

# Oxidation of cyclohexene with *tert*-butylhydroperoxide and hydrogen peroxide catalyzed by alumina-supported manganese(II) complexes

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## Abstract

Alumina-supported Mn(II) complexes with ligands of acetylacetonato (acac), *N,N'*-ethylenebis(salicylideneiminato) (salen), ethylenediamine (en) and 2,2'-bipyridine (bpy) catalyze the oxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP) and hydrogen peroxide. Oxidation of cyclohexene with TBHP gave 2-cyclohexene-1-ol, 2-cyclohexene-1-one and 1-(*tert*-butylperoxy)-2-cyclohexene whereas, oxidation with H<sub>2</sub>O<sub>2</sub> resulted in the formation of cyclohexeneoxide and cyclohexene-1,2-diol. Mn(II) catalysts with the nitrogen donor ligands show significantly higher catalytic activity than oxygen donor ligands at the same surface coverage. The mechanism of oxidation has also been discussed. © 2002 Published by Elsevier Science B.V.

**Keywords:** Mn(II) complexes; Acidic-alumina; Oxidation of cyclohexene; Heterogeneous catalyst; TBHP; H<sub>2</sub>O<sub>2</sub>

## 1. Introduction

One of the most important current topics of catalysis research has been to find an efficient catalyst for the selective insertion of an oxygen atom from oxygen donors, such as sodium hypochlorite (NaOCl), iodosobenzene (PhIO), dioxygen (O<sub>2</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and *tert*-butylhydroperoxide (TBHP) into various organic molecules under mild condition [1–8]. For this, the use of transition metal complexes as homogeneous catalyst are very effective and selective [9,10]. Among the transition metal complexes chiefly used as catalysts, manganese complexes were currently of considerable interest to promote oxidation reactions [11]. First developed by Jacobsen [12],

manganese chiral salen complexes combined with oxygen donors, constitute a valuable new family of homogeneous systems for enantioselective epoxidation of olefins.

One of the major problems in the application of homogeneous transition metal complexes as catalysts for selective olefin epoxidation results from catalyst decomposition or degradation. Deactivation pathways include autooxidation, dimerization through the formation of  $\mu$ -oxo bridges [13], and oxidative degradation via the formation of multi nuclear  $\mu$ -oxo complexes [14]. Decrease of the degradative dimerization of the active site has been achieved by methods such as covalent anchorage of the transition metal complexes on the polymeric matrix [15], metal complexes entrapped inside porous metal oxide framework (e.g. silica, alumina and layered double hydroxide) [16], and transition metal ligands anchored

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on the miscelle-templated silicas (MTS) [17,18]. Also, extensive research was devoted to immobilize transition metal complexes on solid supports, because such heterogenization of homogeneous catalysts may combine the ease of product separation with the selectivity of the complexes. Heterogenized catalysts would combine the advantages of homogeneous and heterogeneous catalysts, and sometimes might minimize the drawbacks of both.

In this study, we synthesized several Mn(II) complexes of various ligands of ethylenediamine, acetylacetonato, *N,N'*-ethylenebis(salicylideneiminato) and bipyridine supported on acidic alumina. These solids were then used as catalysts in cyclohexene oxidation reaction by  $\text{H}_2\text{O}_2$  and TBHP.

## 2. Experimental

### 2.1. Materials

All solvents used for synthesis were purchased from Merck (pro analysi) and were dried with molecular sieves (Linde 4 Å). Ethylenediamine (en), acetylacetonato (acac), salicylaldehyde (sal) and bipyridine (bpy) were purchased from Merck and were used as received. Acidic alumina was purchased from Merck. It was activated at 500 °C for 8 h before use. The  $\text{H}_2$  salen ligand, (*N,N'*-bis (salicylidene)ethylenediamine), was obtained in 85% yield by mixing salicylaldehyde (2 eq.) and ethylenediamine (1 eq.) in ethanol [19]. Cyclohexene was distilled under nitrogen and stored over molecular sieves (4 Å) before use.

### 2.2. Physical measurements

The products were analyzed by GC-mass, using a Philips Pu 4400 Chromatograph (1.5 m 3% OV-17 Column), Varian 3400 Chromatograph (25 m DB-5 Column) coupled with a QP Finnigan MAT INCOF 50, 70 ev. Atomic absorption spectra (AAS) were recorded on a Perkin-Elmer 4100-1319 spectrophotometer using a flame approach, after acid (HF) dissolution of known amount of the alumina material in Parr digest pump. FTIR spectra were recorded on a Shimadzu Varian 4300 spectrophotometer in KBr pellets containing alumina compounds or free complexes.

### 2.3. Preparation of alumina catalysts

#### 2.3.1. Preparation of $\text{MnCl}_2\text{-Al}_2\text{O}_3$

Acidic alumina (6 g) was added to a well stirred solution of manganese chloride tetrahydrate (1 g) in methanol (25 ml). The mixture was then heated at 40 °C for 24 h. The light pink solid was filtered, washed with methanol and dried at 50 °C under vacuum. The resulting light pink powder was stored in a tightly closed bottle and used without reactivation. The concentration of Mn(II) determined by AAS was 0.74 mmol g<sup>-1</sup>.

#### 2.3.2. Preparation of $[\text{Mn}(\text{en})_2]\text{Cl}_2\text{-Al}_2\text{O}_3$ and $[\text{Mn}(\text{bpy})_2]\text{Cl}_2\text{-Al}_2\text{O}_3$

$\text{MnCl}_2\text{-Al}_2\text{O}_3$  was stirred with two-fold of ethylenediamine (under argon atmosphere) or bipyridine in  $\text{CH}_3\text{OH}$ , and after 4 h reflux, the solid colour changed to light yellow. It was then washed with  $\text{CH}_3\text{OH}$  and dried at 50 °C under vacuum.

#### 2.3.3. Preparation of $[\text{Mn}(\text{salen})]\text{-Al}_2\text{O}_3$ (method-A)

The  $\text{MnCl}_2\text{-Al}_2\text{O}_3$  was added to a solution of the  $\text{Na}_2$  salen ligand (1 eq.) in methanol.

The suspension was heated at 40 °C for 4 h under argon atmosphere. The yellow solid was filtered, washed with methanol and soxhelt extracted with  $\text{CH}_3\text{OH}/\text{CHCl}_3$  (1:1) to remove the unreacted ligands.

#### 2.3.4. Preparation of $[\text{Mn}(\text{salen})]\text{-Al}_2\text{O}_3$ (method-B)

*N,N'*-ethylenebis(salicylideneiminato) manganese (II), Mn(salen), was prepared in a manner similar to that reported by Bailes and Calvin [20]. A solution of the Mn(salen) in  $\text{CHCl}_3$  was added to a suspension of  $\text{Al}_2\text{O}_3$  in  $\text{CHCl}_3$ . The resulting suspension was stirred at 40 °C under argon atmosphere. The yellow solid was filtered, and washed with  $\text{CHCl}_3$ . The  $[\text{Mn}(\text{salen})]\text{-Al}_2\text{O}_3$  catalyst was dried at 50 °C under vacuum overnight prior to use.

#### 2.3.5. Preparation of $[\text{Mn}(\text{acac})_2]\text{-Al}_2\text{O}_3$

Bis(acetylacetonato) manganese(II),  $\text{Mn}(\text{acac})_2$ , was also prepared according to the literature procedure [21]. Catalyst was prepared by impregnating the dried alumina with a solution of  $\text{Mn}(\text{acac})_2$  in  $\text{CHCl}_3$ . The suspension was stirred for 4 h at 40 °C under argon atmosphere. The solid was filtered and washed

several times with  $\text{CHCl}_3$ . The  $\text{Mn}(\text{acac})_2\text{-Al}_2\text{O}_3$  catalyst was dried at  $50^\circ\text{C}$  under vacuum overnight, prior to use.

#### 2.4. Oxidation of cyclohexene: general procedure

A mixture of 1 g catalyst, 25 ml solvent and 10 mmol cyclohexene was stirred under nitrogen in a 50 ml round bottom flask equipped with a condenser and a dropping funnel at room temperature for 30 min. Then 16 mmol of TBHP (solution 80% in di-*tert*-butylperoxide) or  $\text{H}_2\text{O}_2$  (30% in  $\text{H}_2\text{O}$ ) was added. The resulting mixture was then refluxed for 8 h under  $\text{N}_2$  atmosphere. After filtration and washing with solvent, the filtrate was concentrated by rotary evaporator and then subjected to GC analysis. The concentration of products were determined using cyclohexanone as internal standard.

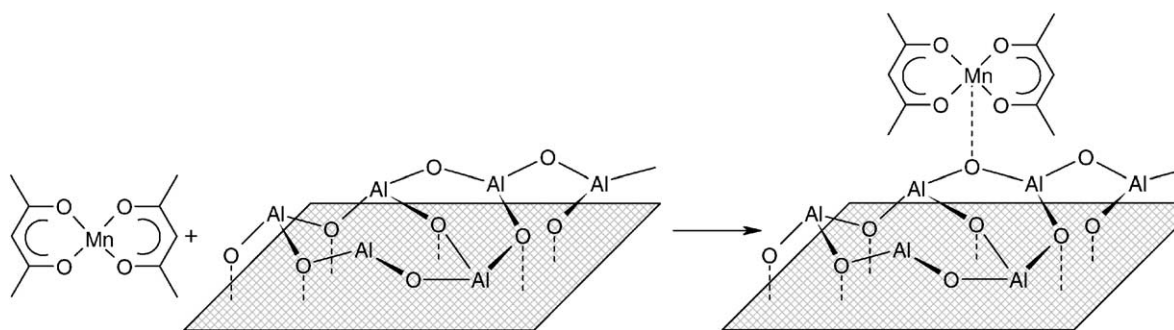
### 3. Results and discussion

We have recently reported the activation of C–H bond with TBHP in the presence of exchanged zeolite NaY with transition metal elements [11,22–25]. We showed that the Mn–NaY catalyzed cyclohexene oxidation with the highest reactivity and selectivity and di(2-cyclohexenyl)ether was formed as the main product. We also showed that some complexes of Mn(II) included in zeolite Y, catalyzed the oxygen transfer from TBHP to cyclohexene and concluded that such simple systems mimic the behavior of Cytochrome P-450 type oxidation systems. Since, alumina-supported metal systems exhibit catalytic

activity in a wide ranging of the industrially important processes and have been extensively studied, we decided to investigate the effect of manganese complexes with different chelates of *N,N*; *N,O* and *O,O* donor atoms, supported on acidic alumina in the oxidation of cyclohexene with TBHP and hydrogen peroxide. Acidic alumina was chosen because either neutral or basic alumina did not adsorb the complex on its surface. The adsorbing tendency of the acidic alumina might arise from the presence of OH groups on the surface in order to coordinate to the metal ion center (Scheme 1). This hypothesis was further confirmed, when we observed that the complex with three bidentate ligand can not be adsorbed on the acidic alumina surface.

The ratio of ligand to metal was chosen 2:1 with the exception of salen which was 1:1. These complexes were then treated with acidic alumina in order to prepare the supported catalysts. That coordination number of Mn–bipyridine complex was 4 not 6, was realized by observing the metal to ligand charge transfer (MLCT) transitions at 495 and 530 nm. Moreover,  $[\text{Mn}(\text{bpy})_2]\text{Cl}_2\text{-Al}_2\text{O}_3$  was synthesized via two different methods [26–28]. The FTIR spectra and the oxidation results on cyclohexene were shown to be similar.

The activity results of these alumina supported catalysts on the oxidation of cyclohexene with TBHP are given in Tables 1–3. At the end of reaction, the catalyst was separated by filtration, thoroughly washed with solvent and reused under similar conditions. Although the analysis of the recovered catalysts by atomic absorption spectroscopy (AAS) showed no reduction in the amount of manganese, they exhibited a slightly lower catalytic activities.



Scheme 1.

Table 1  
Oxidation of cyclohexene with TBHP catalyzed by Mn(II) complexes on alumina in CH<sub>2</sub>Cl<sub>2</sub>

Catalyst	Conversion (%)	Yield (%)		
		Peroxy <sup>a</sup>	Alcohol <sup>b</sup>	Ketone <sup>c</sup>
MnCl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	29.4	8.1	39.6	52.3
[Mn(acac) <sub>2</sub> ]-Al <sub>2</sub> O <sub>3</sub>	44.3	23.2	28.2	48.6
[Mn(en) <sub>2</sub> ]Cl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	52.1	17.4	26.5	56.1
[Mn(salen)]-Al <sub>2</sub> O <sub>3</sub>	65.8	9.83	18.6	71.57
[Mn(bpy) <sub>2</sub> ]Cl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	73.4	7.2	17.4	75.4

<sup>a</sup> 1-(*tert*-butylperoxy)-2-cyclohexene.

<sup>b</sup> 2-cyclohexene-1-ol.

<sup>c</sup> 2-cyclohexene-1-one.

Table 2  
Oxidation of cyclohexene with TBHP catalyzed by Mn(II) complexes on alumina in cyclohexene

Catalyst	Conversion (%)	Yield (%)		
		Peroxy <sup>a</sup>	Alcohol <sup>b</sup>	Ketone <sup>c</sup>
MnCl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	39.7	7.53	37.3	55.17
[Mn(acac) <sub>2</sub> ]-Al <sub>2</sub> O <sub>3</sub>	47.8	20.1	26.7	53.2
[Mn(en) <sub>2</sub> ]Cl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	59.6	16.2	24.2	59.6
[Mn(salen)]-Al <sub>2</sub> O <sub>3</sub>	81.4	8.73	15.36	75.91
[Mn(bpy) <sub>2</sub> ]Cl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	90.3	6.56	11.34	82.1

<sup>a</sup> 1-(*tert*-butylperoxy)-2-cyclohexene.

<sup>b</sup> 2-cyclohexene-1-ol.

<sup>c</sup> 2-cyclohexene-1-one.

When the oxidant was changed to hydrogen peroxide, the oxidation occurred on the double bond and cyclohexene epoxide obtained as the sole product. It seems that the diol resulted from the epoxide ring opening under the aqueous acidic conditions (Table 4).

Table 3  
Oxidation of cyclohexene with TBHP catalyzed by Mn(II) complexes on alumina in CH<sub>3</sub>CN

Catalyst	Conversion (%)	Yield (%)		
		Peroxy <sup>a</sup>	Alcohol <sup>b</sup>	Ketone <sup>c</sup>
MnCl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	17.6	16.3	43.64	40.1
[Mn(acac) <sub>2</sub> ]-Al <sub>2</sub> O <sub>3</sub>	25.5	31.7	31.41	36.89
[Mn(en) <sub>2</sub> ]Cl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	37.8	26.6	29.33	44.1
[Mn(salen)]-Al <sub>2</sub> O <sub>3</sub>	46.2	20.2	23.52	56.28
[Mn(bpy) <sub>2</sub> ]Cl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	54.3	18.5	20.8	60.7

<sup>a</sup> 1-(*tert*-butylperoxy)-2-cyclohexene.

<sup>b</sup> 2-cyclohexene-1-ol.

<sup>c</sup> 2-cyclohexene-1-one.

Table 4  
Oxidation of cyclohexene with H<sub>2</sub>O<sub>2</sub> catalyzed by Mn(II) complexes on alumina in CH<sub>3</sub>CN

Catalyst	Conversion (%)	Yield (%)	
		Epoxide <sup>a</sup>	Diol <sup>b</sup>
MnCl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	23.1	30.1	69.9
[Mn(acac) <sub>2</sub> ]-Al <sub>2</sub> O <sub>3</sub>	28.6	62.63	37.37
[Mn(en) <sub>2</sub> ]Cl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	34.2	81.42	18.58
[Mn(salen)]-Al <sub>2</sub> O <sub>3</sub>	56.4	68.91	31.09
[Mn(bpy) <sub>2</sub> ]Cl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	63.7	37.67	62.33

<sup>a</sup> Cyclohexene-oxide.

<sup>b</sup> Cyclohexene-1,2-diol.

Since both H<sub>2</sub>O<sub>2</sub> and TBHP oxidize cyclohexene in the presence of alumina-supported manganese complexes, but that only H<sub>2</sub>O<sub>2</sub> and not TBHP, gave epoxidation of cyclohexene under the similar conditions leads us to conclude that the two types of reactions do not occur via a common intermediate (Table 4, Fig. 1).

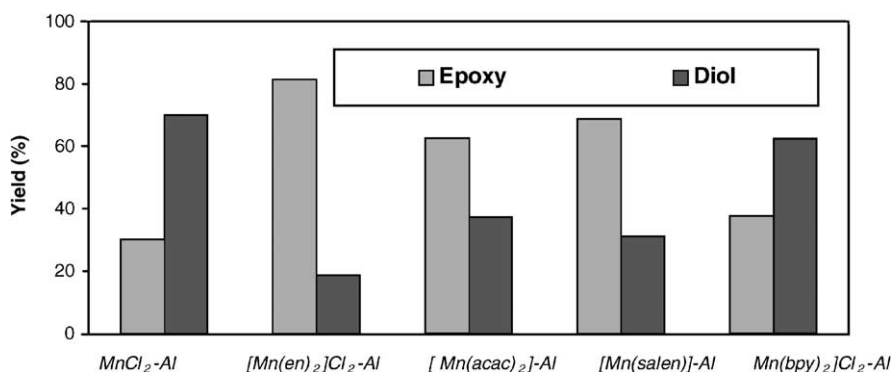


Fig. 1. Oxidation products distribution in cyclohexene with Mn<sup>2+</sup> complexes on Al<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>.

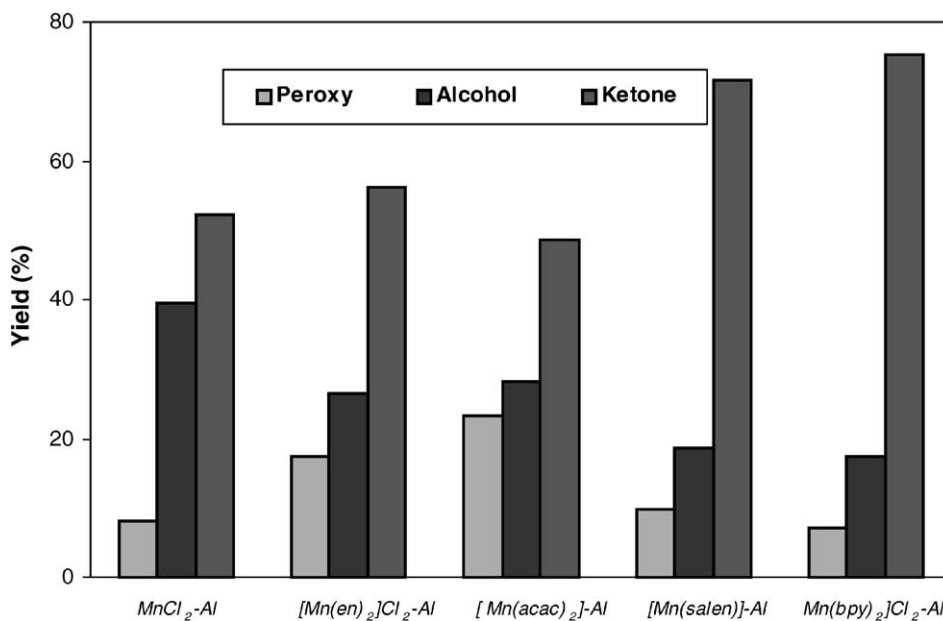


Fig. 2. Oxidation products distribution in dichloromethane with Mn<sup>2+</sup> complexes on Al<sub>2</sub>O<sub>3</sub>/TBHP.

As Valentine and his co-workers have pointed out one possible explanation is that the species responsible for the cyclohexene oxidation are the products formed from cleavage of the O–O bond, whereas, the epoxidation reaction occurs by a direct reaction of olefin

with coordinated HOO radical. Since the O–O bond of HOOH is 5 kcal/mol stronger than that of TBHP, an HOO<sup>−</sup> complex is expected to have a higher activation energy for O–O bond cleavage than a TBOO<sup>−</sup> complex and therefore, to have a longer lifetime [29].

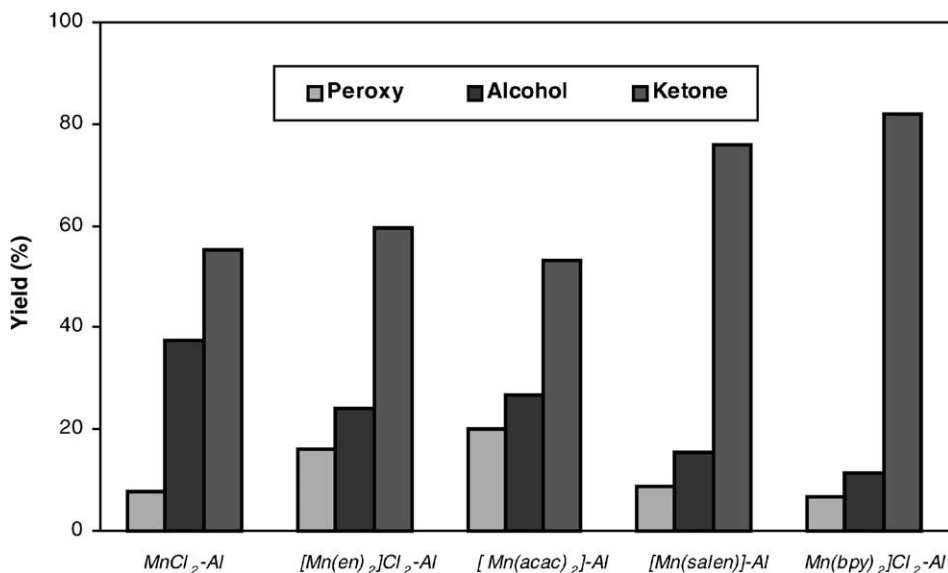


Fig. 3. Oxidation products distribution in cyclohexene with Mn<sup>2+</sup> complexes on Al<sub>2</sub>O<sub>3</sub>/TBHP.

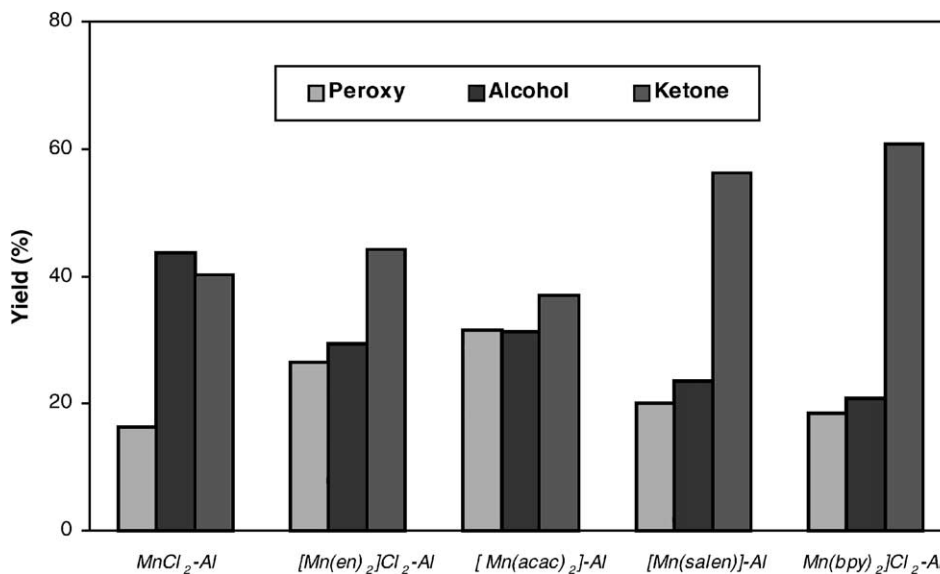


Fig. 4. Oxidation products distribution in acetonitrile with  $Mn^{2+}$  complexes on  $Al_2O_3/TBHP$ .

The trend observed in Figs. 2–4 can be explained on the donor ability of ligands available in the complex catalysts. As Wang and co-workers have pointed out recently in a work similar to our study, the key point in the conversion of cyclohexene to cyclohexene oxide is the reduction of  $L-Mn^{3+}$  to  $L-Mn^{2+}$ . The conversion of  $L-Mn^{2+}$  to  $L-Mn^{3+}$  is facilitated with the system ligands available around the metal cation [30].

When the reaction was carried out in acetonitrile as solvent, the conversion percentages decreased by a factor of 1.2–1.7 (Table 3). This might be attributed to the donor number of acetonitrile (14.1) and therefore, its higher ability to occupy the vacant spaces around the metal center and prevent the approaching of oxidant molecules toward the catalyst center.

#### 4. Conclusion

In this study, we have used a rather simple catalysis system of alumina-supported manganese(II) complexes with a number of bidentate ligands of  $N,N$ ;  $N,O$  of and  $O,O$  atoms in the oxidation of cyclohexene. Oxidation of allylic site and double bond were resulted with the oxidants of TBHP and  $H_2O_2$ , respectively.

The high percentage yield of reactions especially in the presence of alumina-supported manganese bipyridine complex seems promising. The extension of the method to different olefins is currently under investigation in our laboratory.

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