

Oxidation of cyclohexene with *tert*-butylhydroperoxide catalyzed by manganese(II) complexes included in zeolite Y

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Abstract

Mn(II) complexes with ligands of ethylenediamine, tetramethylethylenediamine, 2,2'-bipyridine, tetramethyl-1,8-naphthalenediamine included in zeolite Y were used for oxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP) as oxidant in CH₂Cl₂, CH₃OH, C₂H₅OH, CH₃COCH₃ and CH₃CN. The di(2-cyclohexenyl) ether was identified as the main product. 2-Cyclohexenone and 2-cyclohexene-1-ol were obtained as minor products. It was also found that Mn(bipy)₂²⁺-Y in CH₃OH and CH₃CN had the highest reactivity (98%), although the selectivity was 95% in CH₃OH toward the formation of ether product. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Mn(II) complexes; Zeolite-Y; Oxidation of cyclohexene

1. Introduction

Catalytic oxidation is a major route for the industrial synthesis of functionalized hydrocarbons [1–5]. Oxidation is also one of the most important reactions for the metabolism of biotic substrates and many enzymes are known to catalyze various types of oxidation [6]. The desire to mimic enzymatic systems has prompted an extensive area of research into synthetic porphyrin, phthalocyanine, and Schiff base models of enzyme active sites, especially for monooxygenase enzymes of the cytochrome P-450 family [7–10].

Nowadays, a similar approach has developed on the replacement of the protein portion of natural enzymes by a zeolite framework, which is able to imitate its major function such as shape selectivity and protection of the hem group [11–13].

Using Y-zeolite-encaged complexes contain a variety of different advantages like broad-range application of solvents, inhibition of side reactions, the exertion of shape selectivity of zeolite framework and so on.

2. Experimental

2.1. Materials

All the materials were of commercial reagent grade. TBHP (70% in water) was purchased

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Table 1

Oxidation of cyclohexene with TBHP catalyzed by MnY and [Mn(N-N)₂]⁺²-Y zeolite in CH₂Cl₂

Catalyst	Conversion (%)	Yield (%)			
		peroxide	alcohol	ketone	ether
MnY	51.4	9.78	8.72	33.99	47.51
[Mn(en) ₂] ⁺² -Y	79.1	3.63	5.42	10.52	80.43
[Mn(tmen) ₂] ⁺² -Y	77.8	3.17	5.19	8.57	83.1
[Mn(bpy) ₂] ⁺² -Y	89.32	4.02	3.1	2	91.11
[Mn(phen) ₂] ⁺² -Y	73.4	4.83	11.24	16.95	66.97

Table 2

Oxidation of cyclohexene with TBHP catalyzed by MnY and [Mn(N-N)₂]⁺²-Y zeolite in ethanol

Catalyst	Conversion (%)	Yield (%)			
		peroxide	alcohol	ketone	ether
MnY	57.1	13.96	19.38	–	66.66
[Mn(en) ₂] ⁺² -Y	84.2	5.58	7.27	–	87.2
[Mn(tmen) ₂] ⁺² -Y	80.34	4.69	9.49	–	85.82
[Mn(bpy) ₂] ⁺² -Y	98.1	5.23	5.87	–	88.9
[Mn(phen) ₂] ⁺² -Y	90.33	6.94	10.2	7.7	75.12

from Merck and extraction to the organic phase (methylene chloride) was carried out according to the standard procedure [14].

2.2. Physical measurements

The products were analyzed by GC and 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.

2.3. Preparation of zeolite catalysts

2.3.1. Preparation of MnY

MnY catalysts were prepared and activated according to the procedure described previously [15]. The concentration determination of filtrate solution showed that about 1 mmol of the ion per gram of zeolite has been exchanged.

2.3.2. Preparation of Mn(II) complexes included in zeolite Y; general procedure [16]

One gram of the dried and activated MnY was ground (or mixed in the case of liquid ligands) with 2.176 mmol of the desired ligand. The mixture was then heated at 90°C for 24 h under N₂ atmosphere. The catalyst was then cooled and soxhlet extracted with CH₂Cl₂ to remove unreacted ligands. It was then dried again under N₂ at 125°C for several hours.

2.4. Oxidation of cyclohexene; general procedure

A mixture of 0.5 g catalyst, 25 ml CH₂Cl₂ and 10 mmol cyclohexene was stirred under nitrogen in a 50-ml round-bottom flask equipped with a condenser and a dropping funnel at 40°C for 30 min. Then 16 mmol of TBHP solution in CH₂Cl₂ was added. The resulting mixture was

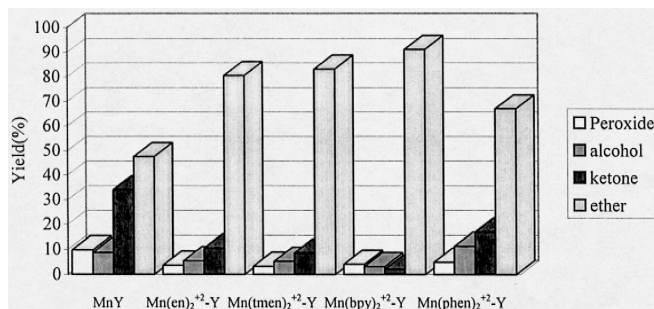


Fig. 1. Oxidation products distribution in dichloromethane with Mn(II) complexes in zeolite Y.

Table 3

Oxidation of cyclohexene with TBHP catalyzed by MnY and [Mn(N-N)₂]²⁺-Y zeolite in methanol

Catalyst	Conversion (%)	Yield (%)			
		peroxide	alcohol	ketone	ether
MnY	53.2	21.7	20.17	–	58.17
[Mn(en) ₂] ²⁺ -Y	71.1	5.21	8.92	9.19	76.68
[Mn(tmen) ₂] ²⁺ -Y	69.4	4.15	7.02	9.48	79.35
[Mn(bpy) ₂] ²⁺ -Y	98.4	2.82	–	2	95.18
[Mn(phen) ₂] ²⁺ -Y	88	4.1	6.2	33.04	56.73

then refluxed for 8 h under N₂ atmosphere. After filtration and washing with solvent, the filtrate was concentrated on a rotary evaporator and then subjected to GC analysis.

3. Results

3.1. Catalytic oxidation of cyclohexene

Oxidation of cyclohexene with TBHP in CH₂Cl₂ in the presence of catalyst yielded di(2-cyclohexenyl) ether as the main product. 1-(*tert*-butyl peroxy)-2-cyclohexene, 2-cyclohexene-1-ol and 2-cyclohexenone were also identified as minor products as shown in Table 1 and Fig. 1.

3.2. The effect of solvent

The effect of solvents of methanol, ethanol, acetone and acetonitrile on the oxidation of

Table 4

Oxidation of cyclohexene with TBHP catalyzed by MnY and [Mn(N-N)₂]²⁺-Y zeolite in acetone

Catalyst	Conversion (%)	Yield (%)			
		peroxide	alcohol	ketone	ether
MnY	60.56	11.95	13.41	11.1	63.54
[Mn(en) ₂] ²⁺ -Y	74.1	3.43	4.92	12.33	79.32
[Mn(tmen) ₂] ²⁺ -Y	72.56	3.97	5.82	9.73	80.49
[Mn(bpy) ₂] ²⁺ -Y	84.5	0.5	2.31	10.8	86.5
[Mn(phen) ₂] ²⁺ -Y	68.1	5.74	7.34	17.12	69.79

Table 5

Oxidation of cyclohexene with TBHP catalyzed by MnY and [Mn(N-N)₂]²⁺-Y zeolite in acetonitrile

Catalyst	Conversion (%)	Yield (%)			
		peroxide	alcohol	ketone	ether
MnY	56.84	21.38	6.11	6.45	66.1
[Mn(en) ₂] ²⁺ -Y	92.32	12.16	4.25	9.6	73.95
[Mn(tmen) ₂] ²⁺ -Y	87.5	12.48	3.7	7.92	75.89
[Mn(bpy) ₂] ²⁺ -Y	98.5	9.52	3.02	8.46	79
[Mn(phen) ₂] ²⁺ -Y	95.4	12.74	2.3	13.77	71.19

cyclohexene with TBHP in the presence of catalysts are provided in Tables 2–5 and Fig. 2.

3.3. The effect of time

The effect of time on cyclohexene oxidation with TBHP in acetonitrile and in the presence of catalyst were studied. The results are shown in Table 6 and Fig. 3.

4. Discussion

In the present investigation, the oxidation of cyclohexene has been carried out under the catalytic effect of Mn(II) complexes in zeolite Y

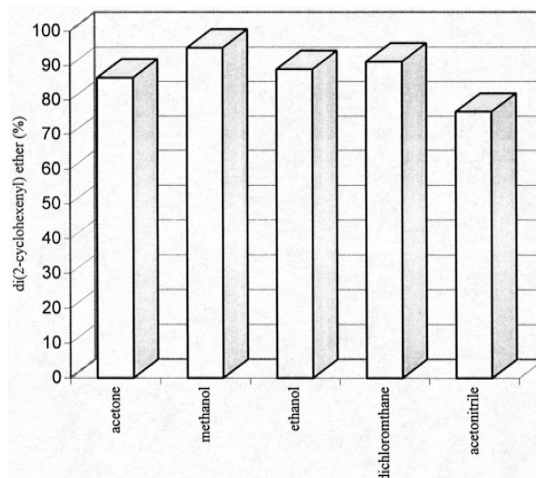


Fig. 2. Effects of solvent on the percentage yield of ether in the presence of Mn(bpy)₂²⁺-Y.

Table 6

Effect of time on the oxidation of cyclohexene with TBHP in the presence of MnY and $[\text{Mn}(\text{N}-\text{N})_2]^{2+}\text{-Y}$

Catalyst	Time (h)	Yield (%)				
		conversion (%)	peroxide	alcohol	ketone	ether
MnY	4	32.1	29.7	7.08	8.5	54.7
MnY	6	45.6	24.2	6.62	8.75	61.64
MnY	8	56.84	21.38	6.11	6.45	66.11
$[\text{Mn}(\text{en})_2]^{2+}\text{-Y}$	4	63.1	12.28	5.34	9.5	72.91
$[\text{Mn}(\text{en})_2]^{2+}\text{-Y}$	6	74.1	12.22	4.8	9.4	73.5
$[\text{Mn}(\text{en})_2]^{2+}\text{-Y}$	8	92.32	12.16	4.25	9.6	73.95
$[\text{Mn}(\text{tmen})_2]^{2+}\text{-Y}$	4	58.6	12.49	4.53	9.27	73.7
$[\text{Mn}(\text{tmen})_2]^{2+}\text{-Y}$	6	70.8	12.43	4.1	8.7	74.7
$[\text{Mn}(\text{tmen})_2]^{2+}\text{-Y}$	8	87.5	12.48	3.7	7.92	75.89
$[\text{Mn}(\text{bpy})_2]^{2+}\text{-Y}$	4	80.3	10.6	4.1	11.83	73.5
$[\text{Mn}(\text{bpy})_2]^{2+}\text{-Y}$	6	91.3	9.96	3.65	9.8	76.55
$[\text{Mn}(\text{bpy})_2]^{2+}\text{-Y}$	8	98.5	9.52	3.02	8.46	79
$[\text{Mn}(\text{phen})_2]^{2+}\text{-Y}$	4	71.4	12.95	3.2	17.2	66.63
$[\text{Mn}(\text{phen})_2]^{2+}\text{-Y}$	6	83.2	12.82	2.8	15.3	69.08
$[\text{Mn}(\text{phen})_2]^{2+}\text{-Y}$	8	95.4	12.74	2.3	13.77	71.19

with TBHP. We recently reported the oxidation of cyclohexene with the same oxidant in the presence of exchanged zeolite NaY with transition metal elements Cr (III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) [17]. We showed later that the similar model system of MY is catalytically active on the oxidation of cyclohexene with TBHP [18]. We also showed that some complexes of Mn(II) included in zeolite Y catalyze the oxygen transfer from TBHP to cyclohexene and concluded that such simple system mimics the behavior of cytochrome P-450 type oxidation system. The enhancement of conversion percentage from 2.4% to 60% was attributed to the effect of ligand either on the increasing electron transfer from Mn(II) com-

plex or stabilizing the oxidized metal formed during the formation of metal–peroxide complex intermediate [18]. Based on these results, it was of interest for us to study the catalytic effect of similar complexes on the oxidation of cyclohexene. This was due to the recent reports in developing catalysts like manganese porphyrin capable of carrying out oxygenation reactions, selectively and under mild conditions [19].

Synthesis of complexes of manganese(II) with bipyridine (bpy), ethylene-diamine (en), tetraethylethylenediamine (tmen) and tetramethyl-1,8-naphthalenediamine (tmnda) and their inclusion in zeolite Y were carried out according to the procedure described before [18]. The structure of complexes were assigned as $\text{Mn}(\text{bpy})_2^{2+}\text{-Y}$, $\text{Mn}(\text{en})_2^{2+}\text{-Y}$, $\text{Mn}(\text{tmen})_2^{2+}\text{-Y}$ respectively [16].

The effect of Mn(II) complexes included in zeolite Y were studied on the oxidation of cyclohexene with TBHP in methylene chloride and the results are shown in Table 1. As is shown in Fig. 1, the allylic oxidation has occurred with the formation of 2-cyclohexene-1-ol, 2-cyclohexenone, 1-(*tert*-butyl peroxy)-2-cyclohexene and di(2-cyclohexenyl) ether. The activity of MnY catalyst has also been included

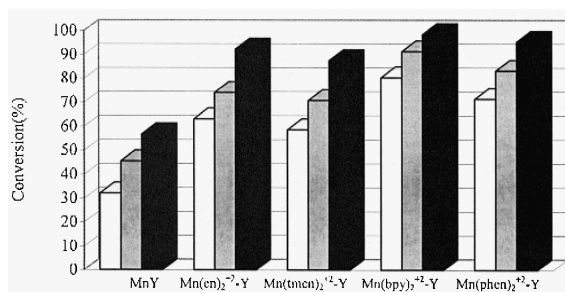


Fig. 3. Effect of time on the oxidation of cyclohexene with TBHP in acetonitrile.

in Table 1 and Fig. 1 to compare the effect of the ligand on the activity of catalyst. The increase of conversion percentage from 57.76% to 89.32% compared to MnY with $\text{Mn}(\text{bpy})_2^{2+}\text{-Y}$ indicates that the existence of ligand has increased the activity of catalyst by a factor of 1.6. From the results indicated in Table 1, it is evident that ether has been formed selectively in the presence of all catalysts although $\text{Mn}(\text{bpy})_2^{2+}\text{-Y}$ shows the most tendency toward the formation of this product. In the present study, it is observed that compared to the MY catalyst system, the ketone yield is lower and the reaction has led mostly to the formation of alcohol and ether.

As was suggested before, the ether product has arisen from the etherification of 2-cyclohexene-1-ol [20]. This idea was confirmed by using 2-cyclohexene-1-ol instead of cyclohexene as starting material and observing the formation of the ether as the main product under the reaction conditions. That the acidity of zeolite catalyst has catalyzed the formation of di(2-cyclohexenyl) ether was ruled out since there was hardly any reaction in the absence of oxidant under our reaction conditions. Therefore, the combination of zeolite catalyst and oxidant has been responsible for the conversion of alcohol to the ether product.

As we mentioned in our previous paper, one can draw a plausible mechanism on the basis of allylic position oxidation [17]. That TBHP as oxidant promotes allylic position oxidation pathway and epoxidation route is minimized, especially under the highly acidic properties of zeolite Y exchanged with divalent and trivalent transition metal ions, has been observed by us and others [17,21]. It should be emphasized that the destructive oxidation of alkenes via epoxidation pathway with hydrogen peroxide under the catalytic effect of zeolite-encapsulated Mn(II) complexes seems interesting [16]. Although the two systems are alike, it is the oxidant structure that has changed the fate of the reaction. Such a conclusion can be drawn based on recent communication concerning the epoxidation of cyclo-

hexene under the effect of a manganese(II)–Schiff base complex supported on clay [19]. The authors have shown that epoxidation is the main path if iodosylbenzene, hypochlorites, *p*-cyano-*N,N*-dimethylaniline *N*-oxide and perhalates are used as oxidants. However, with TBHP, two competing reactions of epoxidation and homolytic decomposition of the hydroperoxide with the subsequent oxidation on the allylic position will occur. Moreover, Nam et al. [22] have observed that in contrast to the hydrogen peroxide which catalytically oxidizes cyclohexene mainly to the corresponding epoxide, alkyl hydroperoxides gave only allylic oxidation products. The authors have concluded that the two types of reactions do not occur via a common intermediate [22].

To investigate the role of solvent on the fate of reaction and product distribution, we carried out the reaction in two groups of protic and aprotic solvents. The results are given in Tables 2–6. From these results, it is evident that polar protic solvents of methanol and ethanol and polar aprotic solvent of acetonitrile have presented the best media for $\text{Mn}(\text{bpy})_2^{2+}\text{-Y}$ catalyst (see Fig. 2), since the conversion has occurred about 98%. Although methanol ($\epsilon = 32.70$) is more polar than ethanol ($\epsilon = 24.55$), the former is a stronger acid (see their $\text{p}K_a$) [23,24]. Therefore, methanol with its higher hydrogen bond donor acidity parameter ($\alpha = 0.98$) provides a medium similar to that of ethanol, since the latter which is a weaker acid has lower hydrogen bond donor acidity parameter ($\alpha = 0.85$) [25]. On the other hand, compared to acetone with donor number of 17.0, acetonitrile has a donor number of 14.1 and because it is more polar than acetone ($\epsilon_{\text{acetonitrile}} = 37.5$, $\epsilon_{\text{acetone}} = 20.70$), the oxidation take place faster in this solvent.

As mentioned before [17], the higher activity of $\text{Mn}(\text{bpy})_2^{2+}\text{-Y}$ complex might be attributed to the higher activity of aromatic ligand and its more active π -cation radical intermediate with respect to the aliphatic ligand system (ethylenediamine with the conversion percentage of

84.2% in ethanol). The lower activity of $\text{Mn}(\text{tmnda})_2^{2+}\text{-Y}$ can be accounted for by the substantial steric hindrance of methyl groups that prevent the approaching oxidant toward the central metal of the catalyst.

As shown in Fig. 2, $\text{Mn}(\text{bpy})_2^{2+}\text{-Y}$ shows the highest activity in all the different solvent systems. Moreover, the ether product has been selectively formed under the effect of this catalyst from 79% to 95%. Since ether has arisen from the etherification of 2-cyclohexene-1-ol, (see above), and maximum percentage resulted in methanol, it can be concluded that the catalyst $\text{Mn}(\text{bpy})_2^{2+}\text{-Y}$ presents the strongest acidic medium in this reaction.

The effect of time on the reactivity of catalysts is shown in Table 6. Acetonitrile was selected as solvent for this experiment because all four products have been formed under this solvent medium effect. Table 6 shows that during 8 h, maximum conversion of starting material takes place with all catalyst systems.

5. Conclusion

The oxidation of cyclohexene with TBHP and Mn complexes included in zeolite Y selectively affords di(2-cyclohexenyl) ether as the main product. Our studies show that the oxidation exclusively occurs on the allylic position. We believe that the combination of a catalyst and oxidant system like $\text{Mn}(\text{bpy})_2^{2+}\text{-Y}$ and TBHP in a common and highly used solvent like methanol provides a simple route to the allylic site oxidation of cyclohexene. Studies on other olefins are currently under investigation in our laboratory and we believe that the observation of similar results on other olefins is not unexpected.

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