



Catalytic C–H oxidations by nonheme mononuclear Fe(II) complexes of two pentadentate ligands: Evidence for an Fe(IV) oxo intermediate

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ABSTRACT

The oxidation reactions of alkanes with hydrogen peroxide and peracids (peracetic acid (PAA) and *m*-chloroperoxybenzoic acid (mCPBA)) catalysed by two Fe(II) complexes of pentadentate {N₅}-donor ligands have been investigated. Kinetic isotope effect experiments and the use of other mechanistic probes have also been performed. While the total yields of oxidized products are similar regardless of oxidant (e.g. 30–39% for oxidation of cyclohexane), the observed alcohol/ketone ratios and kinetic isotope effects differ significantly with different oxidants. Catalytic reactions in H₂O₂ medium are consistent with the involvement of hydroxyl radicals in the C–H bond cleavage step, and resultant low kinetic isotope effect values. On the other hand, catalytic reactions performed using peracid media indicate the involvement of an oxidant different from the hydroxyl radical. For these reactions, the kinetic isotope effect values are relatively high (within a range of 4.2–5.1) and the C3/C2 selectivity parameters in adamantane oxidation are greater than 11, thereby excluding the presence of hydroxyl radicals in the C–H bond cleavage step. A low spin Fe(III)-OOH species has been detected in the H₂O₂-based catalytic system by UV/Vis, mass spectrometry and EPR spectroscopy, while an Fe(IV)-oxo species is postulated to be the active oxidant in the peracid-based catalytic systems. Computational studies on the C–H oxidation mechanism reveal that while the hydroxyl radical is mainly responsible for the H-atom abstraction in the H₂O₂-based catalytic system, it is the Fe(IV)-oxo species that abstracts the H-atom from the substrate in the peracid-based catalytic systems, in agreement with the experimental observations.

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1. Introduction

The selective functionalization of organic substrate molecules remains a great challenge in catalysis research [1]. For decades, considerable efforts have been made to develop robust and selective homogeneous oxidation catalysts based on transition metals [2]. Nature employs a number of heme and nonheme iron enzymes to carry out analogous vital biological transformations, involving oxidation of substrates that use dioxygen as the ultimate oxidant [3–5]. These metalloenzymes show high regio- and stereoselectivity and operate under mild conditions [4]. Examples of such

enzymes include soluble methane monooxygenases [6] and Rieske oxygenases [4,7] (Fig. 1).

Inspired by Nature, a wide range of mononuclear nonheme iron complexes have been synthesized and investigated as catalysts for the oxidation of alkanes and alkenes, using hydrogen peroxide, peracids, or dioxygen as an external oxidant [8–11]. Amongst these complexes, mononuclear Fe(II) catalysts bearing tetradentate N₄-donor ligands, such as TPA [12], BPMEN [13], BQEN [10b], S,S-PDP [14], Me₂PyTACN, [15] Me₂,MeBzImTACN [16], deserve special mention (Fig. 2). Such Fe(II) complexes exhibit excellent catalytic efficiencies in hydrocarbon oxidation reactions with high stereoregulation and C–H bond selectivity. An important structural feature regarding the above-mentioned catalysts is that the Fe(II) ion has two *cis*-coordinated labile sites, which is considered to be a prerequisite for efficient catalytic oxidation.

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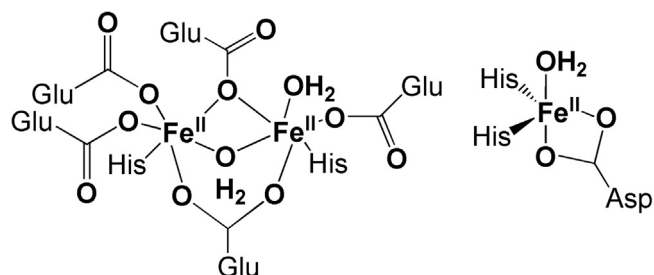


Fig. 1. The active site structures of soluble methane monooxygenase (reduced form, left), and a Rieske oxygenase (right).

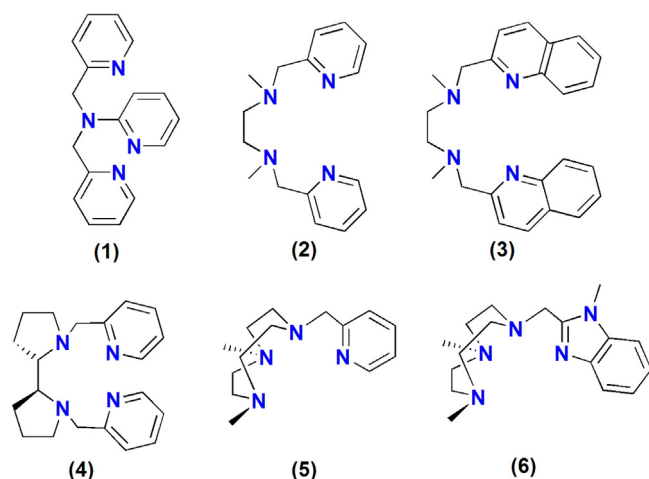


Fig. 2. The structures of the ligands, TPA (1), BPMEN (2), BQEN (3), S,S-PDP (4), Me²PyTACN (5) and Me²,MeBzimTACN (6).

On the other hand, activated bleomycin, a biomolecule and potential antitumor drug that effects the oxidative cleavage of DNA and also the oxidation of hydrocarbons [17], contains a low spin Fe(III)-hydroperoxo unit surrounded by five nitrogen donors [18]. Therefore, oxygen activation and hydrocarbon oxidation by mononuclear Fe(II) complexes containing pentadentate ligands with one labile coordination site have been studied extensively during the last two decades [19–27]. Reactions with suitable oxidants, e.g. O₂, H₂O₂, PhIO, give rise to Fe(III)-OOH or Fe(IV)=O intermediates that have been characterized by various spectroscopic techniques [28–30]. In contrast to the ferrous complexes of tetradentate ligands that have been discussed above, Fe(II) complexes of pentadentate ligands can form high valent Fe(IV)=O intermediates that possess relatively high thermal stability, permitting thorough investigations of such high-valent intermediates in oxidative transformation reactions. In this context, the pentadentate ligand N4Py and its Fe(II)-complex are noteworthy [19]. Both [Fe^{III}(OOH)(N4Py)]²⁺ [19a,28] and [Fe^{IV}(O)(N4Py)]²⁺ [29] have been synthesized from the Fe(II) precursor complex and characterized. The catalytic activities of the Fe(II) complex of N4Py have been studied [20] and the involvement of [Fe^{III}(OOH)(N4Py)]²⁺ and [Fe^{IV}(O)(N4Py)]²⁺ as possible active oxidants during catalysis has been established both experimentally and theoretically [20,27,30,31].

We have previously demonstrated that successive replacement of pyridyl substituents of the ligand N4Py by (*N*-methyl)benzimidazolyl moieties results in an increase in the rates of hydrogen atom abstraction reactions and oxo-transfer reactions by the Fe(IV)-oxo complexes [Fe^{IV}(O)(L¹)]²⁺ and [Fe^{IV}(O)(L²)]²⁺ (L¹ = [*N*-(1-methyl-2-benzimidazolyl)methyl-*N*-(2-pyridyl)methyl-*N*-(bis-2-pyridylmethyl)amine]; L² = [*N*-bis(1-methyl-2-benzimidazolyl)methyl-*N*-(bis-2-pyridylmethyl)amine]; Fig. 3) [32]. Here

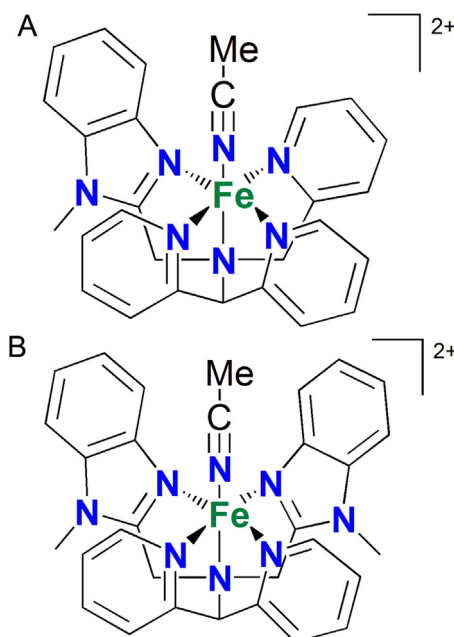


Fig. 3. The structures of the Fe(II)-complexes, [Fe(L¹)(CH₃CN)]²⁺ (1²⁺) (top) and [Fe(L²)(CH₃CN)]²⁺ (2²⁺) (bottom).

we report the oxidation of various hydrocarbons by H₂O₂ or peracids, using the complexes [Fe^{II}(L¹)(CH₃CN)]²⁺ (L = L¹, L²) as catalyst precursors. Spectroscopic studies of possible reactive intermediates operating during catalysis are also described. A detailed theoretical study on the reaction mechanisms involving H₂O₂ and peracids is described.

2. Results and discussion

The catalytic activities of the two ferrous complexes [Fe^{II}(L¹)(CH₃CN)](ClO₄)₂ (1) and [Fe^{II}(L²)(CH₃CN)](ClO₄)₂ (2) (Fig. 3) were studied in oxidation of different alkanes, utilizing hydrogen peroxide, peracetic acid (PAA) or *m*-chloroperoxybenzoic acid (mCPBA) as co-oxidants. The oxidation reactions were carried out under standard catalytic conditions (1:100:1000 ratio for catalyst:oxidant:substrate) in acetonitrile at room temperature, and the results were compared to those for [Fe^{II}(N4Py)(CH₃CN)](ClO₄)₂. The oxidant was added using a syringe pump and a large excess of substrate was used to minimize over-oxidation of the products.

Complex 1 together with H₂O₂ (100 equiv.) oxidizes cyclohexane, and a turnover number (TON) of 21.1 for cyclohexanol and 18.0 for cyclohexanone was obtained with an overall yield of 39% (based on oxidant). Under similar conditions, for complex 2, a TON of 17.4 for cyclohexanol and 14.7 for cyclohexanone was obtained with an overall yield of 32% (Table 1). The alcohol/ketone (A/K) ratio was found to be low (1.2) in both cases, and may be explained by considering the possible involvement of freely diffusing carbon-centered radicals that are trapped by molecular oxygen, followed by a Rus-

Table 1
Catalytic oxidation of cyclohexane carried out by complexes 1 and 2 with H₂O₂^a.

Complex	TON of A ^b	TON of K ^c	Yield (%)	A/K	KIE ^d
1	21.1	18	39	1.2	1.5
2	17.4	14.7	32	1.2	1.7

^a Reaction conditions: see Experimental section.

^b Cyclohexanol.

^c Cyclohexanone.

^d Kinetic isotope effect was determined for the formation of cyclohexanol from a competitive reaction of a (1:1) mixture of cyclohexane and cyclohexane-d₁₂.

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