

Study of the catalytic activity of non-heme manganese complexes toward oxidation of cyclooctene and cyclohexene



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ABSTRACT

The catalytic activity of two manganese(II) complexes, $[\text{MnL1}(\text{H}_2\text{O})](\text{ClO}_4)_2$ (**1**) and $[\text{MnL2}]\text{ClO}_4$ (**2**) *N,O*-donor $\text{L1} = \text{N,N,N}'\text{-tris}(2\text{-methylpyridyl})\text{-N}'\text{-hydroxyethyl-ethylenediamine}$ and $\text{L2} = \text{N}\text{-}(2\text{-hydroxybenzyl})\text{-N,N}'\text{-bis}(2\text{-methylpyridyl})\text{-N}'\text{-hydroxyethyl-ethylenodiamine}$ in the epoxidation of alkenes was investigated in acetonitrile:dichloromethane mixtures at room temperature, using iodosylbenzene as an oxygen source. The epoxidation of cyclooctene in 1 h at the best reactants molar ratio (1:50:1000, catalyst:oxidant:substrate) showed similar yields for catalyst **2** (50%) and catalyst **1** (48%). When cyclohexene was the substrate, catalyst **1** showed best yield of 42% at 1:10:1000 and catalyst **2**, 62% at 1:10:3000. As a hard Lewis base, the phenolato is expected to facilitate the production and the stabilization of catalytic intermediate species with higher oxidation state like Mn(III) or Mn(IV). The presence of the labile water molecule along with the tension imposed by the heptacoordination of L1 in (**1**) favors the formation of oxo or hydroxo Mn(II)-dimers as the catalytically active species. Conversely, the robust nature and the hexacoordination of L2 compared to L1 favors the stabilization of mononuclear active species. Oxidation reactions were monitored with Electron Paramagnetic Resonance (EPR) technique and plausible oxidation states for the manganese-catalysts are discussed as well.

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1. Introduction

The use of coordination compounds as catalysts to oxidation of hydrocarbons with oxygen donors such as iodosylbenzene (PhIO), peroxides, peracids, molecular oxygen, hypochlorite and iodate has been extensively studied. It is especially relevant because of the industrial importance of epoxides, which are essential for the preparation of highly functionalized organic compounds [1–3]. A major goal in epoxidation continues to be the search for better catalysts that are rapid, selective, and inexpensive. In this sense catalysts bioinspired by the performance of highly selective metalloenzymes, are among the most studied and transition metal complexes are good examples of catalysts promoting reactions under mild conditions [4–8]. Manganese is catalytically active in a variety of metalloenzymes [9] and is also less damaging to the environment compared with many other transition metals. Hence, a large number of reports can be found in the literature about manganese complexes as oxidation catalysts [10–13]. Despite the success of manganese porphyrins to catalyze the epoxidation of

olefins with high efficiency [14–17], a limited number of non-heme manganese catalysts are described as efficient catalysts for epoxidation and more information about the intermediate species in the plausible mechanisms is needed.

Recently, Saravanan and Palaniandavar [4] studied the effect of diazacycloalkane backbone in a series of manganese(II) tetraazate-tradentate ligands on the catalytic activity of the complexes toward epoxidation of unfunctionalized olefins using PhIO as oxygen source. The epoxidation of cyclooctene catalyzed by Saravanan's catalysts occurs with yields from 17.4% to 54%. When cyclohexene was the substrate, the selectivity was 18–30.3% for the epoxide and best yields were observed at 22.5% and 53.3% for the epoxide and the ketone products, respectively. The epoxide yield and product selectivity increased upon increasing the Lewis acidity of the Mn(II) center as the ligands varied. Seyedi et al. [18] described the use of manganese(III)–salen complexes containing crown ether rings as catalysts for epoxidation of cyclooctene and cyclohexene by KHSO_5 as oxidant in a water/chloroform mixture at room temperature. Best yields were about 95% with reaction times less than 20 min. The effect of pyridine as the axial base and different alkali metal salts was also investigated. Impressive results were reported by Bahramian et al. for the catalytic activity of a water-soluble Mn(salen)OAc complex in the epoxidation of alkenes in acetonitrile/water 1:1 (v:v), at room temperature, using sodium

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¹ In memoriam.

periodate as oxygen source [19]. In that work, the effect of various axial ligands as co-catalyst was also investigated and imidazole provided the best results with yields as high as 98% for epoxidation of cyclooctene in 10 min. Oxidation of cyclohexene was reported to occur with a 100% yield for the epoxide in a 10 min reaction.

In an earlier publication we demonstrated the catalytic activity of a binuclear carboxylate bridged manganese complex containing the heptadentate ligand *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)-2-ol-1,3-propanediamine ($H_3bbppnol$), in oxidation reactions of cyclohexene and cyclooctene [10]. The investigation revealed epoxide yields of 26% and 37% for cyclohexene and cyclooctene in dichloromethane/acetonitrile 1:1 (v:v) at a 1(cat):10(PhIO):1000(substrate) molar ratio.

Many manganese-porphyrin complexes have also been intensively reported as catalysts in homogeneous conditions [6]. More recently, catalytic activity of Mn(III) complexes of meso-tetra(*n*-propyl)porphyrin in oxidation of olefins with tetra-*n*-butylammonium periodate at room temperature has been reported by Zakavi et al. [14]. Oxidation of cyclooctene led to the exclusive formation of the epoxide with 33.6% yield in a 4 h reaction at alkene:oxidant:catalyst molar ratio of 1000:170:1. Oxidation of cyclohexene gave a moderate selectivity of 38.6% for epoxide, 12% yield and 2-cyclohexene-1-ol as products. Alemohammad et al. [20] showed that meso-tetraphenylporphyrinmanganese(III) acetate ($MnTPPOAc$) and a series of meso-tetrakis(2-,4-,2,3-,2,6-,3,4- and 2,4,6-hydroxyphenyl) porphyrinmanganese(III) acetate can be used as catalysts in the epoxidation of various alkenes with tetra-*n*-butylammonium hydrogen monopersulfate ($n-Bu_4NHSO_5$) as oxidant and tetra-*n*-butylammonium acetate ($n-Bu_4NOAc$) as the axial ligand. Under optimum conditions, cyclooctene oxide was formed in 68% yield. When cyclohexene was used, the yield to epoxide was 49.5% and 2.5% selectivity to the corresponding ketone. Recently Ucoski et al. [17] showed the catalytic activity of the low-cost 5,10,15,20-tetrakis(acetalphenyl)porphyrin manganese(III) in oxidation of cyclooctene and cyclohexane. Best yields of 77% for the cyclooctene oxide was observed in dichloromethane/acetonitrile 1:1 (v:v) mixture at room temperature and at a 1(cat):10(PhIO):5000(substrate) molar ratio.

Herein we describe the catalytic activity of two manganese(II) complexes, $[MnL1(H_2O)](ClO_4)_2$ (**1**) and $[MnL2]ClO_4$ (**2**) containing *N,O*-donor ligands, L1 = *N,N,N'*-tris(2-methylpyridyl)-*N'*-hydroxyethyl-ethylenediamine and L2 = *N*-(2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)-*N'*-hydroxyethyl-ethylenediamine toward the oxidation of cyclooctene and cyclohexene by iodosylbenzene. The structures of the ligands (Fig. 1) are based on the *N*-hydroxyethyl-ethylenediamine group with pyridine and/or phenolic arms. The hydroxyethyl group may promote a more labile site for PhIO activation in the metal coordination sphere since in copper and

vanadium complexes with the same ligands, the hydroxyl groups remains uncoordinated [21,22]. Ligand L1 contains three nitrogen donor atoms from pyridine residues and ligand L2 can coordinate through two pyridines and one phenolic group. The coordination ability of the ligands L1 and L2 was established through single crystal X-ray crystallography [23] and we have considered their relative potential to stabilize higher oxidation states of the manganese ion, usually observed as intermediates in oxidation reactions. The performances of the catalysts were discussed based on reaction yields and selectivity. EPR was used to monitor the oxidation reactions and the spectral features discussed to infer about the nature of the reaction intermediates.

2. Experimental

2.1. Materials

The chemicals used in this work were purchased from Sigma–Aldrich and Merck and used as supplied.

The preparation of complexes (**1**) $[MnL1(H_2O)](ClO_4)_2$ and (**2**) $[MnL2]ClO_4$ was described in a previous publication [23].

Iodosylbenzene (PhIO) was prepared by the hydrolysis of iodosylbenzene diacetate following the method of Sharefkin and Saltzman [24] and the purity was shown to be 98% by iodometric titration. The solid was dried under vacuum at 5 °C and stored at –22 °C in the dark.

2.2. Homogeneous catalysis of oxidation of cyclooctene and cyclohexene

2.2.1. Oxidation by iodosylbenzene (PhIO)

The oxidation reactions of cyclooctene and cyclohexene by iodosylbenzene (PhIO) catalyzed by (**1**) and (**2**) were carried out in 4 mL samples in the solvent mixture (dichloromethane/acetonitrile 1:1, v/v). In a typical experiment 1 mg of $[MnL1(H_2O)](ClO_4)_2$, 3.5–35 mg of PhIO and 220–1320 μ L of cyclooctene or 160–560 μ L of cyclohexene were mixed under argon and kept at 25 °C under stirring in a dark chamber for 1 h. Saturated solution of sodium sulfite was added to the reaction in order to eliminate the excess of iodosylbenzene and to quench the reactions after the experiment time was completed. The resulting solution (1 mL) was transferred to a volumetric flask and the volume adjusted to 2 mL with the mixture DCM:MeCN (1:1, v/v) and 100–300 μ L of methanol, depending on the proportion of PhIO used in the reaction. This procedure is to dissolve any unreacted PhIO and is it necessary before injection into the chromatograph. A volume of 30–100 μ L of this solution was then collected and mixed with 10–40 μ L of the internal standard (*n*-octanol, $9.63 \times 10^{-3} \text{ mol L}^{-1}$ in acetonitrile) and the final volume completed to 500 μ L. The products were analyzed by gas-chromatography. The yields were based on PhIO. Control reactions (without the catalyst) were carried out using the same procedure. Different solvent ratios DCM:MeCN of 10:0, 4:1, 2:3, 1:1, 1:4 and 0:10 for the condition 1:50:1000 (cat:PhIO:substrate) were also carried out. Furthermore, a study of reaction times at 30 min up to a 5 h period was investigated. In this case, 40 μ L samples were extracted at a given time and immediately mixed with a sodium sulfite solution. The resulting solution was then transferred to a 1 mL volumetric flask to chromatographic analysis. The results herein presented represent an average of at least two measurements.

2.2.2. Oxidation by H_2O_2

The oxidation of cyclooctene by H_2O_2 catalyzed by (**1**) and (**2**) was carried out in the solvent mixture (dichloromethane/acetone 1:1, v/v). In a 2 mL vial were mixed 1 mg of the catalyst, 140–170 μ L of H_2O_2 (11.04 mol L^{-1}) and 220 μ L (when cat=(**1**)) or 265 μ L (when cat=(**2**)) of cyclooctene. The final volume of the reaction

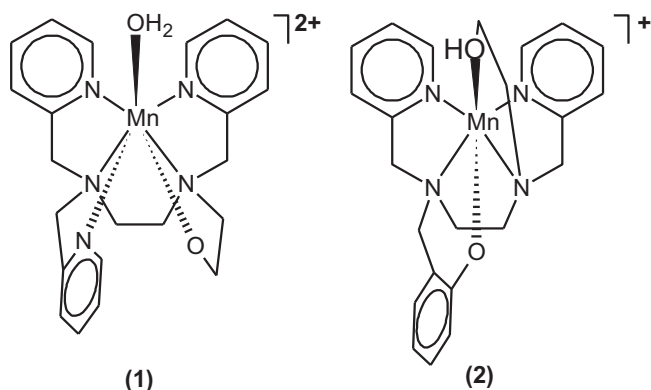


Fig. 1. Representation of the molecular structures of compounds (**1**) and (**2**).

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