

Letter

# Catalase and epoxidation activity of polynuclear manganese(III)–Schiff base complexes

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## Abstract

Polynucleating Schiff base ligands, poly(2,5-dihydroxyterephthalaldehyde ethylenediamine diprotonated) (Pdhter $\text{enH}_2$ ) and poly(2,5-dihydroxyterephthalaldehyde propyldiamine diprotonated) (Pdhter $\text{pnH}_2$ ) were synthesized by condensation reactions of 2,5-dihydroxyterephthalaldehyde (dhter $\text{H}_2$ ) with ethylenediamine and propylenediamine, respectively. Insoluble polynuclear manganese(III)–Schiff base complexes,  $[\text{Mn}_n(\text{Pdhter}\text{en})(\text{OAc})_n]$  **1** and  $[\text{Mn}_n(\text{Pdhter}\text{pn})(\text{OAc})_n]$  **2** were prepared by refluxing manganese(III)–acetate and the respective polymeric Schiff bases in ethanol. The catalase activity of these complexes were studied in aqueous, dimethylformamide and methanol medium. These complexes catalyze the epoxidation of cyclohexene with  $\text{H}_2\text{O}_2$  in the presence of imidazole. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Manganese; Polynuclear; Schiff base; Imidazole;  $\text{H}_2\text{O}_2$ ; Epoxidation

## 1. Introduction

For aerobic living systems, superoxide dismutase [1] and catalase [2] are the key enzymes involved in the control of superoxide anion and hydrogen peroxide, two species derived from the reduction of molecular oxygen and precursors of the highly toxic hydroxyl radical. In many organisms the catalase activity is related to a hemoprotein [3], but recently Mn-containing catalases have been isolated in some microorganisms [4,5].

Polynuclear manganese complexes are essential for disproportionation of  $\text{H}_2\text{O}_2$  catalyzed by manganese catalases (Mn-CATs), in thermo-

philic bacteria [6] and a lactobacillus [7]. Similar catalase activity was observed at the  $\text{S}_2$  state of the photosynthetic water oxidation enzyme [8], which has a tetranuclear manganese core [9]. Attempts have been made to understand the catalytic decomposition of hydrogen peroxide in aqueous medium by manganese(III) ions [10] and their complexes [11]. For a better understanding of the mechanism of this biological process, synthetic models were studied [12]. Biomimetic oxidation catalysis has largely focused on metal complexes with planar tetradentate ligands such as manganese or iron porphyrins and related macrocyclic *trans*-chelates [13]. In spite of the great emphasis given to the study of the homogeneous catalysts [14] its heterogenization using organic and inorganic matrices has been receiving increasing attention

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because these systems present many advantages such as prevention of intermolecular reaction and easy recovery of the catalyst, which can be reused later, in addition to the simplicity in working with it [15]. Currently there is a lot of 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]. Herein we report the catalytic decomposition of hydrogen peroxide and epoxidation of cyclohexene catalyzed by polynuclear manganese(III)–Schiff base complexes in a heterogenized homogeneous condition.

## 2. Experimental

All the solvents were purified by standard methods [19]. Ethylenediamine and propylenediamine were distilled under nitrogen atmosphere before use. 2,5-Dihydroxyterephthalaldehyde (dhterH<sub>2</sub>) was prepared from dimethylhydroquinoneether using literature methods [20]. Polymeric Schiff base ligands PdhterenH<sub>2</sub> [poly(2,5-dihydroxyterephthalaldehyde ethylenediamine diprotonated)] and PdhterpnH<sub>2</sub> [poly(2,5-dihydroxyterephthalaldehyde propyldiamine diprotonated)] were prepared by condensation of 2,5-dihydroxyterephthalaldehyde with ethylenediamine and propyldiamine, respectively, using the reported procedure with some modifications [21]. Mn(OAc)<sub>3</sub> · 2H<sub>2</sub>O (E. Merck) was used as such. Hydrogen peroxide was 30% solution. Infrared spectra were recorded on a Bruker IFS 66V FT-IR and thermal analysis on Delta series TGA-7. Products were analyzed on a Nucon model 5765 gas chromatograph using an OV 17 column and FID. WinAcids 5.0 software was used for data processing.

### 2.1. Synthesis of polynuclear manganese(III)-complexes

Manganese(III)–Schiff base complexes were obtained by refluxing appropriate free Schiff

base polymer, PdhterenH<sub>2</sub> or PdhterpnH<sub>2</sub>, with the manganic acetate (two-fold excess) in dry ethanol for 24 h. The brown solid obtained were filtered, washed thrice with hot ethanol, CH<sub>2</sub>-Cl<sub>2</sub>, and ether in that order and dried at vacuum. [Mn<sub>n</sub>(Pdhteren)(OAc)<sub>n</sub>] **1** [Found: Mn, 17.91; C, 46.30; N, 8.53, H, 3.65%] and [Mn<sub>n</sub>(Pdhterpn)(OAc)<sub>n</sub>] **2** [Found: Mn, 17.14; C, 47.62; N, 8.17; H, 3.93%].

### 2.2. Decomposition of H<sub>2</sub>O<sub>2</sub> in standard dismutation reactions

All reactions were carried out in a thermostated 25 ml reactor. To 50 mg of catalyst 4 ml of solvent (water, dimethylformamide or methanol) and 1 ml of hydrogen peroxide (30% in aqueous solution) were added. Evolved oxygen was measured in a gas burette.

### 2.3. Epoxidation of cyclohexene

Epoxidation of cyclohexene was carried out in a double-necked, round-bottomed flask by mixing cyclohexene (1 ml), catalyst (30 mg), imidazole (20 mg) and hydrogen peroxide (8 ml, 30%) in acetone (10 ml). The contents were stirred at room temperature (25°C) for 24 h. After the reaction was complete the contents were filtered and the products were analyzed by GC.

## 3. Results and discussion

The polynuclear manganese(III)–Schiff base complexes are shown in Fig. 1. The polynucleating Schiff base ligands, PdhterenH<sub>2</sub> and

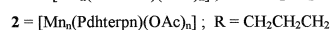
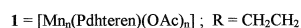
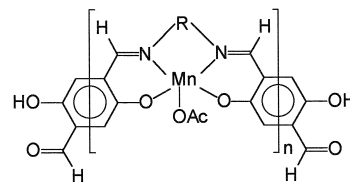


Fig. 1. Schematic representation of manganese complexes.

PdhterpnH<sub>2</sub>, were prepared by reacting 2,5-dihydroxyterephthalaldehyde with ethylenediamine and propylenediamine, respectively, in dimethylformamide.

### 3.1. IR study

The complexation reaction of the Schiff base polymers with Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O in ethanol showed a sharp color change from dark brown to light brown while refluxing. The complexes exhibited IR bands at 1628 cm<sup>-1</sup>, 1595 cm<sup>-1</sup>, 631 cm<sup>-1</sup> and 527 cm<sup>-1</sup>. The strong bands at 1628 cm<sup>-1</sup> and 1595 cm<sup>-1</sup> are assigned to  $\nu_{C=N}$  and acetate group stretching mode, respectively. The bands at 631 cm<sup>-1</sup> and 527 cm<sup>-1</sup> were assigned to the coordinated acetate group deformation mode and Mn–O stretching mode, respectively [22]. The intensity of the aldehydic C=O stretching band at 1670 cm<sup>-1</sup> is very weak compared to the imine stretching band which is attributed to high molecular weights of the chelate polymers.

### 3.2. Thermal analysis

Thermal analysis of **1** and **2** do not show any weight loss up to 200°C indicating the absence of coordinated solvent molecules in the complexes. Thermal stability of the ethylenediamine bridged Schiff base polymer, PdhterenH<sub>2</sub>, is higher than that of the propylenediamine bridged ligand, PdhterpnH<sub>2</sub>. On complexation with manganese(III)-ion the stability of both the Schiff base polymers were found reduced. The complexes **1** and **2** decomposed in the temperature range 250–410°C and 280–410°C, respectively. The higher decomposition temperature range for **2** suggests that the acetate group decomposes faster in complex **1** whereas in **2** it is strongly coordinated.

### 3.3. Hydrogen peroxide decomposition

Decomposition of hydrogen peroxide was more rapid with Mn(III)–Schiff base complexes

as catalyst than the manganese(III)–acetate. This behaviour suggests that the ligand environment around the Mn(III)-center plays an influential role in the oxidation reaction.

Studies on the two complexes **1** and **2** in the hydrogen peroxide decomposition reveal that **2** has much lower activity than **1** (Fig. 2). This is due to the dissociation of the coordinated acetate group is involved in the rate-determining step of the catalytic decomposition of hydrogen peroxide [23]. In complex **2**, due to the presence of  $-(CH_2)_3-$  chain, the acetato group, CH<sub>3</sub>COO<sup>-</sup> is bound more tightly to the more stable conformation of the manganese centre. Aqueous and organic solvents were chosen to study the decomposition of hydrogen peroxide.

The rate of decomposition of hydrogen peroxide by the catalyst **1** in different solvents is in the order: water > dmf > methanol (Fig. 3). At 0°C the catalase activity is decreased in aqueous medium and negligible in dmf. Temperature dependence of the catalytic activity in different solvents suggest the coordination of hydrogen peroxide to the metal [24]. The active form of [Mn(III)] catalyst is formed by dissociation of acetate in water to yield [Mn(III)H<sub>2</sub>O] species.

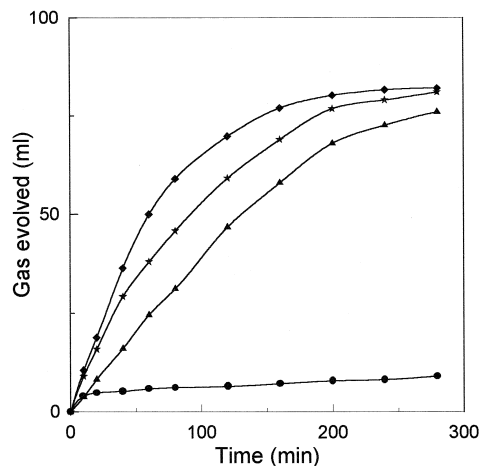


Fig. 2. Time course of oxygen evolution from hydrogen peroxide (1 ml, 30%) in water (5 ml) catalyzed by (◆) catalyst **1** (50 mg), (★) catalyst **2** (50 mg), and (●) manganese(III)-acetate (50 mg) at 25°C; (▲) catalyst **1** (50 mg) at 0°C.

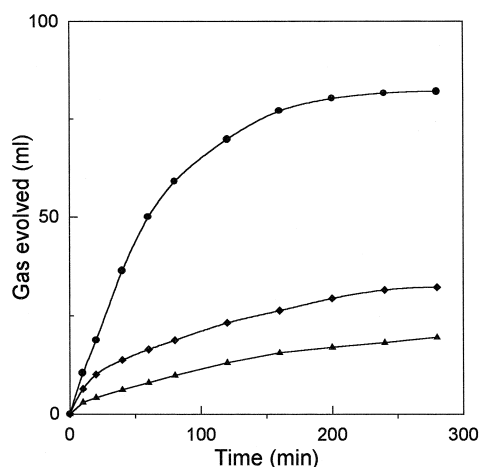
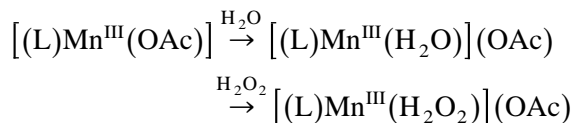


Fig. 3. Time course of oxygen evolution from hydrogen peroxide (1 ml, 30%) catalyzed by catalyst **1** in (●) water, (◆) dmf, and (▲) methanol at 25°C.

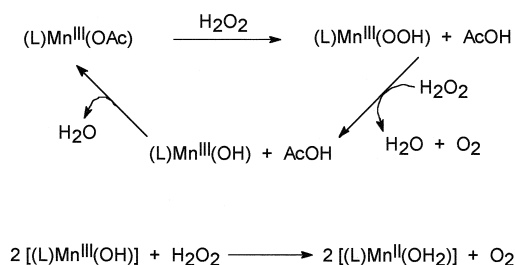
Hydrogen peroxide binds to this aquo species by displacement of bound water.



There is no change of color of the complex during the hydrogen peroxide decomposition suggesting that the high-valent Mn species are not formed [25]. Epoxidation of cyclohexene is not observed in the presence of catalyst and hydrogen peroxide alone. This rules out the formation of metal-oxo species,  $[Mn(V)=O]$  in the higher oxidation state which is responsible for the oxygen transfer to the substrate.

The catalase activity of **1** in methanol is less than in water and dmf, under similar conditions. This decreased catalytic activity in methanol is attributed to leaching of the metal from the polymer. In aqueous or dmf solvent no leaching was observed and the catalyst is robust.

The lower activity of catalyst in methanol and leaching of metal from the ligand may be due to the formation of acetic acid by dissociation of acetate and subsequent protonation of  $CH_3COO^-$  by  $H^+$  from  $H_2O_2$ . Stabilization of  $CH_3COOH$  by  $CH_3OH$  through hydrogen bonding hinders the donation of proton by acetic acid



Scheme 1.

to  $[Mn(III)-OH]$ . As a result regeneration of the catalyst is hindered. The intermediate,  $2[Mn(III)-OH]$  reacts with a molecule of  $H_2O_2$  and releases  $O_2$  and  $[Mn(II)]$  (Scheme 1). The  $[Mn(II)]$  is leached from the ligand due to the increased local concentration of acetic acid.

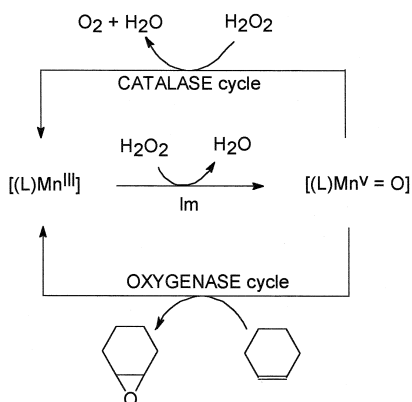
### 3.4. Epoxidation of cyclohexene

Epoxidation of cyclohexene using  $Mn(III)$ -Schiff base complexes with hydrogen peroxide as oxidant has been studied (Table 1). In control experiments, in which either catalyst, imidazole or hydrogen peroxide was excluded, epoxidation did not occur. Thus oxidant, catalyst and base are essential for the reaction. Epoxidation in triphase conditions consisting catalyst (solid)-organic phase (dichloromethane and cyclohexene)-aqueous phase ( $H_2O_2$  in water), yielded 27% and 22% conversion of cyclohexene with **1** and **2** as catalysts, respectively. With acetone as solvent, under homogeneous condi-

Table 1  
Epoxidation of cyclohexene catalyzed by the manganese(III)-Schiff base polymers with hydrogen peroxide<sup>a</sup>

Catalyst	Additive	Solvent	Conversion (%)	Selectivity (%)
<b>1</b>	–	$CH_2Cl_2$	3	–
<b>1</b>	Im	$CH_2Cl_2$	27	82
<b>2</b>	Im	$CH_2Cl_2$	22	80
<b>1</b>	–	Acetone	5	–
<b>1</b>	Im	Acetone	100	93
<b>2</b>	Im	Acetone	100	88
–	Im	Acetone	–	–

<sup>a</sup>In 10 ml of solvent containing 30 mg of catalyst, 20 mg of imidazole (Im), 1 ml of cyclohexene and 8 ml  $H_2O_2$  (30%) at 25°C.



Scheme 2.

tion conversion was 100% in 24 h with good epoxide selectivity at room temperature. Analysis indicates that cyclohexene was oxidized to cyclohexene oxide, cyclohexenol, and cyclohexenone. The products cyclohexenol and cyclohexenone are produced as a result of allylic oxidation [26]. The catalytic activity of the manganese complexes as epoxidation catalyst depends on the ease of formation of higher oxidation state, manganese-oxo intermediate and its ability to transfer oxygen to the substrate. The catalyst is regenerated in its original form after the reaction which is confirmed by analysis.

For efficient epoxidation of cyclohexene both the Mn–Schiff base and imidazole are required. Under identical conditions but in the absence of either, no epoxidation occurs. Cyclohexene is epoxidized by polynuclear manganese(III)–Schiff base complexes to cyclohexene epoxide as major product with hydrogen peroxide as oxidant, allylic oxidation products are formed in very low amounts. It is remarkable that these  $H_2O_2$ -dependent oxidation of cyclohexene could be performed with almost identical results in the presence or absence of dioxygen. Cyclohexene is prone to undergo allylic oxidation by auto-oxidation in the presence of metal complexes [27].

Biomimetic oxygenation reactions using a metal complex as catalyst are generally much more efficient when a nitrogen-base ligand, like imidazole, is added as cocatalyst [28]. Imidazole

facilitates the deprotonation of hydrogen peroxide and donates electrons to the metal enhancing the cleavage of the O–O bond of the coordinated hydroperoxide group. Manganese(III)-complexes decompose  $H_2O_2$  and transfer one oxygen atom to alkenes via high valent Mn(V)=O intermediate only in the presence of imidazole [29] (Scheme 2). This assistance can be compared to the ‘push–pull mechanism’ of catalase itself [30].

#### 4. Conclusion

The catalase activity of the manganese complexes is influenced by ligand environment around the metal centre and the solvent. Cyclohexene oxidation with hydrogen peroxide has been observed using polymeric manganese(III)–Schiff base complexes with good selectivity towards epoxide formation. The inter-communicable manganese polynuclear complexes are good models for the heterogenized homogeneous oxidation catalysts.

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