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Selective hydroxylation of cyclic ethers with *tert*-butylhydroperoxide and hydrogen peroxide catalyzed by iron(III) and manganese(II) bipyridine complexes included in zeolite Y and bentonite

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Abstract

The oxidation of cyclic ethers such as tetrahydrofuran (THF), tetrahydropyran (THP), 2,3-dihydropyran (DHP) and 1,4-dioxan (DO), with hydrogen peroxide (H_2O_2) and *tert*-butylhydroperoxide (TBHP) in the presence of iron(III) and manganese(II) bipyridine complexes included in zeolite Y and bentonite are described. The products are mainly cyclic ether-2-ols and cyclic ether-2-ones with minor amounts of 2,3-dihydrocyclic ether. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxylation; Cyclic ethers; Zeolite Y; Bentonite

1. Introduction

Transition metal ions exchanged with zeolites have been used frequently in catalytic oxidative functionalization of C–H bands either α to a double bond (allylic position) or of a saturated hydrocarbon [1–6].The key point in designing of such catalysis systems are based on the remarkable ability of Cytochrome P-450 to activate dioxygen with resultant oxygen transfer to unreactive C–H bonds of organic substrates [7].

In recent years, oxidation of ethers catalytically and photochemically with the formation of corresponding esters or acids have been reported [8–10]. We envisaged that similar oxidation with H_2O_2 and TBHP in the presence of our recent reported zeolite catalysis system can be efficiently carried out under mild conditions [11–13]. With the exception of 1,4-dioxane, cyclic ether-2-ols were formed as the major product which is in contrast to the previously reports that cyclic ether-2-ones were almost resulted from the oxidation of cyclic ethers.

2. Experimental

2.1. Materials

All the materials were of commercial reagent grade. Cyclic ethers were purified by standard procedures.

2.2. Preparation of catalysts

2.2.1. Preparation of MY catalysts

These catalysts were prepared and activated according to the procedure described previously [11]. Analysis of the filtrate solution showed that about

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1 mmol of the ion per each gram of zeolite has been exchanged.

2.2.2. Preparation of M-bentonite catalysts

Bentonite (Fluka) was activated with 1 M NaCl solution before using 5 g of Na-bentonite was slowly added to 0.06 M solution of the metal salt (FeCl$_3$ and MnCl$_2$) in 100 ml methanol. The suspension was stirred at room temperature for 21 h. The colored solid was filtered, washed with methanol and dried at 50°C under vacuum.

2.2.3. Preparation of M(bpy)$_2{}^{n+}$-Y catalysts (M = Mn^{2+}, Fe^{3+})

These catalysts were prepared and dried according to the procedure described previously [12].

2.2.4. Preparation of M(bpy)$_2{}^{n+}$-bentonite catalysts (M = Mn^{2+}, Fe^{3+})

About 1 g of M-bentonite was added to a solution of 2,2-bipyridine (2.176 mmol) in 100 ml CH$_2$Cl$_2$. The suspension was heated under reflux condition for 24 h. The solid was separated, washed with CH$_2$Cl$_2$ and then soxhlet extracted with CH$_2$Cl$_2$ to remove unreacted ligands. It was then dried at 125°C under nitrogen atmosphere for several hours.

2.3. Oxidation of cyclic ethers; general procedure

In a typical procedure, a mixture of catalyst (0.5 g) and cyclic ether (0.05 mol) was stirred in a 50 ml round bottom two-necked flask equipped with a condenser and dropping funnel for 30 min, under nitrogen atmosphere. Then 0.05 mol of the oxidant (TBHP, 70% in H$_2$O or H$_2$O$_2$, 30% in H$_2$O) was added through the dropping funnel. The mixture was then refluxed for 8 h. After filtration and washing with solvent, the filtrate was subjected to GC (Philips, Pu-4400 chromatograph, 1.5 m, 3% OV-17 column) and GC–MASS (Varian 3400 chromatograph, 25 m CBP-5 column coupled with a QP 1100EX MAT INCOF 50, 70 eV).

3. Results and discussion

In our recent publications, we reported the role of some transition metals and their complexes included within zeolite Y as catalysts in the oxidation of cyclohexane and cyclohexene [11–13]. In both cases, it was observed that these catalysts were able to transfer oxygen from TBHP to substrate and hydroxylate the hydrocarbons. Since the oxidation of cyclic ethers either in the presence of titanium silicate and H$_2$O$_2$ [8] or photochemically with benzil and dioxygen [10] was shown to lead almost to the corresponding lactones, we decided to investigate these oxidation reactions with the aid of our recent reported catalysis systems.

Table 1 shows the substrate conversions and product percentages of oxidation of some cyclic ethers with H$_2$O$_2$ in the presence of Fe^{3+}, [Fe(bpy)$_2$]$^{3+}$-Y, Fe^{3+}-bentonite, and [Fe(bpy)$_2$]$^{3+}$-bentonite. We included the results with bentonite catalysts in order to compare two systems. As is shown in Fig. 1, using metal complex exchanged in zeolite or bentonite enhanced the conversion percentage especially in the case of THF. It is evident that in most cases, cyclic ether-2-ol has been formed as the major product.

The formation of cyclic ether-2-ol implicates the existence of putative [(L)Fe^V=O] intermediate which appear to drive from the heterolytic cleavage of H$_2$O$_2$ by catalyst [14]. Hydrogen abstraction by the [(L)Fe^V=O] species generates [(L)Fe^{IV}–OH···•S] in the solvent cage (S denotes the substrate). The transient radical would then have the choice of combining with OH in the cage and forming cyclic ether-2-ol or diffuses out of the cage and forming 2,3-dihydrocyclic ether. On the basis of results shown in Table 2, the formation of cyclic ether-2-one could have arisen from the oxidation of cyclic ether-2-ol under the reaction conditions [11–13] although its partly formation through the cyclic ether without the intermediacy of cyclic ether-2-ol can not be ruled out [15].

The effects of the complexes of iron instead of lone metal inside the zeolite supercages and increasing the conversion percentage can be attributed to the effect of bipyridine ligand. As L. Que and his co-workers have explained, the greater basicity of the ligands may help to stabilize the putative [(L)Fe^V=O] intermediate [14].

The results obtained from the oxidation of cyclic ethers with H$_2$O$_2$ in the presence of iron and its bipyridine complex included within bentonite are listed in Table 1. It can be seen that both reactivity and selectivity are improved. These might have happened since more available space between the layers of bentonite

Table 1
Substrate conversions and product selectivities in the oxidation of cyclic ethers with H_2O_2 in the presence of iron(III) catalysts[a]

Substrate	Catalyst	Conversion (%)	Yield (%)		
			1	2	3
THF	Fe^{3+}-Y	52.1	82.1	10.8	7.1
THF	$[Fe(bpy)_2]^{3+}$-Y	59	87.1	9.4	3.5
THF	Fe^{3+}-bentonite	76.3	79	11.3	9.7
THF	$[Fe(bpy)_2]^{3+}$-bentonite	91	94.4	3.8	1.8
THP	Fe^{3+}-Y	41	69.9	24.5	5.6
THP	$[Fe(bpy)_2]^{3+}$-Y	49.3	77.7	19.2	3.1
THP	Fe^{3+}-bentonite	53.7	55	34	11
THP	$[Fe(bpy)_2]^{3+}$-bentonite	59.5	90.2	7.3	2.5
DHP	Fe^{3+}-Y	68	28.6	34.1	–
DHP	$[Fe(bpy)_2]^{3+}$-Y	78.1	39.4	28.1	–
DHP	Fe^{3+}-bentonite	71.5	22.6	38.5	–
DHP	$[Fe(bpy)_2]^{3+}$-bentonite	89.1	51.6	21.6	–
DO	Fe^{3+}-Y	6.2	2.1	95.1	–
DO	$[Fe(bpy)_2]^{3+}$-Y	8.4	1.3	93.6	–
DO	Fe^{3+}-bentonite	9.8	–	100	–
DO	$[Fe(bpy)_2]^{3+}$-bentonite	11.3	–	100	–

[a] THF: tetrahydrofuran; THP: tetrahydropyran; DHP: dihydropyran; DO: 1,4-dioxan; (1) cyclic ether-2-ol; (2) cyclic ether-2-one; (3) 2,3-dihydro cyclic ether.

accommodates a higher concentration of the oxidative catalysis molecules.

Using TBHP as oxidant in the presence of iron(III) ion or its bipyridine complex included in zeolite Y or bentonite did not show an efficient reaction. This might be explained by the fact that TBHP undergoes a homolytic cleavage and forms a *tert*-BuO radical as the active species instead of the expected $[(L)Fe^V=]$ intermediate [16].

The compatibility of iron(III) ion and its bipyridine complexes included within zeolite Y or bentonite was reversed when Mn(II) ion was substituted
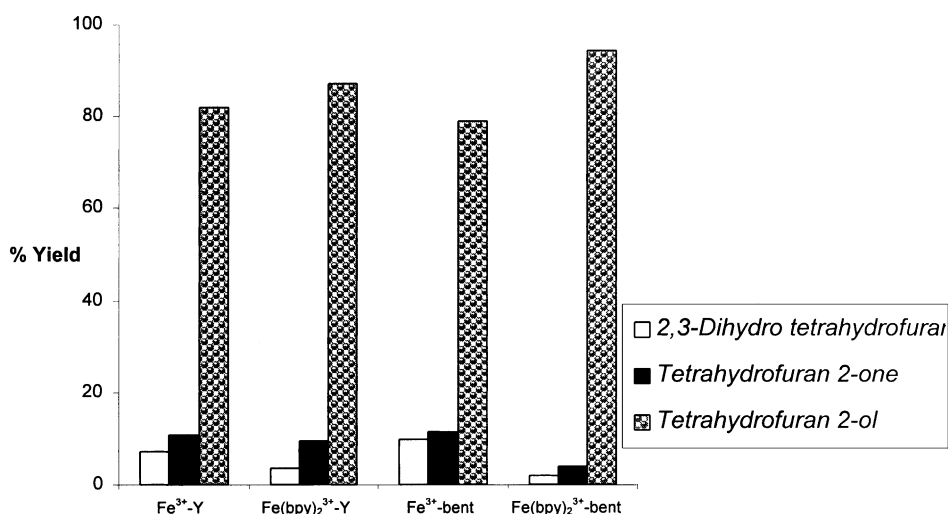

Fig. 1. Oxidation products distribution of THF with iron catalyst.

Table 2
Effect of time on the oxidation of THF with H_2O_2 in the presence of iron(III) catalysts[a]

Substrate	Catalyst	Time (h)	Conversion X (%)	Yield (%)		
				1	2	3
1	Fe^{3+}-Y	4	37.4	89.7	7.1	3.2
2	Fe^{3+}-Y	6	46.3	86.3	8.3	5.4
3	Fe^{3+}-Y	8	52.1	82.1	10.8	7.1
4	$[Fe(bpy)_2]^{3+}$-Y	4	39.6	91.4	7.3	1.3
5	$[Fe(bpy)_2]^{3+}$-Y	6	48.5	89.3	8.6	2.1
6	$[Fe(bpy)_2]^{3+}$-Y	8	59	87.1	9.4	3.5
7	Fe^{3+}-bentonite	4	58.6	86.8	9.2	4.0
8	Fe^{3+}-bentonite	6	69	82.8	10.1	7.1
9	Fe^{3+}-bentonite	8	76.3	79	11.3	9.7
10	$[Fe(bpy)_2]^{3+}$-bentonite	4	73.4	97.3	1.9	0.75
11	$[Fe(bpy)_2]^{3+}$-bentonite	6	86.3	96.7	2.1	1.2
12	$[Fe(bpy)_2]^{3+}$-bentonite	8	91.0	94.4	3.8	1.8

[a] (1) Tetrahydrofuran-2-ol; (2) tetrahydrofuran-2-one; (3) 2,3-dihydrofuran.

with iron(III) in the system. In other words, while TBHP/Mn(II) combination system catalyze the oxidation process efficiently, H_2O_2/Mn(II) pair system is almost unable to catalyze the same oxidation reaction. The results are listed in Table 3 and Fig. 2. Comparison of the results of Tables 1 and 3 indicates that with a few exceptions, iron(III) system displays better

oxidation reactivity and selectivity than manganese(II) system.

The formation of 2-cyclic ether *tert*-butyl peroxide in low to moderate amount of 3–25% (see Table 3) clearly indicate that a radical pathway at least partly is operative in the case of THF and THP substrates. This conclusion is based on the fact that the peroxide

Table 3
Substrate conversion and product selectivities in the oxidation of cyclic ethers with TBHP in the presence of manganese(II) catalysts[a]

Substrate	Catalyst	Conversion (%)	Yield (%)			
			P	A	B	C
THF	Mn^{2+}-Y	45	3.2	4.1	8.3	84.4
THF	$[Mn(bpy)_2]^{2+}$-Y	57	14.2	3.2	7.1	75.5
THF	Mn^{2+}-bentonite	63	4.5	5.2	12.1	78.2
THF	$[Mn(bpy)_2]^{2+}$-bentonite	71.3	17.1	1.2	6.5	75.2
THP	Mn^{2+}-Y	21.3	12.3	–	18.5	11.3
THP	$[Mn(bpy)_2]^{2+}$-Y	38.5	17.1	–	26.5	18.2
THP	Mn^{2+}-bentonite	49.6	13.2	–	3.1	12.1
THP	$[Mn(bpy)_2]^{2+}$-bentonite	54.5	24.7	–	8.2	58.3
DHP	Mn^{2+}-Y	57.6	43.2	–	31.5	12
DHP	$[Mn(bpy)_2]^{2+}$-Y	63.4	55.3	–	42	1.1
DHP	Mn^{2+}-bentonite	62.5	45.6	–	34.2	7.5
DHP	$[Mn(bpy)_2]^{2+}$-bentonite	76.7	60.1	–	30.2	9
DO	Mn^{2+}-Y	15	50.3	–	31.4	1.3
DO	$[Mn(bpy)_2]^{2+}$-Y	21.2	72	–	12.1	2.1
DO	Mn^{2+}-bentonite	17.5	56	–	23	3.2
DO	$[Mn(bpy)_2]^{2+}$-bentonite	25.1	75	–	16.1	4.5

[a] THF: tetrahyrofuran; THP: tetrahydropyran; DHP: dihydropyran; DO: 1,4-dioxane; P: peroxy cyclic ether; A: 2,3-dihydro tetrahydrofuran; B: tetrahydrofuran-2-one; C: tetrahydrofuran-2-ol.
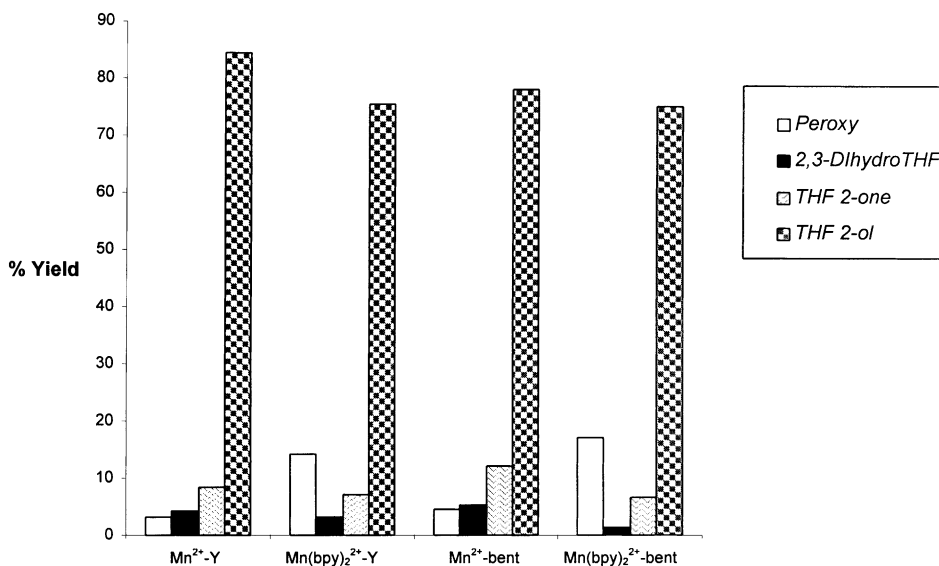
Fig. 2. Oxidation products distribution of THF with manganese catalyst.

formation implicates the intermediacy of *tert*-BuO and *tert*-BuOO radicals that can be generated by the homolytic cleavage and results in the active *tert*-BuOO intermediate [14]. The simultaneous operation of the Haber–Weiss reaction can not be ruled out [12]. In this mechanism, metal ions undergo one-electron oxidation and reduction [17]. Since peroxide products have been formed in the higher amount of DHP and DO, the exclusive operation of a radical mechanism seems likely, that radicals generated by DHP and DO are more stable than those resulted from THF and THP seems resonable since the presence are of either a double bond. This in turn facilitates the conversion rate of tight transient radical to a free radical that combines easily with *tert*-BuOO species available in solution [18].

Finally, we can draw the following conclusions on the basis of these results:

- The activity of THP is less than THF. This might be attributed to the better co-planarity of five-membered ring transition state in THF for hydrogen abstraction, since this step was shown to be the rate-determining step on the basis of kinetic isotope experiments [19].
- DHP shows lower reactivity with respect to THF since DHP with its double bond is more electron

donating and therefore stabilizes the putative iron-oxo intermediate better than THF. This in turn retards the reaction rate [14].
- 1,4-Dioxane shows the least reactivity in both systems. This can be attributed to the electronegativity of the second oxygen in the molecule that decreases the tendency for the complexation with the metal center during the hydrogen abstraction. The smaller donation number of 1,4-dioxane (DN = 14.8) than tetrahydrofuran (DN = 20.0) supports this proposal [20].

4. Conclusion

In this study, we have developed a simple procedure for the oxidation of cyclic ethers to the corresponding hemiacetals and lactones. The mildness and selectivity character of our catalysis model is promising and is recommended for oxidation processes.

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