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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 $[Mn(phox)_2(CH_3OH)_2]ClO_4$ and $Mn(phox)_3$ (Hphox = 2-(2′-hydroxylphenyl)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. $[Mn(phox)_2(CH_3OH)_2]ClO_4$ catalyst with low steric properties has higher catalytic activity than $Mn(phox)_3$. The highest epoxide yield (95%) was achieved for indene at the presence of $[Mn(phox)_2(CH_3OH)_2]ClO_4$ within 5 min. The proximal and distal interactions of strong π-donor axial ligands such as imidazole with the active intermediate are efficiently increased activity of the catalytic system.

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], H_2O_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 H_2O_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

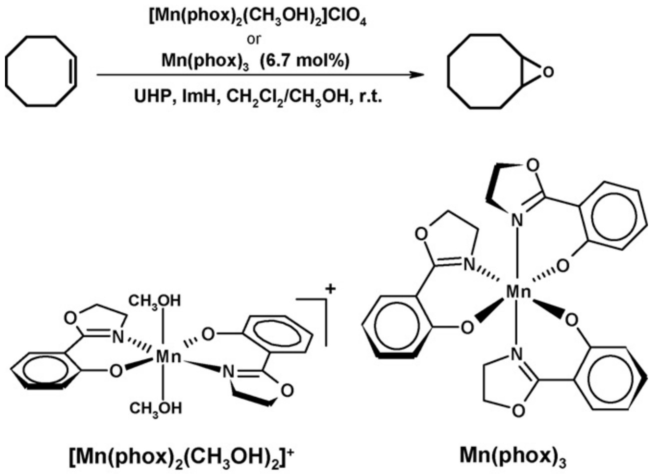
All of the reagents were supplied by Merck and employed without further purification. 2-(2′-Hydroxylphenyl)oxazoline (Hphox) [23] and its manganese complexes [bis{(2-oxazolinyl)phenolato}dimethanol manganese(III)] perchlorate [Mn (phox)$_2$(CH$_3$OH)$_2$]ClO$_4$ [22c] and [tris{(2-oxazolinyl) phenolato}manganese(III)] Mn(phox)$_3$ [22e] have been synthesized according to published procedures.

2.2. Instrumentations

IR spectra were recorded on Unicam Matson 1000 FT-IR paragon 1000 spectrophotometer. ^{1}H and ^{13}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)$_2$(CH$_3$OH)$_2$]ClO$_4$ or Mn(phox)$_3$ (0.01 mmol) in (1:1) mixture of CH$_3$OH/CH$_2$Cl$_2$ (1mL) 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)$_2$ (CH$_3$OH)$_2$]ClO$_4$ or Mn(phox)$_3$.

Table 1
The epoxidation of styrene with [Mn(phox)$_2$(CH$_3$OH)$_2$]ClO$_4$/ImH/UHP in various solvents[a]

Entry	Solvent	Epoxide yield (%)[b]
1	CH$_3$COCH$_3$	53
2	CH$_2$Cl$_2$	30
3	CHCl$_3$	10
4	CH$_3$OH	70
5	CH$_3$CN	63
6	CH$_3$OH/CH$_2$Cl$_2$ (1:1)	76

[a] Conditions: The molar ratio for Mn(phox)$_2$(CH$_3$OH)$_2$]ClO$_4$:ImH:styrene: oxidant are 1:20:15:60. The reactions were run for 5 min at room temperature.
[b] 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)$_2$(CH$_3$OH)$_2$]ClO$_4$

To find the optimised conditions in UHP epoxidation of olefins catalysed by [Mn(phox)$_2$(CH$_3$OH)$_2$]ClO$_4$, 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)$_2$(CH$_3$OH)$_2$]ClO$_4$ was carried out in various solvent. Among the solvents, in which the manganese complexes are soluble (1:1) mixture of CH$_3$OH/CH$_2$Cl$_2$ 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$_2$O$_2$ in the reaction medium. The catalytic oxidation system in CH$_3$OH has reasonable yield, but the (1:1) mixture of CH$_3$OH/CH$_2$Cl$_2$ 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$_2$O$_2$ 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