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Synthesis, characterization and catalytic activity of polynuclear manganese complexes of 2,5-dihydroxyterephthalaldehyde for epoxidation of olefins with H_2O_2

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Abstract

Polynuclear manganese complexes of 2,5-dihydroxyterephthalaldehyde (dhterH_2) and its Schiff base polymer ligand (PdhterenH$_2$) [Mn^{II}(dhter)]$_n$, [Mn^{II}_n(Pdhteren)] and [Mn^{III}_n(Pdhteren)(OAc)$_n$] were synthesized. The manganese complexes were characterized by elemental analysis, thermal analysis, IR and EPR spectroscopic techniques. Catalytic epoxidation of olefins with hydrogen peroxide was studied using the above manganese complexes under heterogenized homogeneous reaction conditions in the presence of a base. The effect of imidazole and olefin concentrations on effective oxygen transfer were studied. [Mn^{II}_n(Pdhteren)] and [Mn^{III}_n(Pdhteren)(OAc)$_n$] are more efficient than the oxygen-bonded manganese complex [Mn^{II}(dhter)]$_n$ for the activation of hydrogen peroxide.

Keywords: Polynuclear manganese complexes; Schiff base; Catalyst; Epoxidation; Hydrogen peroxide

1. Introduction

Hydrogen peroxide is notably a very good oxidizing agent in being cheap and readily available. In addition, products cause no pollution problems. The direct synthetic application of hydrogen peroxide is, however, limited mainly to the epoxidation of active alkenes. This mild activity is significantly enhanced by the addition of various metal catalysts [1]. Oxidation of hydrocarbons is of immense interest in the era of transition metal complexes mediated reactions, under milder reaction condition. Two main oxidation reactions viz. epoxidation and hydroxylation have been reported using hydrogen peroxide as source of oxygen atom and a transition metal complex as catalyst. The epoxidation of olefins is a useful reaction that has numerous applications in organic synthesis [2].

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 oxidation catalysts.

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Manganese is involved in many biological processes; in particular, it is the active site of several enzymes [3]. In order to mimic these enzymes, many manganese complexes containing porphyrin, phthalocyanin, triazamacrocycle and Schiff base ligands have been synthesized and studied in connection with oxidation state [4–8], coordination number [9] and number of manganese sites present in these biological catalysts [10].

Inspite 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 catalyst 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 [11–13]. However, in the polymer-supported catalytic systems, the number of active metal sites are less, which limits their catalytic behaviour. This limitation could be minimized by the use of suitable polynuclear metal complexes with large number of active metal centres [14].

Recently, much attention has been paid to transition metals as possible units for new polymers [15]. There is much interest in the preparation and characterization of multinuclear manganese complexes as models for the structural, spectral and functional properties of the biological enzymes [16–18].

In this study preparation, characterization and catalytic activity of polynuclear manganese complexes of 2,5-dihydroxyterepthalaldehyde (dhterH_2) and its Schiff base have been studied.

2. Experiment

dhterH_2 was prepared as reported [19]. Commercial sample of ethylene diamine was distilled under N_2 atmosphere before use. Schiff base polymer PdhterenH_2 (**PL**) was prepared as reported with some modification [20]. Polynuclear manganese(III) Schiff base complex, [Mn^{III}_n(Pdhteren)$(OAc)_n$] was prepared from $Mn(OAc)_3 \cdot 2H_2O$ and **PL** in ethanol [21]. Hydrogen peroxide was 30% solution. Infrared spectra were recorded on a Bruker IFS 66V FT-IR, electron paramagnetic spectra were recorded on Varian E-112 spectrometer and thermal analysis on Delta series TGA-7. Cyclohexene, cyclooctene, styrene, 1-hexene and 1-pentene were distilled before use. 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. WinAcds 5.0 software was used for data processing.

2.1. Preparation of manganese(II) Schiff base complex, [Mn^{II}_n(Pdhteren)]

Schiff base polymer, PdhterenH_2 (500 mg) was suspended in distilled water (20 ml). NaOH (210 mg) in 10 ml water was added. When the suspension was stirred at room temperature for 5 min, a violet solution was obtained. $MnCl_2 \cdot 4H_2O$ (520 mg) in 15 ml water was added to the violet solution. The reaction mixture was stirred at room temperature for 2 h. A reddish brown manganese complex, **[Mn^{II}_n(Pdhteren)]**, formed was filtered, washed with water and dried under vacuum. Yield = 626 mg (98%). Elemental analysis (Found, %): C, 49.63; H, 3.29; N, 11.16 and Mn, 2185.

2.2. Preparation of polymeric manganese(II)-dhterH_2 complex, [Mn^{II}(dhter)]$_n$

dhterH_2 (500 mg, 3 mmol) was added to 20 ml of an aqueous solution of NaOH (240 mg, 6 mmol). The mixture was stirred for 10 min and filtered. An aqueous solution of $MnCl_2 \cdot 4H_2O$ (595 mg, 3 mmol in 10 ml) was added to the pink filtrate. The mixture was stirred at room temperature for 3 h. A black solid that formed

was filtered, washed with water and dried under vacuum. The entire reaction was carried out under nitrogen atmosphere. Yield = 590 mg (83%). Elemental analysis (Found, %): C, 41.14; H, 2.57 and Mn, 22.28.

2.3. Epoxidation of cyclohexene catalyzed by manganese complexes

Epoxidation was carried out in a two neck round bottom flask by mixing cyclohexene (10 mmol), catalysts (30 mg), imidazole (30 mg) and hydrogen peroxide (4 ml, 30%) in acetone (10 ml). The contents were stirred at room temperature for 12 h. After the reaction, the contents were filtered and the products were analyzed by GC.

2.4. Decomposition of H_2O_2

Hydrogen peroxide (1 ml, 30%) was added to 30 mg of manganese complex (**$[Mn^{III}_n$-(Pdhteren)(OAc)$_n]$**, **$[Mn^{II}_n$(Pdhteren)]**, **$[Mn^{II}$-(dhter)$]_n$**) in 4 ml of acetone. The reaction mixtures were stirred in a thermostated reactor. Evolved oxygen gas was measured in a gas burette.

2.5. Epoxidation of cyclohexene in the presence of nitrogen bases

Hydrogen peroxide (4 ml, 30%) was added to catalyst, **$[Mn^{II}_n$(Pdhteren)]** (30 mg), cyclohexene (10 mmol) and axial ligand (imidazole, benzimidazole, pyridine, 4-methyl pyridine, 2,4,6-trimethyl pyridine or triethylamine) (44 mmol) in acetone (10 ml). The reaction mixtures were stirred at room temperature for 12 h. The products were filtered and analyzed by GC.

2.6. Epoxidation of cyclohexene in the presence of imidazole

Hydrogen peroxide (4 ml, 30%) was added to catalyst, **$[Mn^{II}_n$(Pdhteren)]** (30 mg), cyclohexene (10 mmol) and imidazole at various concentrations (0–1.76 mmol) in 10 ml of acetone. The reaction mixtures were stirred at room temperature for 12 h. The products were filtered and analyzed by GC.

2.7. Epoxidation of cyclohexene at various olefin concentrations

In a typical experiment, hydrogen peroxide (14.61 mmol) was added to cyclohexene, catalyst, **$[Mn^{II}_n$(Pdhteren)]** (30 mg) and imidazole (60 mg) in 10 ml of acetone. Concentration of cyclohexene was varied from 9.87 to 98.72 mmol. The reactions were carried out at 25°C for 12 h. The products were analyzed by GC. The percentage efficiency is calculated using the following equation:

$$\text{Efficiency}\,(\%) = \frac{\text{mmol of cyclohexene conversion}}{\text{mmol of } H_2O_2 \text{ used}} \times 100$$

2.8. Epoxidation of olefins

Hydrogen peroxide (4 ml, 30%) was added to a reaction mixture containing olefin (cyclohexene, cyclooctene, styrene, 1-hexene or 1-pentene) (10 mmol), catalyst, **$[Mn^{II}_n$(Pdhteren)]** (30 mg) and imidazole (60 mg) in 10 ml of acetone. The reactions were carried out at room temperature for 12 h. The products were analyzed by GC.

2.9. Complete oxidation of olefins with H_2O_2

Hydrogen peroxide (30%) was added progressively at a rate of 1 ml/h to the reaction mixture containing olefin (10 mmol), catalyst (30 mg) and imidazole (60 mg) in 10 ml of acetone. The olefin conversions were monitored using GC.

3. Results and discussion

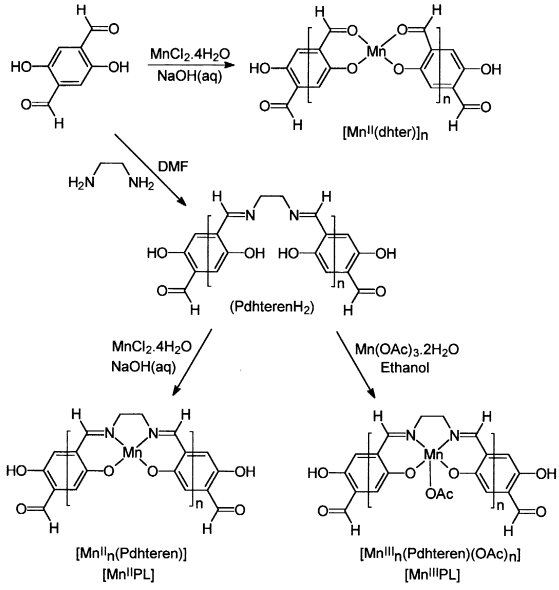
3.1. Synthesis and characterization of manganese complexes

3.1.1. Synthesis and characterization of manganese Schiff base complexes

Schiff base polymer, Poly(dihydroxyterephthalaldehyde ethylenediamine), (PdhterenH_2 or PL) was synthesized from dhterH_2, through condensation polymerization with ethylenediamine (en) in dimethylformamide solvent at ambient temperature. The Schiff base polymer, PdhterenH_2 was used as a polynucleating ligand to synthesize polynuclear manganese(II) and manganese(III) Schiff base complexes. This ligand provides tetradentate chelating environment with two replaceable proton to form strong ligand to metal interaction.

Direct reaction between ligand PdhterenH_2 and manganese(II) chloride or manganese(II) acetate in ethanol did not lead to complexation even after refluxing with stirring for 24 h. However, the Schiff base polymer forms a violet sodium salt with aqueous NaOH. Addition of manganese(II) chloride to the sodium salt of the Schiff ligand gave a brown manganese(II) Schiff base complex, **[Mn^{II}_n(Pdhteren)]**or **[Mn^{II}PL]**, in quantitative yield (Scheme 1). The reaction carried out under nitrogen or aerobic atmosphere gave same manganese(II) complex without oxidation at the metal center. The polynuclear manganese(III) Schiff base complex, **[Mn^{III}_n(Pdhteren)(OAc)$_n$]** or **[Mn^{III}PL]** was prepared by refluxing the ligand PdhterenH_2 with manganese(III) acetate in ethanol.

The manganese complex **[Mn^{II}PL]** and **[Mn^{III}PL]** were studied by IR spectroscopy. The complex **[Mn^{II}PL]** showed a broad band around 3400 cm^{-1} due to the hydrogen bonded ν_{O-H}, hydroxyl group stretching. Absorptions due to C–H bond stretchings appeared at 2922 cm^{-1} and 2879 cm^{-1}. A strong band at 1624 cm^{-1} is attributable to the coordinated imine band stretching, $\nu_{C=N}$. A weak band at 1657 cm^{-1} is assigned to the carbon–oxygen double bond stretching vibration, $\nu_{C=O}$, of the uncoordinated terminal carbonyl group. The presence of absorption due to carbon–oxygen double bond reflects that the end groups of the manganese complex polymeric chain are carbonyl or aldehyde. The manganese(III) Schiff base complex, **[Mn^{III}PL]** shows similar IR pattern like that of the corresponding manganese(II) complex with additional bands at 1590 cm^{-1} and 1421 cm^{-1} due to acetate group [21]. The bands at 1590 cm^{-1} and 1421 cm^{-1} are assigned to the asymmetric and symmetric stretching modes of coordinated acetate group, respectively [22]. The intensity of the $\nu_{asym}(COO^-)$ is much higher than that attributable to the $\nu_{sym}(COO^-)$. Thus, the acetate group is attached to the manganese center through monocoordination or in highly unsymmetrical fashion [23].



Scheme 1.

The manganese complexes **[Mn^{III}PL]** and **[Mn^{II}PL]** were studied by EPR spectroscopy. The manganese(III) Schiff base complex is EPR silent at room temperature and at liquid nitrogen temperature, which is expected for d^4 metal ions [24]. The X-band EPR spectra of **[Mn^{II}PL]** recorded at room temperature and at liquid nitrogen temperature are shown in Fig. 1. The

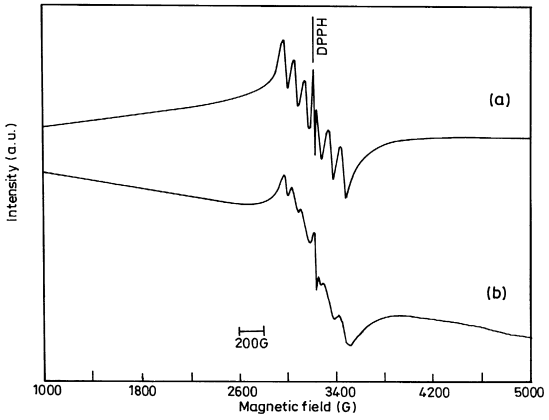


Fig. 1. X-band EPR spectra of [Mn^{II}PL]: (a) at room temperature and (b) at liquid nitrogen temperature.

room temperature spectrum exhibited a six-line manganese hyperfine pattern centered at $g = 2.0129$, $A = 95$ G, which is expected of an odd unpaired electron system ($S = 5/2$, $m_S = \pm 5/2, \pm 3/2, \pm 1/2$; and $I = 5/2$, $m_I = \pm 5/2, \pm 3/2, \pm 1/2$) resulting from ''allowed'' transitions ($\Delta m_S = \pm 1$, $\Delta m_I = \pm 0$). The 77-K spectrum exhibits a six-line signal with reduced g value, $g = 1.9943$, $A = 86$ G. The spectrum is typical of a mononuclear manganese(II) complex [25]. Perhaps this is due to a very weak magnetic exchange interaction between manganese(II) centers.

3.1.2. Synthesis of manganese(II)-dhterH_2 complex

dhterH_2 was used as a bridging ligand to prepare oxygen-coordinated polynuclear manganese complex, **[Mn^{II}(dhter)]$_n$**. The aldehyde is a golden yellow compound that is insoluble in water. Addition of NaOH into dhterH_2 suspension in water produced a purple sodium salt of dhterH_2, dhterNa_2, which is soluble in water. Reaction of dhterNa_2 solution with manganese(II) chloride in aqueous medium gave a polynuclear manganese(II) complex, **[Mn^{II}(dhter)]$_n$** or **[Mn^{II}L]**, as a black solid that is insoluble in common organic solvents.

IR spectrum of the complex **[Mn^{II}L]** showed a broad band in the region, 3680–2900 cm^{-1}. This high-frequency band is characteristic of a stretching vibration mode of hydrogen-bonded hydroxyl group. A weak shoulder at 1689 cm^{-1} is attributed to the $\nu_{C=O}$ of terminal carbonyl group. The internal coordinated carbonyl group showed a strong band at 1628 cm^{-1}. A medium intensity band at 1360 cm^{-1} is due to the ν_{C-O} (phenolic). A weak band at lower frequency, 540 cm^{-1} is characteristic of metal-oxo stretching mode.

The X-band EPR spectra of the complex, **[Mn^{II}L]**, were recorded on the polycrystalline powder at room temperature and liquid nitrogen temperature. The compound showed a temperature-independent featureless single broad signal around $g = 2$. The broadness of this isotropic EPR absorption indicates the existence of magnetically coupled manganese ions [26].

3.1.3. Thermal analysis

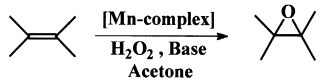
Thermal analysis of the polynuclear manganese complexes was studied under N_2 atmosphere. The manganese Schiff base complexes **[Mn^{II}PL]** and **[Mn^{III}PL]** showed major decomposition in the temperature range 300–480°C and 250–410°C, respectively. There is no sharp weight loss up to 250°C, which suggests the absence of coordinated water molecule in these complexes. The oxygen-coordinated manganese complex, **[Mn^{II}L]**, started to decompose around 180°C. Thermal stability decreases in the order: **[Mn^{II}PL]** > **[Mn^{III}PL]** > **[Mn^{II}L]**. Thus, the thermal stability of the manganese complexes with *N,N,O,O*-tetradentate chelating ligand, **[Mn^{II}PL]**, and **[Mn^{III}PL]** is higher than that of *O,O*-bidentate ligand, **[Mn^{II}L]**.

3.2. Epoxidation

Epoxidation of olefins with hydrogen peroxide catalyzed by polynuclear manganese complexes was studied in acetone in the presence of a nitrogen base (Scheme 2).

3.2.1. Epoxidation of cyclohexene catalyzed by manganese complexes

Epoxidation of cyclohexene with 30% hydrogen peroxide catalyzed by solid polynuclear



Scheme 2.

manganese complexes was studied. The results of epoxidation of cyclohexene catalyzed by various manganese complexes are given in Table 1. For comparison, epoxidation of cyclohexene was carried out under identical condition for different manganese catalysts. In a typical experiment, 4 ml of hydrogen peroxide (30%) was added at a time to the reaction mixture containing cyclohexene (10 mmol), catalyst (30 mg) and imidazole (30 mg) in 10 ml acetone. Manganese(III) Schiff base complex, **[Mn^{III}PL]**, gave 28% conversion of cyclohexene with 94% of epoxide selectivity in 12 h. Manganese(II) Schiff base complexes, **[Mn^{II}PL]**, gave 49% conversions of cyclohexene with 92% selectivity. However, oxygen-coordinated manganese complex, **[Mn^{II}L]**, gave only 12% conversion of cyclohexene in 12 h.

Manganese(II) complex, **[Mn^{II}PL]**, is more effective for conversion of cyclohexene than the manganese(III) complex under same Schiff base ligand environment. Nitrogen-coordinated manganese Schiff base complexes are better epoxidation catalysts than the oxygen-coordinated complex, **[Mn^{II}L]**. Evolution of oxygen was observed during the reaction. The low conversion of cyclohexene in these reactions is due to catalytic decomposition of hydrogen peroxide in a competitive parallel reaction.

Table 1
Epoxidation of cyclohexene with H_2O_2 catalyzed by manganese complexes[a]

Run	Catalyst	Conversion (%)	Selectivity (%)
1	[Mn^{III}PL]	28	94
2	[Mn^{II}PL]	49	92
3	[Mn^{II}L]	12	91

[a]Cyclohexene (10 mmol), catalyst (30 mg), Imidazole (30 mg) and hydrogen peroxide (4 ml, 30%) in acetone (10 ml) for 12 h.

3.2.2. H_2O_2 decomposition by manganese complexes in acetone

The catalytic activity of manganese complexes towards hydrogen peroxide decomposition in acetone was studied at room temperature. Fig. 2 shows the amounts of oxygen evolved against time curves for hydrogen peroxide decomposition catalyzed by various manganese complexes. The catalytic activities of the manganese complexes are in the following order: **[Mn^{III}PL] > [Mn^{II}PL] > [Mn^{II}L]**. Nitrogen-coordinated manganese(III) complex, **[Mn^{III}PL]**, is more active towards catalytic decomposition of hydrogen peroxide than the analogous manganese(II) complex, **[Mn^{II}PL]**. This suggests that the coordination of hydrogen peroxide at manganese center is important for the activation of hydrogen peroxide. Oxygen-bonded manganese complex, **[Mn^{II}L]**, is less active than the nitrogen-bonded manganese complexes.

3.2.3. Nature of axial ligand on epoxidation

Cyclohexene epoxidation with hydrogen peroxide catalyzed by manganese complex, **[Mn^{II}PL]**, in acetone in the presence of various nitrogen bases were studied. Table 2 shows the results obtained for epoxidation of cyclohexene using various nitrogen donors as axial ligands.

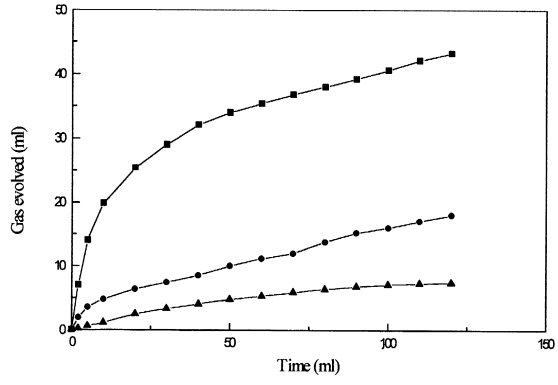


Fig. 2. Time course on O_2 evolution from H_2O_2 (1 ml, 30%) catalyzed by (■) [$Mn^{III}PL_1$], (●) [$Mn^{II}PL_1$] and (▲) [Mn^{II}L].

Table 2
Nature of axial ligand on epoxidation of cyclohexene with H_2O_2 catalyzed by $[Mn^{II}PL]$[a]

Ligand	Conversion (%)	Selectivity (%)
Imidazole	49	92.5
Benzimidazole	26	86
Pyridine	19	87
4-Methyl pyridine	23	81
2,4,6-Trimethyl pyridine	11	78
Triethylamine	4	–
–	5	–

[a]Cyclohexene (10 mmol), H_2O_2 (4 ml, 30%), ligand (0.44 mmol), catalyst (30 mg), in 10 ml of acetone at 25°C for 12 h.

In the absence of any axial ligand, only 5% of cyclohexene oxidation is observed without any epoxidation product. Imidazole and benzimidazole gave 49% and 26% of cyclohexene conversions with 92% and 86% selectivity towards epoxidation, whereas pyridine showed only 19% conversion of cyclohexene, which is less than imidazole. However, substituted pyridine, having electron-releasing methyl group such as 4-methyl pyridine showed 23% conversion of cyclohexene, which is higher than the unsubstituted pyridine; but activity is decreased when substituent is introduced at *ortho*-positions; for example, 2,4,6-trimethyl pyridine showed only 11% of cyclohexene conversion. This suggests the coordination of nitrogen base, as an axial ligand, at the manganese center for activation of hydrogen peroxide. In the presence of tri-ethylamine, only 4% conversion of cyclohexene was observed without any selectivity towards epoxidation. Among nitrogen bases, which are used as axial ligands, imidazole exhibited maximum activity towards epoxidation of cyclohexene with hydrogen peroxide. The lower rates of epoxidation found with other bases such as pyridine could be due to their weaker ligand affinity for manganese complex [27].

Comparison of the catalytic activity of the manganese complex in the presence of various nitrogen bases shows that imidazole has a strong proximal effect than pyridine on the acceleration of the oxygen transfer to the olefin. Strong coordination of axial ligand, imidazole, should result in an increase of electron density on the metal and a facile heterolytic cleavage of the O—O bond of H_2O_2 [28].

3.2.4. Effect of imidazole concentration on epoxidation

The influence of imidazole on the catalytic activity of **$[Mn^{II}PL]$** towards olefin epoxidation with hydrogen peroxide was studied by changing the concentration of imidazole by keeping other parameters, viz. catalyst, cyclohexene, hydrogen peroxide and reaction time constant. The reactions were carried out at room temperature in acetone solvent. In a reaction manganese complex, **$[Mn^{II}PL]$** (30 mg, 0.12 mmol), hydrogen peroxide (4 ml, 30%), cyclohexene (10 mmol) and imidazole concentration that varied from 0 to 1.76 mmol, were reacted at 25°C. The products were analyzed after 12 h reaction. No epoxidation of olefin was observed in the absence of imidazole. On the addition of imidazole, epoxidation was observed. This suggests the importance of coordination of imidazole on to the metal for epoxidation. Imidazole coordinates to the manganese by electron donation, and hence, favors the formation and stabilization of higher oxidation state manganese-oxo intermediate. Manganese-oxo intermediate is the key species for oxygen transfer reaction [29].

Conversion of cyclohexene was found to increase with increasing concentration of imidazole. Oxidation of cyclohexene with hydrogen peroxide catalyzed by **$[Mn^{II}PL]$** in the presence of 0.88 mmol of imidazole ([Im]/[catalyst] = 7.3) gave 57% conversion of cyclohexene in 12 h. However, it was only 5% in the absence of imidazole under identical conditions (Table 3). This suggests that the role of imidazole, in addition to coordination at the axial position, is to abstract a proton from hydrogen peroxide, which facilitates heterolytic cleavage of peroxide O—O bond. At high concentration of imidazole, the activity of the catalyst is also consistent with hydrogen bonding between nitrogen of free imidazole and hydrogen of coordinated imidazole, which increases the electron density at

Table 3
Effect of concentration of imidazole in the epoxidation of cyclohexene[a]

Im		[Im]/[Mn]	Conversion (%), 12 h
mg	mmol		
0	0	–	5
5	0.07	0.58	12
8	0.12	1.00	23
20	0.29	2.40	37
30	0.44	3.66	49
40	0.59	5.00	54
60	0.88	7.30	57
80	1.18	10.00	55
100	1.47	12.20	51
120	1.76	14.60	48

[a]Cyclohexene (10 mmol), H_2O_2 (4 ml, 30%), Imidazole, catalyst (30 mg, 0.12 mmol), in 10 ml of acetone at 25°C.

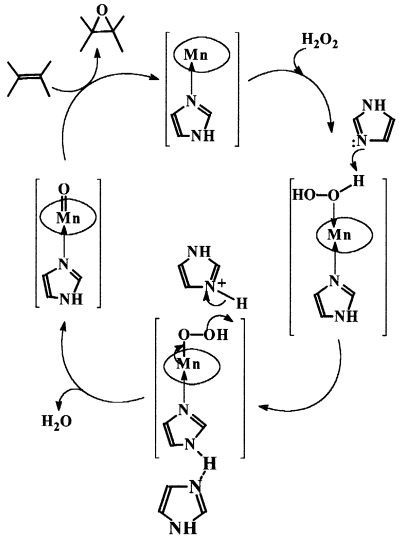
the manganese and consequently facilitates O—O bond cleavage [30] (Scheme 3). When the imidazole concentration was very high, the olefin conversion was decreased. At higher imidazole concentration, competitive oxidation of imidazole is also possible in addition to the oxidation of cyclohexene [31].

3.2.5. Effect of concentration of olefin on epoxidation

Oxidation of cyclohexene with hydrogen peroxide catalyzed by **[Mn^{II}PL]** in the presence of imidazole was studied by varying the concentration of cyclohexene to study the effective use of oxidant, hydrogen peroxide, for cyclohexene oxidation. The results are shown in Table 4. The catalytic efficiency was calculated from the number of moles of cyclohexene conversion per mole of hydrogen peroxide used at the end of 12 h. At lower cyclohexene concentration, the efficiency or effective use of hydrogen peroxide for cyclohexene oxidation was low. When $[\text{cyclohexene}]/[H_2O_2] = 0.68$, the efficiency was only 38.6%, that is, only 38.6% of added hydrogen peroxide was effectively utilized for cyclohexene oxidation. The rest of hydrogen peroxide decomposed into molecular oxygen in a parallel reaction. The efficiency increased with increasing concentration of cyclohexene. At higher olefin concentration, $[\text{cyclohexene}]/[H_2O_2] = 6.76$, high efficiency was observed, 85.5%.

It has been shown that manganese complexes in the presence of imidazole are prone to catalyze the dismutation of H_2O_2 [30,31]. It is very likely that the variation in the cyclohexene oxidation is due to competition between the substrate and hydrogen peroxide for reaction with the oxo-manganese intermediate (Scheme 4).

At higher concentration of cyclohexene, oxygen transfer from manganese-oxo intermediate to cyclohexene is more facile. On the other hand, at higher hydrogen peroxide concentration, manganese-oxo intermediate reacts with hydrogen peroxide and releases molecular oxy-

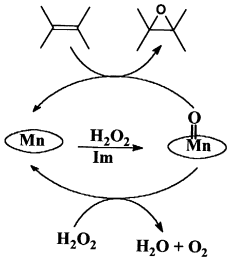


Scheme 3.

Table 4
Efficiency of epoxidation of cyclohexene with H_2O_2

Cyclohexene (mmol)	H_2O_2 (mmol)	Olefin conversion		Efficiency (%)
		%	mmol	
9.87	14.61	57	5.63	38.55
19.744	14.61	36.9	7.29	49.89
29.617	14.61	27.8	8.23	57.94
39.489	14.61	23.12	9.13	64.28
49.361	14.61	19.96	9.85	69.36
59.233	14.61	17.6	10.43	73.46
98.72	14.61	12.3	12.14	85.52

[a]Calculated based on oxidant consumed assuming that one mole of oxidant reacts with one mole of substrate.

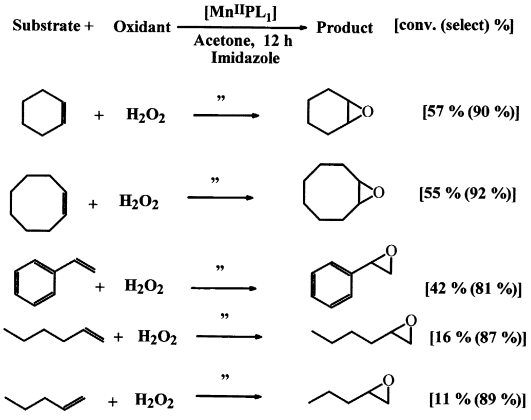


Scheme 4.

gen. Therefore, at higher concentration of olefin, epoxidation reaction is faster than the oxygen evolution. Hence, for effective utilization of hydrogen peroxide for oxidation reaction, the concentration of cyclohexene should be kept high.

3.2.6. Epoxidation of olefins with H_2O_2

Epoxidation of simple olefins with hydrogen peroxide catalyzed by manganese complex, **[Mn^{II}PL]** was achieved in acetone in the presence of imidazole as axial ligand. Linear, cyclic and phenyl substituted olefins were used as substrates. The results are shown in Scheme 5. Cyclic olefins, such as cyclohexene and cyclooctene gave 57% and 55% conversions of olefin with selectivity of 90% and 92%, respectively, towards epoxidation at room temperature for 12 h. Styrene yielded 42% conversion with 81% selectivity for styrene oxide. Terminal olefins such as 1-hexene and 1-pentene gave only 16% and 11% olefin conversion, respectively.



Scheme 5.

The oxygen transfer activity of the catalyst, **[Mn^{II}PL]**, towards various olefins is decreasing in the following order. cyclohexene > cyclooctene > styrene > 1-hexene > 1-pentene. Thus, electron-rich cyclic olefins are more active than the electron-poor terminal olefins. This reflects the electrophilic nature of oxygen transfer from manganese-oxo intermediate to the olefinic double bond.

3.2.7. Complete oxidation of olefins with H_2O_2 catalyzed by [Mn^{II}PL]

Fig. 3 shows the percentage of olefin conversion against the amount of hydrogen peroxide used for various olefins. Hydrogen peroxide was added in drops into the reaction mixture containing substrate, catalyst and imidazole in acetone at 25°C. The reaction was followed by monitoring the conversion of cyclohexene after the addition of each 1 ml hydrogen peroxide (30% solution). Hydrogen peroxide added slowly at the rate of 1 ml/h. The reaction was carried to 100% conversion of olefin. 10 mmol of cyclohexene consumed 7 ml of 30% hydrogen peroxide for 100% conversion. Cyclooctene, styrene and 1-hexene were oxidized in this manner under identical conditions. Cy-

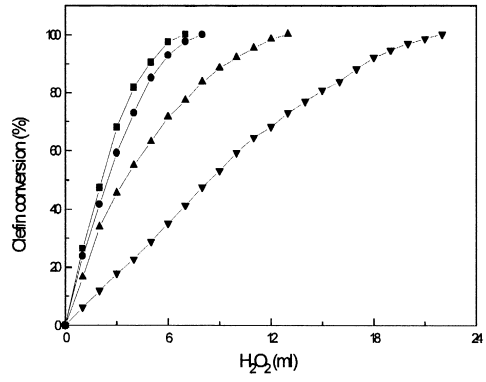


Fig. 3. Plot of hydrogen peroxide concentration against olefin conversion: (■) cyclohexene, (●) cyclooctene, (▲) styrene and (▼) 1-hexene. Olefin (10 mmol), catalyst, [$Mn^{II}PL_1$] (30 mg) and Imidazole (60 mg) in acetone at 25°C.

clooctene, styrene and 1-hexene required 8, 13 and 22 ml of 30% hydrogen peroxide, respectively, for complete conversion. Thus, 1-hexene is a poor substrate in $[Mn^{II}PL_1]$-catalyzed epoxidation with hydrogen peroxide.

4. Conclusions

Epoxidation of simple olefins with hydrogen peroxide was achieved using polynuclear manganese complexes as catalysts under heterogenized homogeneous condition. The presence of a nitrogen base is always necessary to induce heterolytic cleavage of H_2O_2 and obtain efficient reactions. Imidazole influencing the epoxidation reaction with hydrogen peroxide in the presence of a manganese complex as a proximal as well as distal ligand. During competitive hydrogen peroxide dismutation and olefin epoxidation reactions, the dismutation reaction is more rapid than the olefin oxygenation in the absence of imidazole. Complete olefin conversion is possible in this system without deactivation of the catalyst. Manganese Schiff base complexes are more efficient than oxygen-bonded manganese complexes for the activation of hydrogen peroxide. Epoxidation with hydrogen peroxide catalyzed by solid polynuclear manganese complexes is an environmental friendly process.

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