

# Catalytic activity of manganese(III)-oxazoline complexes in urea hydrogen peroxide epoxidation of olefins: The effect of axial ligands

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## Abstract

The catalytic activity of two manganese(III)-oxazoline complexes  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  and  $\text{Mn}(\text{phox})_3$  (Hphox = 2-(2'-hydroxy-phenyl)oxazoline), was studied in the epoxidation of various olefins. All of epoxidation reactions were carried out in (1:1) mixture of methanol:dichloromethane at room temperature using urea hydrogen peroxide (UHP) as oxidant and imidazole as co-catalyst. The epoxide yields clearly demonstrate the influence of steric and electronic properties of olefins, the catalysts and nitrogenous bases as axial ligand.  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  catalyst with low steric properties has higher catalytic activity than  $\text{Mn}(\text{phox})_3$ . The highest epoxide yield (95%) was achieved for indene at the presence of  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  within 5 min. The proximal and distal interactions of strong  $\pi$ -donor axial ligands such as imidazole with the active intermediate are efficiently increased activity of the catalytic system.

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**Keywords:** Manganese(III)-oxazoline; Urea hydrogen peroxide; Axial ligand; Catalysis; Epoxidation

## 1. Introduction

Oxidative functionalization of hydrocarbons into useful organic compounds is of immense interest in the era of transition metal complexes mediated reaction [1–4]. Epoxidation of olefins is a useful reaction that has numerous applications in organic synthesis [5]. Over the past three decades transition complexes of a variety of ligand systems such as porphyrins [6], Schiff bases [7] and oxazolines [8] have been used as catalysts for the catalytic oxygen transfer reactions in the oxidation of hydrocarbons. The catalytic oxidations have been carried out using a variety of oxidants such as PhIO [9], NaOCl [10],  $\text{H}_2\text{O}_2$  [11], UHP [12] and molecular oxygen [13]. Aqueous hydrogen peroxide has high relative oxygen content and leaves only water as waste product. However, in some cases the use of aqueous hydrogen peroxide decreases the selectivity of the desired epoxide due to isomerization and hydrolysis of the epoxide and also the formation of other cleaved products. Hence, it was thought that instead of aqueous hydrogen peroxide, anhydrous urea hydrogen peroxide adduct (UHP) can be used as the oxidizing reagent [14].

Given the considerable usefulness of hydrogen peroxide in many fields, such as atmospheric chemistry, photodissociation dynamics, and oxidation reactions, and of urea in biological processes because of potential hydrogen-bonding and acid–base properties associated with both the amine and the carbonyl groups, the urea hydrogen peroxide (UHP) 1:1 complex has been widely used in several oxidation processes and also as a safe source to produce hydrogen peroxide [15]. The major advantages of UHP lie in its stability, low price and potential for releasing anhydrous  $\text{H}_2\text{O}_2$  into solution in a controlled manner [16]. Therefore, we decided to examine its use in this study.

The chemistry of oxazoline-based ligands continues to be an area of interest due to their use as chirality-transfer auxiliaries in combination with several transition metals in a wide range of asymmetric catalytic reactions [17]. In nature, these groups have been found in microbial metal-transporting agents with a high affinity for Fe(III) [18]. In recent years, other metal-oxazoline complexes such as oxo-vanadium [18a,19], oxo-molybdenum [20], oxo-rhenium [21] and manganese [22] have been demonstrated as efficient catalysts in oxygen transfer reactions. Control of the stereo-selectivity of the catalytic process of these complexes mainly depends on the steric or electronic nature of the ligands around the metal center [20,22]. This paper reports studies the catalytic activity of two manganese(III)-oxazoline

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complexes during olefin epoxidation with urea hydrogen peroxide, showing the effect of axial ligand on the catalytic efficiency.

## 2. Experimental

### 2.1. Materials

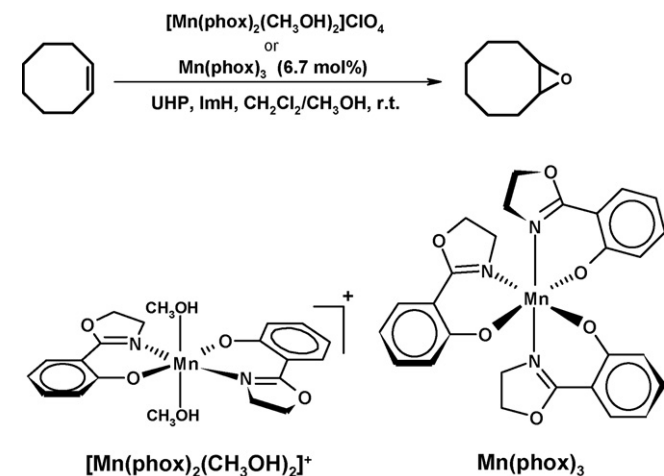
All of the reagents were supplied by Merck and employed without further purification. 2-(2'-Hydroxyphenyl)oxazoline (Hphox) [23] and its manganese complexes [bis{(2-oxazoliny)phenolato}dimethanol manganese(III)] perchlorate [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]ClO<sub>4</sub> [22c] and [tris{(2-oxazoliny)phenolato}manganese(III)] Mn(phox)<sub>3</sub> [22e] have been synthesized according to published procedures.

### 2.2. Instrumentations

IR spectra were recorded on Unicam Matson 1000 FT-IR paragon 1000 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the ligands and products of epoxidation were recorded on a Bruker FT-NMR 500 MHz spectrometer. Gas chromatography (GC) analyses were performed on Agilent Technologies 6890N, 19019 J-413 HP-5, 5% phenyl methyl siloxane, capillary 60.0 m × 250 μm × 1.00 μm.

### 2.3. Catalytic experiments

The following procedure is typical: to a solution of olefin (0.15 mmol), nitrogenous bases (0.2 mmol) as axial ligand, chlorobenzene (0.15 mmol) as internal standard and [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]ClO<sub>4</sub> or Mn(phox)<sub>3</sub> (0.01 mmol) in (1:1) mixture of CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added 0.6 mmol urea hydrogen peroxide as oxidant. The mixture was stirred at room temperature and the reaction progress was monitored by GC. Assignments of products were made by comparison with authentic samples. All the reactions were run at least in duplicate (Scheme 1).



Scheme 1. Epoxidation of cyclooctene with UHP catalysed by [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]ClO<sub>4</sub> or Mn(phox)<sub>3</sub>.

Table 1

The epoxidation of styrene with [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]ClO<sub>4</sub>/ImH/UHP in various solvents<sup>a</sup>

Entry	Solvent	Epoxide yield (%) <sup>b</sup>
1	CH <sub>3</sub> COCH <sub>3</sub>	53
2	CH <sub>2</sub> Cl <sub>2</sub>	30
3	CHCl <sub>3</sub>	10
4	CH <sub>3</sub> OH	70
5	CH <sub>3</sub> CN	63
6	CH <sub>3</sub> OH/CH <sub>2</sub> Cl <sub>2</sub> (1:1)	76

<sup>a</sup> Conditions: The molar ratio for Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]ClO<sub>4</sub>:ImH:styrene:oxidant are 1:20:15:60. The reactions were run for 5 min at room temperature.

<sup>b</sup> GC yields based on the starting styrene.

## 3. Results and discussion

### 3.1. The effect of solvent on the epoxidation of styrene with UHP catalysed [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]ClO<sub>4</sub>

To find the optimised conditions in UHP epoxidation of olefins catalysed by [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]ClO<sub>4</sub>, styrene was used as the model substrate. The molar ratio 1:20:15:60 of the catalyst:imidazole:styrene:UHP was found as the optimum molar ratio for the catalytic system. To obtain the appropriate solvent in UHP-epoxidation of olefins, catalysed by the manganese-oxazoline complexes, the epoxidation of styrene in the presence of [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]ClO<sub>4</sub> was carried out in various solvent. Among the solvents, in which the manganese complexes are soluble (1:1) mixture of CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> was chosen as the reaction medium. Urea hydrogen peroxide is not completely soluble in less polar organic solvents such as acetone, dichloromethane, chloroform and acetonitrile, so the epoxidation yield is low in these solvents (Table 1). In the other hand, the epoxidation yield is increased with polarity of the solvents. High polar solvents like methanol have an important role in breaking of adduct between urea and hydrogen peroxide and releasing of active H<sub>2</sub>O<sub>2</sub> in the reaction medium. The catalytic oxidation system in CH<sub>3</sub>OH has reasonable yield, but the (1:1) mixture of CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> acts better than pure methanol.

### 3.2. The effect of nature of axial ligands on the epoxidation

A study on the epoxidation of styrene with aqueous H<sub>2</sub>O<sub>2</sub> catalysed by Mn(III)-oxazoline complexes indicates the oxidation reaction is accelerated in the presence of a base such as 1-methylimidazole [22c,22e]. To better understanding the role of nitrogenous bases in activating manganese(III)-oxazoline complexes, we investigated the co-catalytic effects of various nitrogen donors with different steric and electronic properties upon the epoxidation of styrene. As the result in Table 2 shown, pure σ-donor amines are very poor co-catalysts in the epoxidation of styrene. Within this group, it seems that steric properties are the dominant factor in determining their co-catalytic activities (Table 2, entries 2–4). Pyridine and methyl-substituted pyridines with weak π-donating ability [24] show co-catalytic activities similar to those of σ-donor amines (Table 2, entries 5–8). Aminopyridines are much better co-catalysts than pyridines and

Table 2

The effect of various axial ligands in the epoxidation of styrene by  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4/\text{UHP}$  and  $\text{Mn}(\text{phox})_3/\text{UHP}^{\text{a}}$

Entry	Nitrogenous bases <sup>b</sup>	$[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4^{\text{c}}$	$\text{Mn}(\text{phox})_3^{\text{c}}$
1	None	0	0
2	Quinuclidine	2	0
3	$\text{Et}_2\text{NH}$	4	6
4	$\text{Et}_3\text{N}$	0	3
5	Py	3	6
6	4-MePy	4	7
7	2-MePy	2	2
8	2,6-Me <sub>2</sub> Py	5	2
9	4-CNPy	2	4
10	PyO	2	12
11	4-NH <sub>2</sub> Py	69	50
12	4-NMe <sub>2</sub> Py	44	25
13	ImH	78	64
14	2-MeImH	54	4
15	BzImH	14	31
16	1-MeIm	59	55

<sup>a</sup> The molar ratios for  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  or  $\text{Mn}(\text{phox})_3$ :axial ligand:substrate:oxidant are 1:20:15:60. The reactions were performed in (1:1) mixture of  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (1 mL) under air at 25 °C.

<sup>b</sup>  $\text{Et}_2\text{NH}$ , diethylamine;  $\text{Et}_3\text{N}$ , triethylamine; Py, pyridine; 4-CNPy, 4-cyanopyridine; 4-MePy, 4-methylpyridine; 2-MePy, 2-methylpyridine; 2,6-Me<sub>2</sub>Py, 2,6-dimethylpyridine; 4-NH<sub>2</sub>Py, 4-aminopyridine; 4-NMe<sub>2</sub>Py, 4-*N,N*-dimethylpyridine; PyO, pyridine-*N*-oxide; ImH, imidazole; 2-MeImH, 2-methylimidazole; BzImH, benzimidazole; 1-MeIm, 1-methylimidazole.

<sup>c</sup> The GC epoxide yields (%) are measured relative to the starting olefins after 5 min.

pure  $\sigma$ -donor amines. Apparently the  $\pi$ -resonance effect of the lone pair on the amino-substituent makes the nitrogen donor site of 4-NH<sub>2</sub>py and 4-NMe<sub>2</sub>py both good  $\sigma$ - and  $\pi$ -donor [24] (Table 2, entries 11 and 12). Among the various nitrogenous bases investigated in this study imidazole and substituted imidazole with strong  $\pi$ -donating ability [24,25] show the high accelerating effect on the epoxidation of styrene and the best epoxide yield was achieved in the presence of imidazole as axial ligand. These results may suggest the importance of  $\pi$ - rather than  $\sigma$ -interactions of nitrogenous donors with the metal center [25b].

The epoxide yields for different ImH/Mn ( $\text{Mn} = [\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$ ) molar ratio are plotted in Fig. 1. As ImH/Mn molar ratio is increased up to 20 the epoxide yield increases probably due to increasing of the concentration of  $[\text{Mn}(\text{phox})_2(\text{ImH})]^+$  that can be coordinated by  $\text{H}_2\text{O}_2$  to produce  $[\text{Mn}(\text{phox})_2(\text{ImH})(\text{HOO})]$  that is a precursor to high-valent Mn-oxo species as the active intermediate to transfer oxygen to olefinic substrate. From various mechanistic studies have been revealed that a  $\text{Mn}^{\text{V}}$ -oxo intermediate is formed during  $\text{H}_2\text{O}_2$ -epoxidation catalysed by Mn-complexes such as manganese-porphyrins [26] and manganese-Schiff base [27] catalysts. As seen in Fig. 1 further increase in amount of imidazole results in a decrease of  $[\text{Mn}(\text{phox})_2(\text{ImH})]^+$  and increases the inactive entity concentration, i.e.  $[\text{Mn}(\text{phox})_2(\text{ImH})_2]^+$ , that do not have any vacant site for coordination of  $\text{H}_2\text{O}_2$  to the central metal, resulting in a decrease on the epoxide yield.

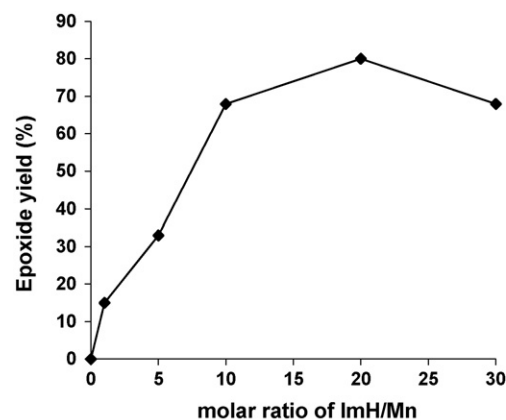
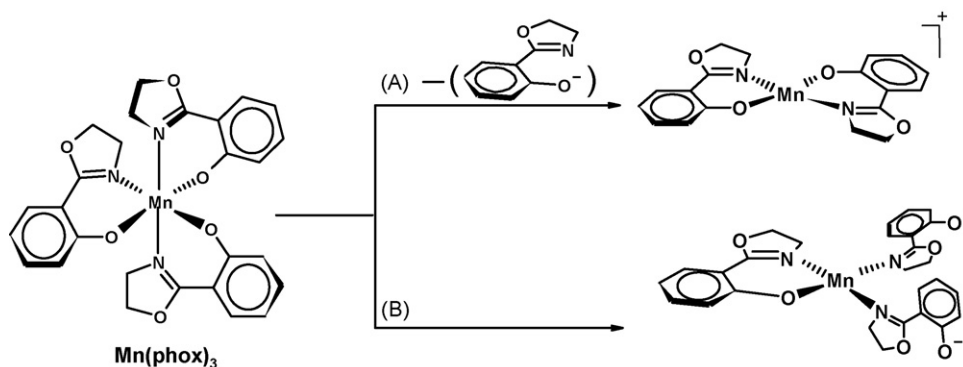


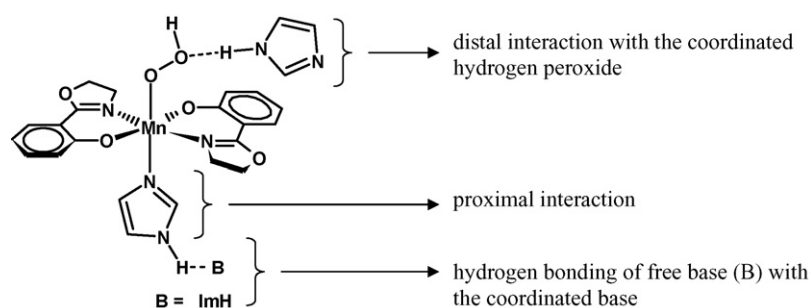
Fig. 1. Epoxide yields as function of molar ratio of ImH/Mn for the epoxidation of styrene with  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4/\text{UHP}/\text{ImH}$  catalytic system.

Reedijk and co-workers have reported that due to  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]^+$  complex that containing  $[\text{Mn}(\text{phox})_2]^+$  unit is less effective catalyst than  $[\text{Mn}(\text{phox})_3]$ , the availability of free coordination sites is not of crucial importance for the bis- and tris-oxazoline complexes [22c]. Indeed, in molar ratio 143:1 for 1-MeIm/Mn used in the  $\text{H}_2\text{O}_2$  epoxidation of olefins [22c], the inactive species  $[\text{Mn}(\text{phox})_2(1\text{-MeIm})_2]^+$  is dominant entity that cannot activate the oxidant through its coordination to the manganese atom. Thus, Reedijk and co-workers proposed [22c] the presence of a base does decrease the acidity of the solution caused by hydrogen peroxide, resulting in an increase of the  $\text{HOO}^-$  concentration, which might react more easily with a manganese compound to form a  $\text{Mn}-\text{O}-\text{O}-\text{H}$  entity as an active intermediate species. But much lower epoxide yields, for diethylamine with more basic property ( $\text{p}K_{\text{a}}(\text{BH}^+) 11.02$ ) than imidazole ( $\text{p}K_{\text{a}}(\text{BH}^+) 6.95$ ) (Table 2, entries 3 and 13) indicate nitrogenous bases have to affect on the epoxidation reaction through coordination to the metal complex.

Various studies on the effect of a nitrogenous base in manganese complex-catalysed epoxidation reactions have shown proximal effect of the base is effective in the formation of a high valent Mn-oxo intermediate and transferring of oxygen from this species to the olefins [28]. To form this metal-oxo intermediate essentially needs free coordination site on metal center, however there must be another site for coordination of an axial ligand. Comparing of epoxidation yields in the absence and presence of axial ligand (Table 2, entries 1 and 13) confirms that connecting of imidazole to manganese increases catalytic activity of the catalyst by increasing of electron density on the metal.  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  has higher epoxidation yield with various olefins than  $\text{Mn}(\text{phox})_3$ . This directly can be related to availability of two sites for forming of oxo-intermediate and coordination of axial ligand in  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$ , but the tris-complex has to prepare free sites for these connections. These sites can be created by one of following ways: first, the tris-complex losses one of its oxazoline ligands and converts to bis-complex (Scheme 2, pathway A). The second pathway can be related to formation of dangling ligands through breaking of two oxazolate ligands (Scheme 2, pathway B).



Scheme 2. Two pathways for activation of Mn(phox)<sub>3</sub>. (A) Remove of one oxazoline ligand and conversion to the bis-complex. (B) Dangling of two oxazoline ligands.



Scheme 3. The proximal and distal effect of imidazole on the epoxidation of olefins catalysed by [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]/ClO<sub>4</sub>.

Due to formation of these species requires some activation energy prior to formation of the oxo-manganese intermediate, the bis-complex is shown greater catalytic activity than the tris-complex in the epoxidation reaction.

The much lower co-catalytic activity of 2-methylimidazole than imidazole is due to the steric effects between methyl substituent and plane of oxazoline ligands [29], which is more clearly shown in the presence of bulky Mn(phox)<sub>3</sub> (Table 2, entry 14). In addition to the proximal interaction, possible distal hydrogen bonding between the coordinated hydrogen peroxide and imidazole should also be considered [25b,30] (Scheme 3). Among imidazole derivatives used 1-methylimidazole is the only nitrogenous base that lacks N–H bond, so it cannot form N–H···HO–O–Mn hydrogen bond (distal effect) with coordinated hydrogen peroxide [31] (Scheme 3). The other type of hydrogen bonding is formation of N–H···B hydrogen bond leads to a shift of electron density from free base (B) to the coordinated base, increasing donating ability of the axial ligand [32], whereas 1-methylimidazole is also chemically incapable of such bonding. Good co-catalytic activity of 1-MeIm in the epoxidation of styrene (Table 2, entry 16) clearly shows the proximal interaction of axial ligand has more important role of its distal effect. Also the difference between co-catalytic activity of 4-NH<sub>2</sub>py (Table 2, entry 11) and 4-NMe<sub>2</sub>py (Table 2, entry 12) can be related to the lack of distal interaction of the latter with coordinated hydrogen peroxide and the hydrogen bonding with coordinated base (Scheme 3).


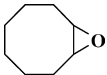

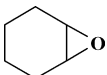
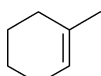
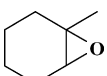
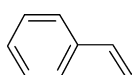
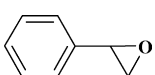
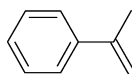
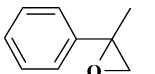
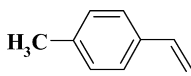
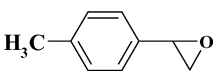
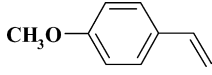
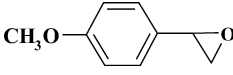
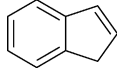
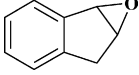
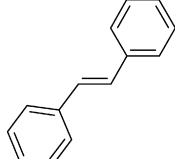
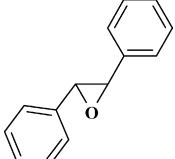
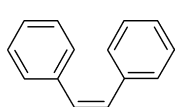
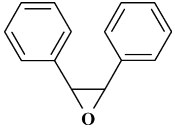
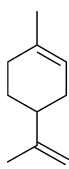
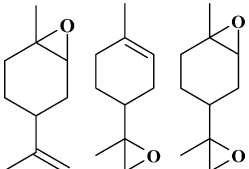
### 3.3. Catalytic olefins epoxidation by [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]/ClO<sub>4</sub>/ImH/UHP and Mn(phox)<sub>3</sub>/ImH/UHP

Epoxidation of various olefins was performed at room temperature in 1:1 mixture of CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> containing the manganese(III)-oxazoline complex, imidazole, olefin and the oxidant in 1:20:15:60 molar ratio, respectively. The results are shown in Table 3. Monitoring the epoxide yield versus the time for the styrene epoxidation with [Mn(phox)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>]/ClO<sub>4</sub>/ImH/UHP and Mn(phox)<sub>3</sub>/ImH/UHP catalytic systems indicates that the reactions proceed in a rapid rate in which 55%, and 60%, respectively, of the epoxidations occur within 1 min followed by rapid loss of activity up to 5 min concomitant with catalyst bleaching (Fig. 2).

As the data in Table 3 indicate, electron rich olefins are more reactive than electron-poor ones. For instance α-methylstyrene with methyl group as electron donating substituent gives higher epoxidation yield than styrene (Table 3, entries 4 and 5). The observed order of epoxidation yields of 4-methoxystyrene > 4-methylstyrene > styrene is also directly related to electron releasing ability of methoxy and methyl groups. These results may indicate the Mn<sup>V</sup>=O intermediate to transfer its oxygen atom to the olefinic double bond in an electrophilic reaction. According to the results in Table 3, olefinic substrates which are conjugated with phenyl ring (Table 3, entries 4–8), are more reactive than non-conjugated cyclic olefins.

Table 3

Epoxidation of olefins catalysed by  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4/\text{ImH}/\text{UHP}$  and  $\text{Mn}(\text{phox})_3/\text{ImH}/\text{UHP}^{\text{a}}$ 

Entry	Substrate	Product	$[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4^{\text{b}}$	$\text{Mn}(\text{phox})_3^{\text{b}}$
1			<b>63</b>	<b>48</b>
2			<b>69</b>	<b>39</b>
3			<b>67</b>	<b>49</b>
4			<b>76</b>	<b>63</b>
5			<b>86</b>	<b>76</b>
6			<b>87</b>	<b>79</b>
7			<b>89</b>	<b>80</b>
8			<b>95</b>	<b>63</b>
9			<b>81</b>	<b>66</b>
10			<b>30</b> ( <i>cis</i> -epoxide), <b>30</b> ( <i>trans</i> -epoxide)	<b>21</b> ( <i>cis</i> -epoxide), <b>21</b> ( <i>trans</i> -epoxide)
11			<b>26</b> (1,2-epoxide), <b>26</b> (8,9-epoxide), <b>23</b> (1,2-8,9-epoxide)	<b>20</b> (1,2-epoxide), <b>20</b> (8,9-epoxide), <b>18</b> (1,2-8,9-epoxide)

<sup>a</sup> The molar ratios for  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  or  $\text{Mn}(\text{phox})_3$ :imidazole:substrate:oxidant are 1:20:15:60. The reactions were performed in (1:1) mixture of  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (1 mL) under air at 25 °C.

<sup>b</sup> The GC epoxide yield (%) are measured relative to the starting olefin after 5 min.

While epoxidation of *trans*-stilbene stereospecifically proceeds with complete retention of configuration, epoxidation of *cis*-stilbene was associated with loss of stereochemistry to afford a mixture of *cis*-stilbene oxide and *trans*-stilbene oxide with ratio of (1:1) (Table 3, entries 9 and 10). Apparently, formation of the thermodynamically more stable *trans*-stilbene oxide requires a free rotation about the alkene C–C bond at some intermediate step. It is well known that formation of *cis*-

and *trans*-stilbene oxide in epoxidation of *cis*-stilbene provide an evidence for the radical or cationic mechanism [26]. To explore the intermediacy of the radical species in the epoxidation reaction, 2,6-di-*tert*-butyl-*p*-cresol was used as radical trap in *cis*- and *trans*-stilbene epoxidation with UHP catalysed by  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$ . The results are shown in Table 4. Owing to the epoxidation reaction is not completely inhibited, a free radical chain mechanism is excluded [33]. The reduction in

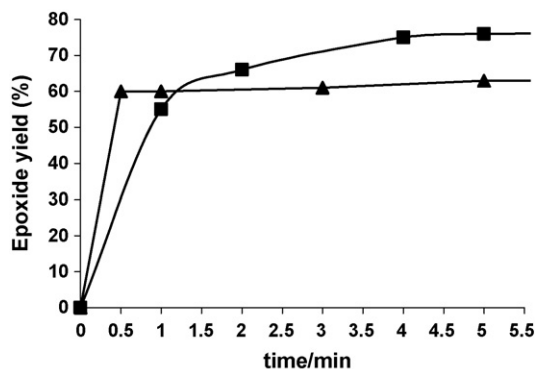


Fig. 2. Epoxide yields as function of reaction time for the epoxidation of styrene with UHP catalysed by  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  (■) and  $\text{Mn}(\text{phox})_3$  (▲) complexes.

Table 4

Epoxidation of *cis*- and *trans*-stilbene catalysed by  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4/\text{ImH}/\text{UHP}$  at the presence of 2,6-di-*tert*-butyl-*p*-cresol as radical scavenger<sup>a</sup>

Entry	Substrate	Epoxide yield (%) <sup>b</sup>
1	<i>Cis</i> -stilbene	16 ( <i>cis</i> -epoxide), 17 ( <i>trans</i> -epoxide)
2	<i>Trans</i> -stilbene	64 ( <i>trans</i> -epoxide)

<sup>a</sup> The amounts of  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$ , imidazole, substrate, 2,6-di-*tert*-butyl-*p*-cresol, and UHP are 0.01, 0.2, 0.15, 0.15 and 0.6 mmol, respectively. The reactions were performed in (1:1) mixture of  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (1 mL) under air at 25 °C.

<sup>b</sup> The GC epoxide yield (%) are measured relative to the starting olefin after 5 min.

epoxide yields in the presence of the radical scavenger (Table 4) may indicate a radicaloid intermediate must be formed during the reaction pathway [33].

#### 4. Conclusions

This study has demonstrated that  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  and  $\text{Mn}(\text{phox})_3$  complexes are efficient catalysts for olefin epoxidation with urea hydrogen peroxide during short reaction times (5 min). The presence of a nitrogenous base is necessary to obtain efficient catalytic activity. Among various nitrogen donor bases used in this study, strong  $\pi$ -donor axial ligands such as imidazole are shown more co-catalytic effect. The co-catalytic effect is caused by the proximal and distal interactions of imidazole with the catalysts. The epoxide yields show the importance of steric and electronic properties of olefins, the catalysts, and axial ligands. Less hindrance  $[\text{Mn}(\text{phox})_2(\text{CH}_3\text{OH})_2]\text{ClO}_4$  catalyst has higher catalytic activity than  $\text{Mn}(\text{phox})_3$ .

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#### References

- [1] B. Meunier, Chem. Rev. 92 (1992) 1411.
- [2] R.E. White, M.J. Coon, Annu. Rev. Biochem. 49 (1980) 315.

- [3] T. Katsuki, J. Mol. Catal. A: Chem. 113 (1996) 87.
- [4] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
- [5] J.T. Groves, in: P. Ortiz de Montellano (Ed.), Cytochrome P-450: Structure, Mechanism and Biochemistry, vol. 7, Plenum Press, New York, 1986, p. 1.
- [6] (a) S.L.H. Rebelo, M.M.Q. Simoes, M.G.P.M.S. Neves, J.A.S. Cavaleiro, J. Mol. Catal. A: Chem. 201 (2003) 9;  
(b) S.L.H. Rebelo, M.M.Q. Simoes, M.G.P.M.S. Neves, A.M.S. Silva, P. Tagliatesta, J.A.S. Cavaleiro, J. Mol. Catal. A: Chem. 232 (2005) 135.
- [7] (a) E.M. McGarrigle, D.G. Gilheany, Chem. Rev. 105 (2005) 1563;  
(b) A. Martinez, C. Hemmert, B. Meunier, J. Catal. 234 (2005) 250;  
(c) K. Kervinen, H. Korpi, M. Leskela, T. Repo, J. Mol. Catal. A: Chem. 203 (2003) 9.
- [8] (a) K. Kandasamy, H.B. Singh, R.J. Butcher, J.P.M. Jasinski, Inorg. Chem. 43 (2004) 5704;  
(b) M.D. Godbole, A.C.G. Hotze, R. Hage, A.M. Mills, H. Kooijman, A.L. Spek, E. Bouwman, Inorg. Chem. 44 (2005) 9253;  
(c) Bagherzadeh, Tetrahedron Lett. 44 (2003) 8943;  
(d) M. Bagherzadeh, J. Chem. Res. (S) (2003) 765.
- [9] J.P. Collman, L. Zeng, J.I. Brauman, Inorg. Chem. 43 (2004) 2672.
- [10] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S. Singh, I. Ahmed, R.V. Jasra, J. Mol. Catal. A: Chem. 218 (2004) 141.
- [11] M.C. White, A.G. Doyle, E.N. Jacobsen, J. Am. Chem. Soc. 123 (2001) 7194.
- [12] (a) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, R.V. Jasra, Tetrahedron: Asymmetry 12 (2001) 433;  
(b) E.D.P. Carreiro, A.J. Burke, M.J.M. Curto, A.J.R. Teixeira, J. Mol. Catal. A: Chem. 217 (2004) 69;  
(c) M.K. Tse, H. Jiao, G. Anilkumar, B. Bitterlich, F.G. Gelalcha, M. Beller, J. Organomet. Chem., in press;  
(d) E.P. Carreiro, G. Yong-En, A.J. Burke, J. Mol. Catal. A: Chem. 235 (2005) 285.
- [13] (a) S.G. Jarboe, P. Beak, Org. Lett. 2 (2000) 357;  
(b) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, P. Iyer, S.T. Patel, Polyhedron 18 (1999) 1773.
- [14] Y. Ding, Q. Gao, G. Li, H. Zhang, J. Wang, L. Yan, J. Suo, J. Mol. Catal. A: Chem. 218 (2004) 161.
- [15] (a) J.A. Dobado, J. Molina, D. Portal, J. Phys. Chem.: A 102 (1998) 778;  
(b) R.P. Wayne, Chemistry of Atmospheres, Clarendon Press, Oxford, 1991;  
(c) D.H. Zhang, J.Z. Zhang, J. Chem. Phys. 98 (1993) 6276;  
(d) J.A. Damavandi, B. Karami, M.A. Zolfigol, Synlett (2000) 933;  
(e) T.R. Boehlow, C.D. Spilling, Tetrahedron Lett. 37 (1996) 2717;  
(f) H. Heaney, Aldrichim. Acta 26 (1993) 35.
- [16] A.M.A.R. Gonsalves, R.A.W. Johnstone, M.M. Pereira, J. Shaw, J. Chem. Res. (S) (1991) 208.
- [17] (a) D. Rechavi, M. Lemaire, Chem. Rev. 102 (2002) 3467;  
(b) J.S. Johnson, D.A. Evans, Acc. Chem. Res. 33 (2000) 325;  
(c) R.M. Moreno, A. Bueno, A. Moyano, J. Organomet. Chem. 671 (2003) 187.
- [18] (a) C. Bolm, T.K. Luoneg, K. Harms, Chem. Ber. Recueil 130 (1997) 887;  
(b) C. Bolm, G. Schlingloff, K. Wieckhardt, Angew. Chem. Int. Ed. Engl. 33 (1994) 1848;  
(c) C. Bolm, G. Schlingloff, J. Chem. Soc. Chem. Commun. (1995) 1247.
- [19] (a) J.J.H. Hwang, M.M. Abu-Omar, Tetrahedron Lett. 40 (1999) 8313;  
(b) K. Kandasamy, H.B. Singh, R.J. Butcher, J.P. Jasinski, Inorg. Chem. 43 (2004) 5704.
- [20] M. Gomez, S. Jansat, G. Muller, G. Noguera, H. Teruel, V. Moliner, E. Cerrada, M. Hursthouse, Eur. J. Inorg. Chem. (2001) 1071.
- [21] J. Arias, C.R. Newlands, M.M. Abu-Omar, Inorg. Chem. 40 (2001) 2185.
- [22] (a) M. Hoogenraad, H. Kooijman, A.L. Spek, E. Bouwman, J.G. Haasnoot, J. Reedijk, J. Eur. J. Inorg. Chem. (2002) 2897;  
(b) M. Hoogenraad, K. Ramkisoensing, S. Gorter, W.L. Driessen, E. Bouwman, J.G. Haasnoot, J. Reedijk, T. Mahabiersing, F. Hartl, Eur. J. Inorg. Chem. (2002) 377;  
(c) M. Hoogenraad, K. Ramkisoensing, W.L. Driessen, H. Kooijman, A.L. Spek, E. Bouwman, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 320 (2001) 117;

- (d) M.G. Simon, S. Jansat, G. Muller, D. Panyella, M.F. Bardia, X. Solans, *J. Chem. Soc. Dalton Trans.* (1997) 3755;
- (e) M. Hoogenraad, K. Ramkisoensing, H. Koojiman, A.L. Spek, E. Bouwman, J.G. Haasnoot, J. Reedijk, *Inorg. Chem. Acta* 279 (1998) 217.
- [23] H.R. Hoveyda, V. Kamnaname, S.J. Rettig, C. Orvig, *Inorg. Chem.* 31 (1992) 5408.
- [24] (a) M.K. Safo, F.A. Walker, A.M. Raitsimring, W.P. Walters, D.P. Dolata, P.G. Debrunner, W.R. Scheidt, *J. Am. Chem. Soc.* 116 (1994) 7760;
- (b) M.K. Safo, G.P. Gupta, C.T. Watson, U. Simonis, F.A. Walker, W.R. Scheidt, *J. Am. Chem. Soc.* 114 (1992) 7066;
- (c) M.K. Safo, G.P. Gupta, F.A. Walker, W.R. Scheidt, *J. Am. Chem. Soc.* 113 (1991) 5497.
- [25] (a) C.K. Chang, T.G. Traylor, *J. Am. Chem. Soc.* 95 (1973) 8477;
- (b) D. Mohajer, G. Karimipour, M. Bagherzadeh, *New J. Chem.* 28 (2004) 740.
- [26] (a) R.D. Arasasingham, G.X. He, T.C. Bruice, *J. Am. Chem. Soc.* 115 (1993) 7985;
- (b) J.T. Groves, J. Lee, S.S. Marla, *J. Am. Chem. Soc.* 119 (1997) 6269;
- (c) A.M.A.R. Gonsalves, A.C. Serra, *J. Mol. Catal. A: Chem.* 168 (2001) 25;
- (d) F.J. Waller, A.J. Bailey, W.P. Griffith, S.P. Marsden, E.H. Smith, *J. Mol. Catal. A: Chem.* 154 (2000) 85.
- [27] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S. Singh, I. Ahmed, R.S. Shukla, R.V. Jasra, *J. Catal.* 219 (2003) 1.
- [28] (a) S.I. Ozaki, M.P. Roach, T. Matsui, Y. Watanabe, *Acc. Chem. Res.* 34 (2001) 818;
- (b) A. Boffi, L. Guarrera, L. Giangiacomo, C. Spagnuolo, E. Chiancone, *Biochemistry* 39 (2000) 3500;
- (c) D.A. Scherlis, D.A. Estrin, *J. Am. Chem. Soc.* 123 (2001) 8436.
- [29] P. Battioni, J.P. Renaud, J.F. Bartoli, M. Reins-Artiles, M. Fort, D. Mansuy, *J. Am. Chem. Soc.* 110 (1988) 8462.
- [30] (a) G.B. Jameson, J.A. Ibers, in: I. Bertini, H.B. Gray, S. Lippard, J. Valentine (Eds.), *Bioinorganic Chemistry*, University Science Books, Mill Valley, CA, 1994, p. 167 (Chapter 4);
- (b) G.A. Tondreau, D.A. Sweigart, *Inorg. Chem.* 23 (1984) 1060.
- [31] (a) L.C. Yuan, T.C. Bruice, *J. Am. Chem. Soc.* 108 (1986) 1643;
- (b) P. O'Brien, D.A. Sweigart, *Inorg. Chem.* 24 (1985) 1405;
- (c) F.A. Walker, M.W. Lo, M.T. Ree, *J. Am. Chem. Soc.* 98 (1976) 5552.
- [32] P. O'Brien, D.A. Sweigart, *Inorg. Chem.* 24 (1985) 1405.
- [33] (a) K.U. Ignold, P.A. Macfaul, in: B. Meunier (Ed.), *Biomimetic Oxidations Catalysed by Transition Metal Complexes*, Imperial College Press, London, 2000, p. 56 (Chapter 2);
- (b) K. Srinivasan, S. Perrier, J.K. Kochi, *J. Mol. Catal. A: Chem.* 36 (1986) 297.