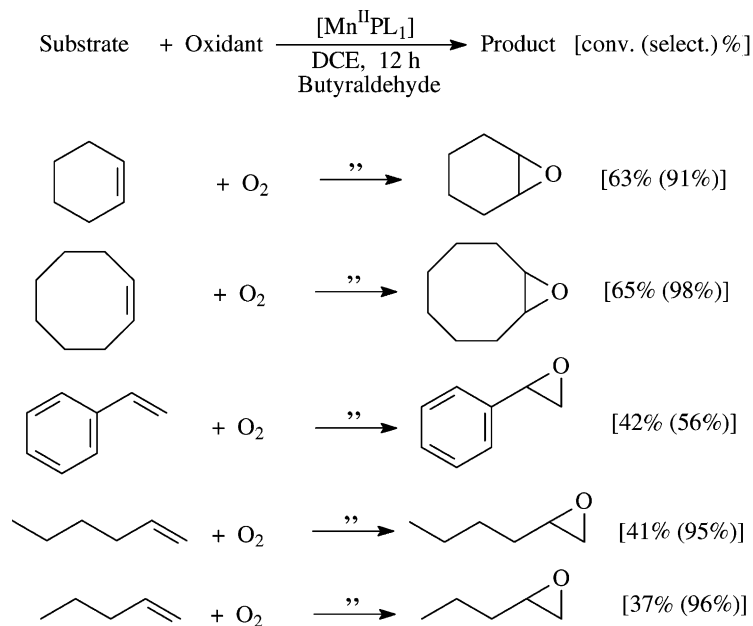
### 3.4. Effect of aldehyde structure on epoxidation

Influence of the structure of the aldehyde on epoxidation of cyclohexene with O<sub>2</sub> catalyzed by manganese complex, [Mn<sup>II</sup>PL<sub>1</sub>] in dichloroethane was studied. The results are shown in Table 3. Various aliphatic aldehydes were used as a sacrificial reductant

for activation of dioxygen toward epoxidation of cyclohexene catalyzed by a manganese complex, [Mn<sup>II</sup>PL<sub>1</sub>]. Linear aliphatic aldehydes, namely, acetaldehyde, propanaldehyde and *n*-butyraldehyde gave 40, 58 and 63% conversions of cyclohexene with 83, 85 and 91% of selectivity towards epoxidation. Thus, by using longer chain aldehydes the epoxidation could be increased. Upon using aldehydes with alkyl substitutions adjacent to the carbonyl carbon, the activity was increased remarkably. Cyclohexene (10 mmol) epoxidation with dioxygen catalyzed by [Mn<sup>II</sup>PL<sub>1</sub>] in dichloroethane in the presence of *iso*-butyraldehyde and pivalaldehyde gave 69 and 74% conversions of cyclohexene, respectively, with 93 and 95% of epoxidation selectivities. The remarkable structural effect of aldehyde on epoxidation with O<sub>2</sub> suggests the direct involvement of the aldehyde on dioxygen activation for the epoxidation of olefins.

### 3.5. Epoxidation of olefins with molecular oxygen

Epoxidation of various olefins with dioxygen catalyzed by manganese complexes in the presence of aldehyde was studied. Scheme 2 shows the results of epoxidation of various olefins by dioxygen,



Scheme 2.

catalyzed by  $[Mn^{II}PL_1]$  in the presence of butyraldehyde as a cocatalyst. The reactions were carried out in dichloroethane medium at room temperature for 12 h. Cyclic olefins such as cyclohexene and cyclooctene showed 63 and 65% conversions of olefin with 91 and 98% of selectivity towards corresponding epoxides, cyclohexene oxide and cyclooctene oxide, respectively. Styrene showed 42% of olefin conversion with 56% of styrene oxide, 29% of benzaldehyde and 13% of phenylacetaldehyde formation. The benzaldehyde and phenylacetaldehyde are the side products in the epoxidation of styrene. Benzaldehyde is the side product formed by olefinic double bond cleavage in styrene oxidation.  $PhCH_2CHO$  is the rearrangement product in styrene oxidation catalyzed by a manganese complex [38].

The terminal olefins like 1-hexene and 1-pentene gave 41 and 37% conversions of olefins, respectively. Cyclic olefins are more active than the terminal olefins. Thus, electron rich olefins are more active than the terminal olefins towards epoxidation. Hence, the oxygen transfer intermediate process should be electrophilic in nature [39]. This suggests the involvement of high valent oxo-manganese intermediate in oxygen transfer process under these conditions [40].

Epoxidation of alkenes with oxygen catalyzed by manganese complex,  $[Mn^{II}PL_1]$  in dichloroethane in the presence of pivalaldehyde as a sacrificial reductant was studied. The results are shown in Table 4. Various olefins were smoothly epoxidized under this condition. Cyclohexene, cyclooctene, styrene, 1-hexene and 1-pentene gave 74, 75, 49, 48 and 40% conversions of olefin, respectively, in 12 h at room temperature. Thus, in all substrates studied, the catalytic epoxidation by

Table 4  
Epoxidation of olefins with  $O_2$  catalyzed by  $[Mn^{II}PL_1]$  in the presence of pivalaldehyde<sup>a</sup>

Run	Olefin	Conversion (%)	Selectivity (%)
1	Cyclohexene	74	95
2	Cyclooctene	75	97
3	Styrene	49	63 (epoxide), 25 (PhCHO) and 10 (PhCH <sub>2</sub> CHO)
4	1-Hexene	48	98
5	1-Pentene	40	97

<sup>a</sup> Olefin (10 mmol), pivalaldehyde (20 mmol), catalyst (30 mg) in dichloroethane (10 ml) under oxygen atmosphere for 12 h.

manganese complex,  $[Mn^{II}PL_1]$  was found to increase when pivalaldehyde was used as a sacrificial reductant in place of butyraldehyde.

### 3.6. Effect of concentration of aldehyde on epoxidation

The effect of aldehyde to olefin ratio on epoxidation with dioxygen catalyzed by a manganese complex was studied. Cyclohexene epoxidation with dioxygen catalyzed by manganese complex,  $[Mn^{II}PL_1]$  in the presence of butyraldehyde was taken as a model reaction. In a typical reaction, oxygen gas was bubbled into a mixture containing cyclohexene (10 mmol) and catalyst (30 mg) in 10 ml of dichloroethane in the presence of butyraldehyde. The butyraldehyde concentration was varied from 0 to 70 mmol. The reactions were carried out at room temperature and the products were analyzed after 12 h reaction. The results are shown in Fig. 2. In the absence of butyraldehyde no epoxidation was observed. In the presence of 10 mmol of butyraldehyde 40% of cyclohexene conversion was observed in 12 h. Upon increasing the ratio of butyraldehyde to cyclohexene, the olefin conversion was found to increase. At  $[butyraldehyde]/[cyclohexene] = 7$ , the conversion of cyclohexene was 100%. However, a decrease in epoxidation selectivity is observed upon increasing the concentration of aldehyde.

### 3.7. Effect of catalyst structure on epoxidation of styrene

Epoxidation of styrene with dioxygen catalyzed by various manganese complexes in the presence of butyraldehyde was studied. The reactions were carried out by passing  $O_2$  into a reaction mixture containing styrene (10 mmol), butyraldehyde (20 mmol) and catalyst (30 mg) in 10 ml of dichloroethane with stirring for 12 h at room temperature. The manganese  $[Mn^{III}PL_1]$ ,  $[Mn^{III}PL_2]$ ,  $[Mn^{II}PL_1]$  and  $[Mn^{II}L]$  gave 33, 31, 42 and 38% conversion of styrene, respectively (Table 5). Three products, namely, styrene oxide, benzaldehyde and phenylacetaldehyde were formed by the aerobic epoxidation of styrene in this process (Scheme 3). Different manganese complexes showed different selectivities under identical reaction conditions. This suggests the direct involvement of the manganese complexes in the oxygen transfer step.

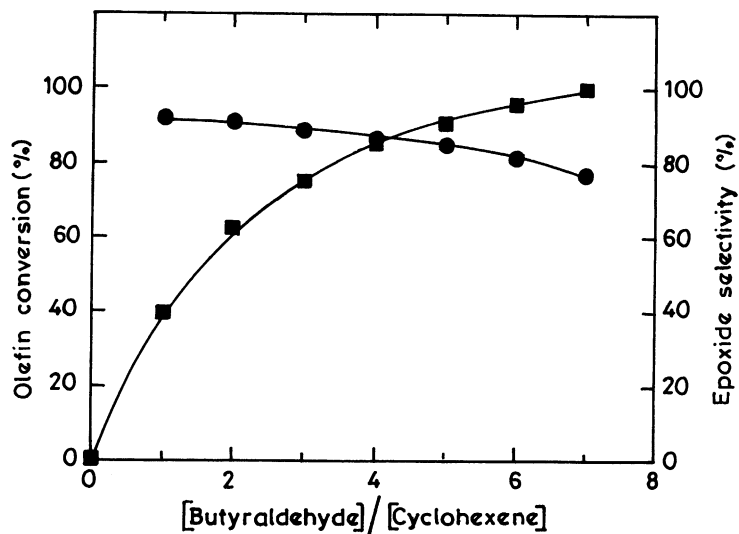


Fig. 2. Effect of butyraldehyde concentration on oxidation of cyclohexene with  $O_2$  catalyzed by  $[Mn^{II}PL_1]$  in dichloroethane at  $25^\circ C$  for 12 h.

Table 5

Effect of catalyst structure on epoxidation of styrene with  $O_2$  in the presence of butyraldehyde<sup>a</sup>

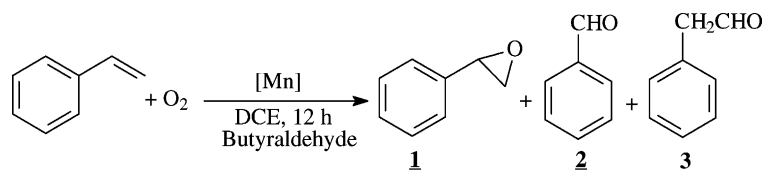
Catalyst	Conversion (%)	Selectivity (%)		
		1	2	3
$[Mn^{III}PL_1]$	33	64	28	8
$[Mn^{III}PL_2]$	31	61	27	12
$[Mn^{II}PL_1]$	42	56	29	13
$[Mn^{II}L]$	38	68	25	7

<sup>a</sup> Styrene (10 mmol), butyraldehyde (20 mmol), catalyst (30 mg) in dichloroethane (10 ml) under oxygen atmosphere for 12 h. 1-Styrene oxide, 2-benzaldehyde and 3-phenylacetaldehyde.

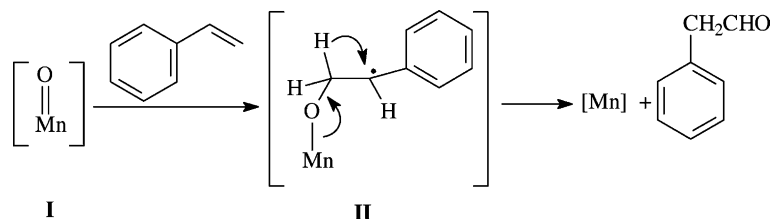
Ethylene diamine bridged manganese(III)–Schiff base complex,  $[Mn^{III}PL_1]$  gave styrene oxide, benzaldehyde and phenylacetaldehyde with selectivity of 64, 28 and 8%, respectively. However, under identical reaction conditions propylene diamine bridged manganese(III)–Schiff base complex,  $[Mn^{III}PL_2]$

showed 61, 27 and 12% selectivity towards styrene oxide, benzaldehyde and phenylacetaldehyde, respectively. Phenylacetaldehyde is a rearrangement side product formed during epoxidation of styrene [41]. Oxygen transfer from high-valent manganese intermediate species to styrene is as shown in Scheme 4. If the ligand environment were sterically favorable around the active metal center,  $PhCH_2CHO$  formation would be more facile than in a sterically restricted environment. Such a situation is favorable for the intermediate II to rearrange. Therefore, the phenylacetaldehyde selectivity is more in the long chain propylene diamine bridged Schiff base complex,  $[Mn^{III}PL_2]$  than the ethylene diamine bridged Schiff base complex  $[Mn^{III}PL_1]$ .

Manganese(II)–Schiff base complex,  $[Mn^{II}PL_1]$  gave 42% conversion of styrene and the products selectivity for styrene oxide, benzaldehyde and phenylacetaldehyde are 56, 29 and 13%, respectively. In the



Scheme 3.



Scheme 4.

styrene oxidation reactions, the  $[\text{Mn}^{\text{III}}\text{PL}_2]$  showed better selectivity towards styrene oxide formation than the  $[\text{Mn}^{\text{II}}\text{PL}_1]$ . This could be attributed to electronic factors. The presence of coordinated axial ligand in manganese(III)-complex facilitates the flow of electron from manganese-oxo intermediate to the olefin and ring closure to form epoxide is more favorable than a rearrangement. Hence, manganese(III)-complex is more selective towards epoxidation than the analogous manganese(II)-complex.

Oxygen coordinated manganese complex,  $[\text{Mn}^{\text{II}}\text{L}]$  gave 38% conversion of styrene. The product selectivity for styrene epoxide, benzaldehyde and phenylacetaldehyde are 68, 25 and 7%, respectively. Epoxide selectivity is high in oxygen coordinating manganese complex,  $[\text{Mn}^{\text{II}}\text{L}]$  than in the nitrogen-coordinating manganese–Schiff base complexes. The phenylacetaldehyde formation is less in  $[\text{Mn}^{\text{II}}\text{L}]$  catalyzed oxidation of styrene. Higher oxidation state intermediate is less stable in oxygen donor complex than in the strong nitrogen donor complexes. Hence, the rearrangement of the intermediate species is less favored and phenylacetaldehyde formation is less.

#### 4. Conclusions

Aerobic epoxidation of olefins catalyzed by polynuclear manganese complexes in the presence of a sacrificial aldehyde were studied under heterogeneous homogeneous condition. Oxygen uptake measurements showed that manganese(II)–Schiff base complex is more active than the corresponding manganese(III) complex under this reaction condition. This oxidation system is more efficient in the non-coordinating solvent like dichloroethane. Effective epoxidation of cyclohexene, cyclooctene, styrene,

1-hexene and 1-pentene is achieved. Cyclic olefins are more reactive than the terminal olefins under this condition. Oxidation of styrene gave three products, namely, styrene oxide, benzaldehyde and phenylacetaldehyde. Manganese complexes under different ligand environment showed different selectivities in the oxidation of styrene. These observations suggest the direct involvement of the metal complex in oxygen transfer reaction. Epoxidation of olefins catalyzed by solid polynuclear manganese complexes using molecular oxygen is an environmental friendly process.

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