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Oxidation of alkanes by *tert*-butyl hydroperoxide catalyzed by polynuclear manganese Schiff base complexes

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Abstract

The polynuclear manganese(III) Schiff base complexes **1**–**7** containing μ-alkoxo and μ-acetato bridging and a variety of structural features were employed as catalysts for oxidation of cyclohexane by *tert*-butyl hydroperoxide in acetonitrile solution at room temperature. Oxidation of cyclohexane using complexes **1** to **5** gave cyclohexanol and cyclohexanone in moderate to high yields. However, the complexes **6** and **7** possessing chloride ligands, were inactive as catalysts. The complexes **1** and **2** were further employed as catalysts for oxidation of other substrates viz. adamantane, toluene, ethylbenzene, cumene, *cis*-cyclooctene, *trans*-stilbene and cyclohexanol. Dual mechanistic pathways involving predominantly a metal based oxidant proceeding in a heterolytic manner and a simultaneous free radical autoxidation are proposed for the oxyfunctionalization of alkanes.

Keywords: Manganese complexes; Catalysts; *tert*-Butyl hydroperoxide; Oxidation; Alkanes

1. Introduction

Homogeneous catalytic oxyfunctionalization of alkanes is a challenging research objective [1]. The present efforts in this area are directed at evolving a practical methodology based on transition metal complex catalysts. Application of enzyme mimetic systems has been a major approach to this problem in the past one and a half decades. Chemical models of cytochrome P-450 have received considerable attention in this context. However, these systems employ expensive porphyrin ligands and oxidants such as iodosylbenzene [2]. Currently, models of methane monooxygenase (MMO) enzyme as alkane oxidation catalysts have attracted much attention (Refs. [3–6] and references therein). Spectroscopic studies have shown that the catalytic site is comprised of a μ-hydroxo diiron core and bridging carboxylate anions together with terminal ligands coordinating through nitrogen and oxygen atoms [7].

The MMO model systems use μ-oxo or hydroxo-bridged diiron complexes as catalysts in the presence of molecular oxygen and electrons or single oxygen atom donors such as *tert*-butyl hydroperoxide (TBHP) for the oxidation of alkanes to alcohols and ketones [3–6]. Manganese analogues of these systems have also been shown to catalyze oxidation of alkanes by TBHP [8–12]. These systems employ μ-oxo bridged binuclear manganese complexes with

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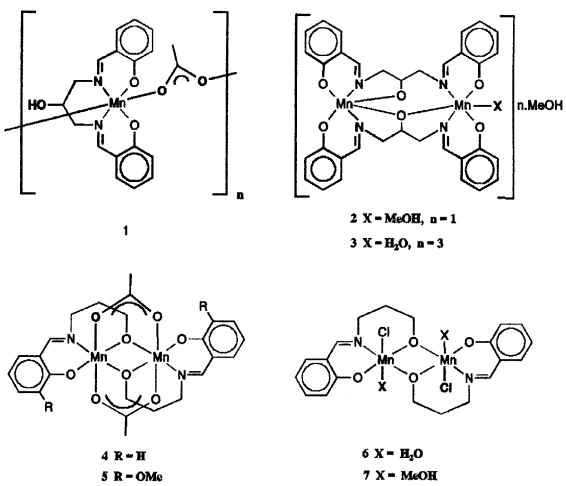
ligands containing nitrogen donor atoms such as 2,2-bipyridyl, 1,10-phenanthroline or tris[(1-methylimidazol-2-yl)methyl]amine. The coordination environment has significant influence on the catalytic activity of the complexes [10]. Recently, in a brief report, we demonstrated that binuclear manganese complexes of multidentate Schiff base ligands containing N and O coordinating atoms are also able to oxidize alkanes in the presence of TBHP [13]. In the present work we have undertaken a detailed study of several oxo-bridged manganese complexes (see the structures **1**–**7**) of Schiff bases as active catalysts for hydroxylation of alkanes with a view to gain more insight into structure–activity relationship in these systems.



2. Experimental

2.1. Materials

The binuclear managanese complexes **1**–**7** are known and have been characterized previously by X-ray studies. These were prepared by the reported procedures [14–18]. The identity of the complexes were confirmed by elemental analysis, IR and UV-VIS spectra. Authentic samples of α-(*tert*-butylperoxy)toluene, 1-(*tert*-butylperoxy)-1-phenylethane and 2-(*tert*-butylperoxy)-2-phenylpropane were prepared by literature methods [19]. Acetonitrile was distilled from P_4O_{10} under N_2. TBHP (70% in aqueous solution, Merck) and hydrogen peroxide (30% in aqueous solution) were analyzed by iodometric titration. All other chemicals were obtained commercially and used as received.

2.2. Oxidation reactions

The metal complex (0.04 mmol) was dissolved in degassed acetonitrile (25 cm^3) by stirring magnetically under argon atmosphere in a 50 cm^3 round bottomed flask. Substrate (40 mmol) followed by TBHP (4 mmol) were added to the above solution. An argon balloon was fitted to the flask and resultant solution was stirred at room temperature for the specified period. The reaction products were analyzed by GC using internal standard method. Chlorobenzene for cyclohexanol, cyclohexanone, *cis*-cyclooctene oxide, benzaldehyde and 1,3,5-trichlorobenzene for all other oxidation products were used as internal standards. The products were identified by GC comparison with the authentic samples. No oxidation of substrate occurred in the absence of the metal complexes.

2.3. Physical methods

UV-visible spectra were recorded as CH_3CN solution on a Shimadzu UV-160A spectrophotometer. IR spectra were recorded as KBr pellets on a Brüker FT-IR, IFS-113 VS model. Gas chromatographic analysis were carried out on Shimadzu GC-7AG with a flame ionization detector and a 10% Carbowax 20 M (2.5 M × 1/8″) column using N_2 as carrier gas.

3. Results and discussion

The polynuclear Mn(III) compounds **1**–**7** with Schiff base ligands containing a variety of oxo-

bridging features were screened for their catalytic activity for the oxidation of cyclohexane by TBHP. These results are compiled in Table 1. The polymeric complex **1** with μ-acetato bridging was found to be the most active (yield 72%) among the complexes employed. The binuclear Mn(III) complex **2** showed marginally lower activity than **1**. The complex **3** which is structurally similar to **2** but with an aqua ligand in place of MeOH showed relatively low activity. This may be due to difference in the relative ligand exchange ability of H_2O and MeOH ligands in these complexes which affects the accessibility of ^{t}BuOOH to the metal centre. Since the initial step in such systems involves the interaction of TBHP with the metal complex to form *tert*-butylperoxometal compound [20,21], the ligand exchange ability of the complex significantly influences the reaction rates. The complexes **4** and **5** have, both, bis-μ-alkoxo and bis-μ-acetato bridges while **6** and **7** have only bis-μ-alkoxo bridges. The remaining coordinating sites in these complexes are occupied by chloride and aqua or MeOH ligands. Whereas, complexes **4** and **5** showed moderate catalytic activity (yield 25%) **6** and **7** were found practically inactive. The presence of axial chloride ligands appears to be detrimental to the activity of these complexes. Comparison of the activities of the complexes **4** and **5** indicates that electron donating methoxyl substituents at 3 position in the aromatic rings cause lowering of the catalytic activity of **5**. This needs further investigation.

Table 1
Comparison of complexes **1**–**7** as catalysts for oxidation of cyclohexane by TBHP [a]

Complex	Yield [b] (%)		TON [c]
	CyOL	CyONE	
1	24	48	72
2	21	39	60
3	11	21	32
4	8	17	25
5	3	7	10
6 [d]	—	—	—
7 [d]	—	—	—

[a] Mn complex (0.04 mmol), TBHP (4 mmol) and cyclohexane (40 mmol) were taken. Reaction time 3 h.
[b] Yields are based on TBHP taken. Yields of ketone are calculated assuming requirement of two moles of TBHP to produce one mole of ketone from the hydrocarbon substrate.
[c] Turnover number = (moles of cyclohexanol + 2 × moles of cyclohexanone)/moles of catalyst.
[d] No reaction occurred.

Table 2
Oxidation of cyclohexane catalyzed by complexes **1** and **2** under different conditions [a]

Run	Complex	TBHP (mmol)	Time (h)	Yield [b] (%)		TON [c]
				CyOL	CyONE	
1	1	2	1	15	28	43
2	1	2	3	24	48	72
3	1	2	6	28	56	84
4	2	2	3	21	39	60
5	2	2	6	23	47	70
6	1	3	3	19	36	83
7 [d]	1	2	3	18	34	52
8 [d]	2	2	3	13	32	45

[a] Mn complex (0.04 mmol), cyclohexane (40 mmol) were taken.
[b c] See Table 1.
[d] 2,6-Di-*tert*-butyl-4-methylphenol (0.8 mmol) added.

The complexes **1** and **2** which showed better activity compared to complexes **3**–**7**, were studied further to investigate the scope and mechanism of the reaction. Table 2 shows results of the oxidation of cyclohexane using **1** and **2** under different conditions. Using the complex **1** the yields of cyclohexanol and cyclohexanone increased rapidly during initial 3 h. Only a marginal increase in the yields was observed in next 3 h and no further increase was observed on continuing the reaction beyond 6 h (see runs 1–3). A similar trend was noticed with complex **2** (see runs 4 and 5). Using higher amounts of TBHP caused an increase in the rates of the reaction leading to similar TON in 3 h (compare runs 3 and 6). Attempts to inhibit the oxidation of cyclohexane by TBHP in the presence of complex **1** or **2** by addition of 2,6-di-*tert*-butyl-4-methylphenol (20 equivalents) as a free radical trap were not successful. However, the yields of the oxidation products were lowered by about 25% with small variations in the ketone to alcohol ratios (Table 2, runs 7 and 8).

The complexes **1** and **2** were further employed for the oxidation of variety of substrates. The results are presented in Table 3. Oxidation of adamantane gave 1-adamantanol as the major product along with small amounts of 2-adamantanone. Oxidation of toluene gave benzaldehyde and minor quantities of α-(*tert*-butylperoxy)toluene. Ethylbenzene under these conditions afforded 1-phenylethanol, acetophenone and substantial amounts of 1-(*tert*-butylperoxy)-1-phenylethane. Oxidation of cumene resulted in the formation of acetophenone and 2-(*tert*-butylperoxy)-2-phenylpropane. However, the other expected product namely, 2-phenyl-2-propanol was not observed at the end of this reaction. Oxidation of *cis*-cyclooctene gave the corresponding epoxide in moderate yields. However, in the case of *trans*-stilbene, benzaldehyde was obtained as the sole oxidation product. Oxidation of cyclohexanol in the presence of **1** gave cyclohexanone selectively. The rate of cyclohexanone formation in this reaction was lower (yield 0.8 mmol in 3 h, Table 3) than that in the oxidation of cyclohexane in the presence of **1** (yield 0.96 mmol in 3 h, Table 1). Such an activity has been observed with μ-oxo-bridged diferric complexes in the oxidation of cyclohexane by TBHP [3].

In the oxidation reactions the initial brown colour of the acetonitrile solution of the metal complex changes to reddish brown on addition of TBHP. The reddish colour of the reaction mixture slowly fades away over a period of 3 h leaving a dark brown precipitate and nearly colourless solution. This indicates the transformation of the metal complex into an insoluble species which causes termination of the catalytic cycle. The analysis of this red–brown solid for C, H and N gave values which did not match with the original catalyst **1** confirming that a new inactive species was generated after the reaction. The stoichiometric composition of this solid could not, however, be established.

Table 3
Oxidation of organic compounds by TBHP catalyzed by **1** and **2** [a]

Substrate	Complex	Products	Yield [b] (%)
Adamantane [c]	**1**	1-Adamantanol	35
		2-Adamantanone	7
Adamantane [c]	**2**	1-Adamantanol	29
		2-Adamantanone	5
Toluene	**1**	Benzaldehyde	20
		α-(*tert*-Butylperoxy)toluene	5
Ethylbenzene	**1**	1-Phenylethanol	8
		Acetophenone	46
		1-(*tert*-Butylperoxy)-1-phenylethane	44
Cumene	**1**	Acetophenone	53
		2-(*tert*-Butylperoxy)-2-phenylpropane	26
cis-Cyclooctene [d]	**1**	*cis*-Cyclooctene oxide	33
cis-Cyclooctene [d]	**2**	*cis*-Cyclooctene oxide [e]	23
trans-Stilbene [c]	**1**	Benzaldehyde	18
Cyclohexanol [f]	**1**	Cyclohexanone	20

[a b] See Table 1.
[c] Substrate (4 mmol) was taken.
[d] Substrate (10 mmol) was taken.
[e] A minor unidentified product was also formed.
[f] Substrate (2 mmol) was taken.

This observation was true even for the residue obtained in the case of reaction with complex **2**. The infra-red spectrum of the red–brown solid obtained at the end of the oxidation reaction was compared with that of the original catalysts **1** and **2**. The IR spectra of **1** and **2** are nearly identical with strong absorption bands appearing in the region 1700–600 cm^{-1}. On the other hand the IR spectra of the residue indicates considerable broadening and significant reduction in intensities of the bands in this region. In particular, the sharp bands at 890 cm^{-1} (M–O–M) and ligand vibrations at 1625 cm^{-1} (C=N) and 1531 cm^{-1} (phenyl) [22,23] in the spectrum of used catalyst are considerably broadened. However, definite inference can not be drawn about the nature of the spent catalyst due to the complexities of the spectra in this region.

The UV-visible absorption spectral profiles of complexes **1** and **2** in acetonitrile were similar. Two prominent bands were observed around 235 and 390 nm. Known concentrations of TBHP were added to solutions of **1** and **2** and the spectral changes monitored periodically. These changes are illustrated in Fig. 1. Mn^{III} complexes in general exhibit a ligand to metal charge transfer band in the 350–600 nm region. For the present complexes this band appears at 390 nm. The other strong absorption band in the UV-region at 235 nm corresponds to a ligand related transition [24–26]. On addition of TBHP the 390 nm band in the spectra of **1** and **2** disappears slowly and is seen as a shoulder on the sharply rising band around 400 nm. Secondly, a very weak band appears around 500 nm in the spectra of either **1** or **2** after the treatment with TBHP. Oxomanganese (V) species as catalytic intermediates were reported to absorb at ~550 nm during olefin epoxidations with mononuclear Mn(III)-Schiff base complexes [27]. d–d transitions in Mn^{II} complexes ($^5E_{2g} \rightarrow {}^5T_{2g}$) also appear in the region above 500 nm. However, an unambiguous assignment for the band in our system can not be made due to the ill-defined shape of the absorption band at 500 nm.

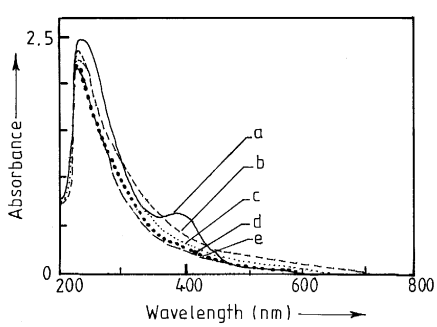
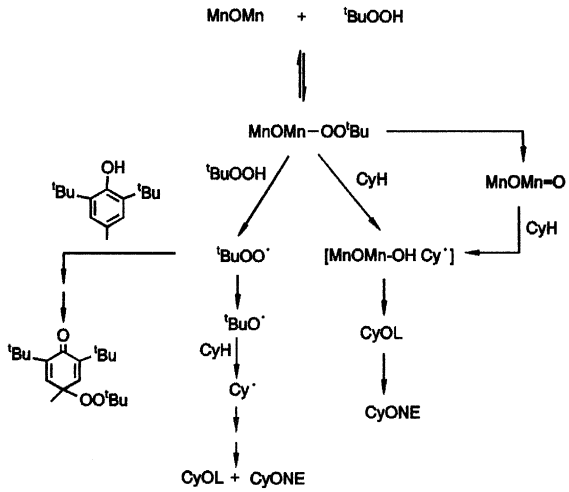


Fig. 1. Absorption spectrum of 0.5×10^{-4} M **1** in CH_3CN (a) and after treatment with 1×10^{-3} M TBHP in CH_3CN; (b) spectrum recorded at 5 min (c) at 1 h (d) at 2 h and (e) at 3 h.



Scheme 1. Proposed mechanism for the oxidation of cyclohexane (Cy = cyclohexane, CyOL = cyclohexanol, CyONE = cyclohexanone).

Recently, mechanisms involving heterolysis of peroxide bond to generate high valent oxometal intermediates have been proposed for the metal catalyzed oxidation of alkanes by hydroperoxides [4,5,9,21,28]. Detailed investigations on non-heme iron complexes has provided definite evidence that the reaction of the complex with TBHP generates an alkylperoxo iron(III) species [20,21]. The proposed mechanism is outlined in Scheme 1. The alkylperoxomanganese(III) complex either abstracts hydrogen directly from the starting alkane or does so after

converting into a metal-oxo species. This is followed by the formation of a C–O bond by the oxygen rebound mechanism [29]. At higher concentrations, TBHP competes with alkane for the metalperoxo oxidizing species. This generates alkylperoxy radicals which results into typical radical chain autoxidation leading mainly to the same products. Therefore, dual mechanistic pathways, one proceeding in a heterolytic manner via metal based oxidant and the other by free radical autoxidation process, operate simultaneously. This leads to complexities of the mechanism in these systems [29]. A similar type of dual mechanism involving alkylperoxomanganese(III) as a common intermediate is proposed in oxidation of cyclohexene by TBHP in the presence of Mn^{III}(salen) catalyst [27]. In the present system, partial suppression of the yields of the oxidation products in the oxidation of cyclohexane by addition of 2,6-di-*tert*-butyl-4-methylphenol (Table 2, runs 7 and 8) indicates such a dual mechanism. 2,6-di-*tert*-butyl-4-methylphenol scavenges alkylperoxy radicals causing suppression of the yields of cyclohexanol and cyclohexanone produced by radical autoxidation pathway [27]. Absence of products such as *tert*-butylperoxycyclohexane or bicyclohexyl which involves substrate free radicals shows that metal based oxidation predominates over the autoxidation pathway.

4. Conclusion

The polynuclear manganese Schiff base complexes described in this paper, which can be conveniently prepared from easily available materials, are as effective as or in some cases even better than those using nitrogen based ligands. Their activity is highly dependent on the ligating environment. However, these complexes suffer deactivation after completing about 85 catalytic cycles. A new approach to the design of Schiff base metal complexes is required to make these systems more practical.

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