



Comparative study of the catalytic thermodynamic barriers for two homologous Mn- and Fe-non-heme oxidation catalysts



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ABSTRACT

Two sets of homologous Mn- and Fe-catalysts, [Mn^{II}LCl₂], [Fe^{II}LCl₂] and [Mn^{II}L(OAc)₂], [Fe^{II}L(OAc)₂] have been synthesized. A detailed comparative study of their catalytic oxidative performance with H₂O₂, *in tandem* with EPR and Low-Temperature UV-vis spectroscopies has been carried out. The [Metal-L(OAc)₂] and [Metal-LCl₂] catalysts did not show any difference in their catalytic behavior i.e. there is no effect of the labile ligands on the studied catalysis. It is found that the Mn-catalysts consistently outcompeted the homologous Fe-catalysts i.e. TOFs (Mn) = 162 vs. TOFs (Fe) = 16. We found that the Fe-catalyst faces a significantly higher activation barrier than the Mn-catalyst i.e. $E_a(\text{Fe}^{\text{II}}\text{L}(\text{OAc})_2) = 91 \text{ kJ/mol} \gg E_a(\text{Mn}^{\text{II}}\text{L}(\text{OAc})_2) = 55 \text{ kJ/mole}$, while the free-energy difference, $\Delta G(\text{Fe}^{\text{II}}\text{L}(\text{OAc})_2) \sim \Delta G(\text{Mn}^{\text{II}}\text{L}(\text{OAc})_2) \sim -145 \text{ kJ/mole}$, did not make difference. Taken altogether the present data clarify that the main thermodynamic barrier, ultimately determining the overall catalytic performance, of these homologous Mn- and Fe-catalysts is the activation energy for the transient intermediates i.e. Mn^{II} to Mn^{IV}=O for the Mn-catalysts and Fe^{II} to Fe^{III}-OOH for the Fe-catalysts. A unified/consistent catalytic thermodynamic concept is discussed, that bears relevance to the catalytic behavior of many non-heme Mn- vs. Fe-oxidation catalysts.

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1. Introduction

In fine chemicals technology, among the end-targets of applied oxidation catalysis is to produce more efficient catalysts *in tandem* with less expensive and more environmentally acceptable processes [1]. Epoxidation reactions of olefins constitute an industrially applicable process for production of epoxides i.e. widely used as raw materials or intermediates for epoxy resin production, paints, surfactants and medicines [2,3]. Environmental regulations on industrial production of chemicals, force companies to diminish environmental pollution [4–7]. Within this environmental/economic context, the use of manganese and iron complexes as active catalysts, associated with hydrogen peroxide as the primary oxidant, is highly desirable. H₂O₂ is increasingly used as oxidant both in industry and in academic research, since its only by-product is water. In the same context, non-heme manganese and non-heme iron catalysts present advantages e.g. convenient synthesis, low production-cost, considerable stability, selectivity toward formation of epoxides [1,8].

In general, the stability and selectivity of a homogeneous catalyst are strongly related to its molecular structure. Consideration of steric, electronic and conformational properties is necessary i.e. in order to design appropriate ligands for metal complexes which will serve as efficient catalysts. Among other properties, the ligands must [i] be resilient to oxidation, and [ii] strongly electron donating, in order to achieve high oxidation states of the active metal [1]. In this context, polydentate ligands containing 2-pyridylmethyl or 2-pyridyl fragments attached to a tertiary nitrogen atom, contain both σ -donor and π -acceptor binding sites. Thus, ligands of this class (e.g. such as tris (2-pyridylmethyl) amine, *tpa* or N,N,N',N'-tetrakis (2-pyridylmethyl) ethylenediamine, *tpen*) are capable of stabilizing both high- and low-oxidation states in their metal complexes [9–11]. Moreover, ligands containing 2,6-di-*tert*-butyl-4-hydroxyphenol groups on the periphery of the ligand frame are also interesting because they might provide antioxidant features [12] and additional endurance to metal oxidation catalysts. 2,6-di-*tert*-butyl-4-hydroxyphenol has been already used as substituent on the porphyrin ring offering remarkable performance in oxidations catalyzed by metalloporphyrins [13–18]. Recently, a new series of non-heme metal complexes with di-(2-picolyl) amine ligand bearing this 2,6-di-*tert*-butyl-4-hydroxyphenol

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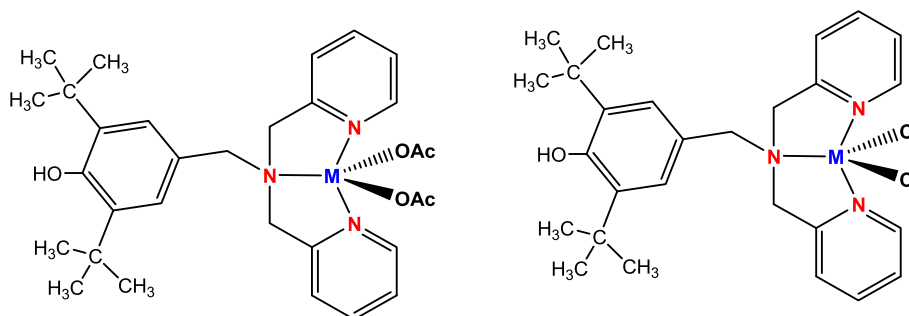


Fig. 1. Structures of $[\text{Mn}^{\text{II}}(\text{L})(\text{OAc})_2]$ (1), $[\text{Mn}^{\text{II}}\text{LCl}_2]$ (2), $[\text{Fe}^{\text{II}}(\text{L})(\text{OAc})_2]$ (3) and $[\text{Fe}^{\text{II}}\text{LCl}_2]$ (4) complexes.

moiety has been reported by one of us [19]. Herein, manganese and iron complexes containing the [N-(3,5-Di-*tert*-butyl-4-hydroxybenzyl)-N,N-di-(2-pyridylmethyl)]amine (L) ligand [19] (Fig. 1) have been evaluated as homogeneous catalysts for alkene epoxidation with hydrogen peroxide.

Herein, we present a method where low-temperature UV–vis spectroscopy was used *in tandem* with low-temperature Electron Paramagnetic Resonance (EPR) to study the transient redox/catalytic intermediates formed during the catalytic cycle of the $[\text{Mn}^{\text{II}}\text{LX}_2]$ and $[\text{Fe}^{\text{II}}\text{LX}_2]$ complexes. EPR is eminently suited for quantitative monitoring of Fe^{III} and Mn^{II} states [20]. Transient oxidation states e.g. ($\text{Fe}^{\text{III}}\text{O}=\text{O}$), Fe^{V} , Mn^{III} , ($\text{Mn}^{\text{IV}}=\text{O}$) can also be detected by EPR [20–22]; however, under ambient temperature, their population is usually rapidly evolving. Therefore they can be trapped only by a systematic freeze-quench protocol that eventually allows optimal detection of these elusive species by EPR. Previously, we have reported the detection of such a catalytic intermediate Fe^{IV} state in a SiO_2 -[Fe-porphyrin] system [15]. In that system, the $\text{Fe}^{\text{IV}}\text{-oxo}$ center was shown to be magnetically coupled with a porphyrin radical i.e. forming the highly-reactive ferryl-species that determines the catalytic performance [15]. In the case of Mn-catalysts, the evolution to higher oxidation states, generated via oxidation of an initial Mn^{III} state has been reported [23] and EPR detection of Mn^{IV} in $\text{Mn}(\text{salen})$ complexes has been also demonstrated [23]. In the aforementioned work [23] the Mn^{IV} state could not be trapped during a ‘standard’ catalytic run; instead, a Mn^{IV} species, was formed by reaction of the initial $\text{Mn}^{\text{V}}\text{-oxo}$ intermediate with the solvent in the absence of a substrate.

Apart from the detection of the elusive transient intermediates, their thermodynamic parameters i.e. activation energy, entropy, enthalpy, Gibbs free energy, are important. Moreover, a direct comparative study of the catalytic and thermodynamic parameters of homologous non-heme Fe and Mn complexes should provide profound insights into the catalytic mechanisms and energetics. Recently, systematic differences have been documented in the catalytic behavior of homologous Mn- vs. Fe-complexes [24–26], however a thermodynamic basis of these observations is still in need. In this context, herein we present the first comparative catalytic/thermodynamic study of the homologous complexes $[\text{Mn}^{\text{II}}(\text{L})(\text{OAc})_2]$ (1) vs. $[\text{Fe}^{\text{II}}(\text{L})(\text{OAc})_2]$ (3) and $[\text{Mn}^{\text{II}}\text{LCl}_2]$ (2) vs. $[\text{Fe}^{\text{II}}\text{LCl}_2]$ (4). A systematic freeze-quench EPR study was carried out to trap the transient intermediates and then to monitor the full time-course of their evolution. In parallel we have performed detailed kinetic studies of the redox evolution of monitoring their UV–vis spectra at a range of temperatures from +25 °C to –45 °C. Low-Temperature UV–vis (LT-UV–vis) spectroscopy allows a *continuous* mapping of the spectral evolution of the complexes. Then, a thermodynamic analysis of the LT-UV–vis data allowed numerical estimates of the activation energies, E_a , as well as ΔS^\ddagger , ΔH^\ddagger , ΔG^\ddagger for the Fe- and Mn-complexes. Based on the EPR and thermodynamic data, we construct a reaction-path scheme which unravels that the

transient intermediates of the Fe-catalysts have higher E_a than the homologous Mn-catalysts, and as result Fe-catalysts have lower catalytic performance than the Mn-catalysts.

2. Materials and methods

2.1. Materials

All synthetic works were carried out under ambient air and at room temperature (25 °C). All solvents were purchased from Aldrich and used as received. The following chemical substrates were obtained in their highest commercial purity, stored at 5 °C and purified by passing through a column of basic alumina prior to use (Aldrich): Cyclohexene, Cyclooctene, Limonene, 1-hexene, *cis*-stilbene, styrene, *trans*- β -methylstyrene. Hydrogen peroxide was 30% (w/w) aqueous solution. GC analysis was performed using an 8000 Fisons chromatograph with a Flame Ionization Detector or a Shimadzu GC-17A gas chromatograph coupled with a GC-MS-QP5000 mass spectrometer. Continuous-flow of H_2O_2 was provided by a digitally-controlled syringe pump (SP101IZ WPI). Solution potential E_h was measured *in situ* by a Metrohm platinum redox electrode (type 6.0401.100).

2.2. Catalytic procedure

In the reactions catalyzed by Mn-complexes 1 and 2, H_2O_2 was slowly added, over a total time of 30 min, in an acetone/MeOH (450/200 μl) solvent mixture under ambient air, at room temperature (25 °C). Then, the alkene (1 mmol), ammonium acetate (1 mmol) as cocatalytic additive, and manganese-catalyst (1 μmol) were added and the resulting reaction solution was vigorously stirred in a glass round-bottom flask for 6 h under ambient conditions. We underline that ammonium acetate is added as an additive that is absolutely required in order to generate efficient Mn-catalytic systems [27]. Acetophenone or bromobenzene was used as internal GC standards. The molar ratio of [Mn-catalyst: H_2O_2 : $\text{CH}_3\text{COONH}_4$:substrate] was equal to [1:2000:1000:1000 μmol]. The total volume of catalytic reaction was about 1 ml.

In the reactions catalyzed by Fe-complexes 3 and 4, H_2O_2 diluted in CH_3CN solvent (1:10 v/v) was slowly added (within a period of 5 min) to a CH_3CN solution containing the catalyst (1 μmol) and the substrate (1000 μmol) under N_2 atmosphere at room temperature (25 °C). The molar ratio [Fe-catalyst: H_2O_2 :substrate] was equal to [1:500:1000 μmol]. Acetophenone or bromobenzene was used as internal GC standards. The total volume of catalytic reaction was approximately 1 ml.

The progress of the catalytic reactions was monitored by GC-MS for 20 μl samples, periodically taken from the reaction mixture. Quantitative analysis of the GC data was done by comparing the integrals of the GC peaks vs. the internal standard, thus providing the substrate conversion and product yield. Reactions were

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