

# Catalytic oxyfunctionalization of saturated hydrocarbons by non-heme oxo-bridged diiron(III) complexes: role of acetic acid on oxidation reaction

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#### Abstract

Oxo-bridged diiron(III) complexes  $[Fe_2O(L^1)_2(H_2O)_2](ClO_4)_4$  (1) and  $[Fe_2O(L^2)_2(H_2O)_2](ClO_4)_4$  (2), where  $L^1$  and  $L^2$  are tetradentate *N*-donor *N*,*N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine and *N*,*N'*-bis(2-pyridylmethyl)ethane-1,2-diamine respectively, have been isolated as synthetic models of non-heme iron oxygenases and characterized by physicochemical and spectroscopic methods. Both the complexes have been studied as catalysts for the oxyfunctionalization of saturated hydrocarbons using green hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant under mild conditions. The selectivity (A/K) and regioselectivity (3°/2°) in oxidative C–H functionalization of alkanes suggests the involvement of metal-based intermediate in the oxygenation reaction. The catalytic efficiency is found to be strongly dependent on the presence of acetic acid. Remarkable increase in conversion and selectivity favoring the formation of alcohols in the oxidation of cyclohexane and cyclooctane and exclusive hydroxylation of adamantane with drastic enhancement of regioselectivity has been achieved by the addition of acetic acid in the presence of H<sub>2</sub>O<sub>2</sub>.

### Introduction

Selective oxyfunctionalization of saturated hydrocarbons using iron complexes as catalysts under mild and environmental friendly conditions is of enormous importance in homogeneous catalysis and synthetic chemistry [1–5]. Nonheme iron enzymes have attracted a great deal of interest to carry out selective oxidative oxygen transfer into the C-H bond of a variety of hydrocarbons [6, 7]. Presence of oxobridged diiron centers in a variety of metalloenzymes like methane monooxygenases [8-10], ribonucleotide reductase [11, 12] and purple acid phosphatase [13, 14] has directed much focus in the chemistry of oxo-bridged diiron(III) complexes. Over the past few years, a large number of µ-oxobridged diiron complexes have been synthesized as structural models and their catalytic activities in the selective functionalization of saturated hydrocarbons using environmentally green oxidant have been widely investigated. These studies include the following model complexes:  $[Fe_2O(tpa)_2X_2]^{m+1}$ 

Uday Sankar Agarwalla udaygrwlla@gmail.com (tpa = tris-(2-pyridylmethyl)amine, X = Br, Cl, H<sub>2</sub>O) [15, 16]; [Fe<sub>2</sub>O(H<sub>2</sub>O)<sub>2</sub>(tmima)<sub>2</sub>]<sup>4+</sup> (tmima = tris[(1-methylimidazol-2-yl)methyl]amine) [17]; [Fe<sub>2</sub>O(mebpa)<sub>2</sub>Cl<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> (mepba = N(2-methoxyethyl)- N,N-bis(pyrid-2-ylmethyl)amine) [18]; [Fe<sub>2</sub>O(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (phen = 1,10-phenanthroline) [19]; [Fe<sub>2</sub>O(L)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (L = L-(-),4,5-pinenebipyridine) [20]. Among the other active systems of non-heme diiron complexes containing Fe–O–Fe unit reported so far, [Fe<sub>2</sub>O(bbp)<sub>2</sub>(MeOH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (NO<sub>3</sub>)<sub>2</sub> (bbp = 2,6-bis(Nmethyl benzimidazol-2-yl)pyridine) [21]; [Fe<sub>2</sub>O(tpoen)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (tpoen = N(2-pyridylmethoxyethyl)- N,N-bis(2-pyridylmethyl)amine) [22] and [Fe<sub>2</sub>O(L)<sub>4</sub>X<sub>n</sub>]<sup>m+</sup> (L = bipyridine, 4,4<sup>'</sup>-(Me)<sub>2</sub>-bipy, X = H<sub>2</sub>O, Cl) [19, 23] are noteworthy.

In our earlier studies, we have reported that nonheme mononuclear iron(III) complexes of N,N'-bis(2pyridylmethyl)-diamine framework have shown moderate catalytic activity with low selectivity toward oxidation of hydrocarbons in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant [24]. The outcome of previous studies suggested that the iron(III)chloride bond is too strong, which makes the mononuclear iron complexes poor catalysts [25]. From the synthetic models reported so far it has also been observed that the catalytic activity of iron complexes in terms of product yield and selectivity requires the presence of exchangeable

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coordination sites in the metal center [25, 26]. This observation encouraged us to design iron complexes with the same ligand framework in order to enhance their catalytic efficiency toward hydroxylation of saturated C-H bond. In the present study, we have synthesized  $\mu$ -oxo-bridged diiron(III) complexes containing exchangeable water molecule in each iron center,  $[Fe_2O(L^1)_2(H_2O)_2](ClO_4)_4$  (1) and  $[Fe_2O(L^2)_2(H_2O)_2](ClO_4)_4$  (2), where  $L^1 = N, N'$ -bis(2pyridylmethyl)-1,2-cyclohexanediamine and  $L^2 = NN,N'$ bis(2-pyridylmethyl) ethane-1,2-diamine, in the hope that they can serve as an efficient catalyst for the oxyfunctionalization of saturated hydrocarbons. The catalytic properties of the complexes have been studied in the oxidation of alkanes with green and benign  $H_2O_2$  as the terminal oxidant under mild conditions. The effect of acetic acid on the selectivity of oxidation products in the hydrocarbon oxygenation has also been reported.

# **Experimental**

#### Instruments and reagents

The electronic spectra were recorded in acetonitrile on a JASCO V-530 spectrophotometer in the 200-800 nm region. The infrared spectra were performed from KBr disk on a JASCO 5300 FT-IR spectrophotometer in the  $4000-400 \text{ cm}^{-1}$  range. Heraeus Carlo Erba 1108 elemental analyzer was used to collect Elemental microanalyses (C, H and N) data. The product analyses were done by Perkin Elmer Clarus-500 Gas Chromatograph with FID (Elite-I, Polysiloxane, 15-meter column).

All chemicals were purchased from Sigma-Aldrich and used as received. Acetonitrile and dichloromethane used for catalytic experiments were distilled under argon and stored over 4 Å molecular sieves. The active oxygen content of  $H_2O_2$  (as ~ 30% solution in water) was determined iodometrically prior to use.

#### Synthesis of the ligands

The ligands  $L^1$  and  $L^2$  were synthesized and characterized using a previously reported procedure [27].

#### Synthesis of the catalysts

Synthesis of  $[Fe_2O(L^1)_2(H_2O)_2](CIO_4)_4$  (1)

A solution of  $Fe(ClO_4)_3.10H_2O(0.540 \text{ g}, 1 \text{ mmol})$  in methanol (5 ml) was added to a stirred solution of L<sup>1</sup> (0.296 g, 1 mmol) in methanol (5 ml). The mixture was stirred for 1 h, then the precipitate was filtered off, washed twice with small quantities of diethyl ether and dried under vacuum.

The brown mass obtained was purified by recrystallization from acetonitrile.

*Yield*: 0.51 g (44%). Anal. Calcd. for  $C_{36}H_{52}Cl_4Fe_2N_8O_{19}$ : C, 37.4; H, 4.5; N, 9.7. Found: C, 37.2; H, 4.3; N, 9.6%. IR (KBr pellet): selected peaks ν (cm<sup>-1</sup>):798 for Fe–O–Fe<sub>asym</sub>, 1096 for ClO<sub>4</sub><sup>-</sup> ion. Uv–vis (in CH<sub>3</sub>CN)  $\lambda_{max}$ /nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 254 (24,150), 327 (9630), 489 (850).

## Synthesis of $[Fe_2O(L^2)_2(H_2O)_2](CIO_4)_4$ (2)

Complex 2 was prepared by the same procedure employed for complex 1, using  $L^2$  (0.242 g, 1 mmol) in place of  $L^1$  as ligand.

*Yield*: 0.50 g (48%). Anal. Calcd. for C<sub>28</sub>H<sub>40</sub>Cl<sub>4</sub>Fe<sub>2</sub>N<sub>8</sub>O<sub>19</sub>: C, 32.2; H, 3.9; N, 10.7. Found: C, 32.4; H, 3.7; N, 10.6%. IR (KBr pellet): selected peaks ν (cm<sup>-1</sup>): 802 for Fe–O-Fe<sub>asym</sub>, 1093 for ClO<sub>4</sub><sup>-</sup> ion. Uv–vis (in CH<sub>3</sub>CN)  $\lambda_{max}/nm$ (ε, M<sup>-1</sup> cm<sup>-1</sup>): 254 (36,500), 324 (18,600), 489 (1500).

#### **Catalytic oxidation reaction**

In a typical run, 7 mM of oxidant  $H_2O_2$  was added to a small screw capped vials fitted with PTFE septa containing 2 ml of acetonitrile solution (or 1:1 mixture of acetonitrile and dichloromethane in case of adamantane oxidation) of catalyst (0.7 mM) and substrate (700 mM) in a catalyst: oxidant: substrate molar ratio of 1:10:1000. After 3 h of stirring at room temperature (1 h when the catalytic oxidation was carried out in the presence of 50 µM AcOH), a standard solution of internal standard, pentafluoroiodobenzene (PFIB), was added to the reaction mixture. The analysis was done by gas chromatographic analysis after injecting an aliquot (1 µl) from the reaction vial into preheated GC. The conversion of alkanes into the oxygenated products was identified and quantified by a comparison of the GC retention times of the authentic reference sample and the reaction sample.

# **Results and discussion**

#### **Synthesis**

Oxo-bridged diiron(III) complexes (1 and 2) containing  $L^1$ and  $L^2$  ligand framework were obtained readily by stirring a reaction mixture of ligand with an equimolar amount of Fe(ClO<sub>4</sub>)<sub>3</sub>.10H<sub>2</sub>O in methanol at room temperature. The resultant brownish yellow precipitate was recrystallized from acetonitrile and was characterized by spectral methods and elemental analysis. The proposed structure of the complexes 1 and 2 is shown in Scheme 1.



Scheme 1 Proposed structure of the complexes  $[Fe_2O(L^n)_2(H_2O)_2]$   $(ClO_4)_4 \ (n=1 \ and \ 2)$ 

#### Characterization

Complexes 1 and 2 display electronic absorption spectra in the region 250-500 nm in acetonitrile. An intense band at 254 nm obtained in both the complexes is attributed to the intra-ligand  $\pi \rightarrow \pi^*$  transition within the pyridine ring [22, 28]. The electronic spectrum of 1 shows absorption bands at 327 nm and 489 nm which are characteristic of oxo-toiron(III) LMCT transitions [18, 29]. Complex 2 shows similar absorption pattern with bands at 324 nm and 489 nm. The less intense band at 489 nm in both the complexes is assigned to the  ${}^{6}A_{1} \rightarrow ({}^{4}A_{1}, {}^{4}E)$  transition and is the signature of the Fe-( $\mu$ -O)-Fe core, suggesting that the dinuclear structure is maintained in solution [30].

The presence of the Fe–O–Fe motif in the diiron(III) complexes **1** and **2** is further confirmed by the vibrational spectroscopy. In the IR spectrum, peak at 798 cm<sup>-1</sup> for complex **1** and at 802 cm<sup>-1</sup> for complex **2** can be assigned to Fe–O–Fe asymmetric stretching mode on the basis of the literature reports [31, 32]. Both the complexes also exhibit intense bands around 1100 cm<sup>-1</sup>, indicating the presence of perchlorate anion [32].

The spectral and elemental analyses data (experimental section) of the complexes **1** and **2** are in agreement with the proposed structures shown in Scheme 1.

# Oxyfunctionalization of saturated hydrocarbons by diiron complexes

The catalytic properties of the synthesized diiron(III) complexes 1 and 2 toward alkane functionalization has been explored at room temperature in the presence of environmentally friendly  $H_2O_2$  as oxidant. The product distributions for cyclohexane, cyclooctane and adamantane oxidation have been compiled Table 1.

The present catalytic system catalyzed the oxidation of cyclohexane affording cyclohexanol (CyOH, A) and cyclohexanone (CyO, K). In the case of complex **1** as catalyst, a combined yield of 22% based on oxidant has been achieved after 3 h of reaction with an A/K ratio of 1.8. The conversion with **2** under similar reaction conditions is lower (17%) than those found for complex 1, A/K ratio remains the same. Similar results are obtained when the catalytic reaction is performed under nitrogen atmosphere. Under the similar reaction conditions, cyclooctane was oxidized to the corresponding alcohol and ketone with selectivity (A/K 2.3 for complex 1 and 2.4 for complex 2) higher than that found for cyclohexane oxidation, the amount of oxidized product formed being almost same (Table 1, entries 3,4). Control experiments performed in the absence of catalyst fail to affect any oxidative transformation of alkanes in the presence of  $H_2O_2$  revealing that complexes 1 and 2 have significant contribution in the oxidation reaction. The catalytic activity with Fe(ClO<sub>4</sub>)<sub>3</sub>.10H<sub>2</sub>O instead of diiron complex has also been tested in alkane oxidation and very little catalytic activities were observed under our experimental conditions. Further, no products are observed in the reaction of cyclohexane and catalyst in the absence of H<sub>2</sub>O<sub>2</sub>.

The behavior of present catalytic system toward adamantane oxidation has also been investigated. The use of adamantane as substrate resulted in oxidation at both secondary and tertiary carbon centers, affording the hydroxylation products 1-adamantanol and 2-adamantanol along with very little amount of subsequent oxidation product 2-adamantanone (Scheme 2).

The regioselectivity is parameterized as a  $3^{\circ}/2^{\circ}$  ratio derived from the amount of 1-adamantanol (1-ol) divided by the amount of 2-adamantanol (2-ol) and 2-adamantanone (2-one) and multiplied by 3 to correct the threefold higher number of secondary C–H bonds.

A high selectivity of the catalytic oxidizing system for the tertiary C–H bonds versus secondary ones has been observed in the oxidation of adamantane with  $H_2O_2$ , as indicated by 3°/2° ratio (Table 1, entries 5, 6). Complex 1 showed much higher efficiency in adamantane oxidation relative to complex 2. A total conversion of 33% with 3°/2° ratio of 11.1 was obtained by  $1/H_2O_2$  system. On the other hand, oxo-bridged dinuclear complex 2 displayed an activity with 24% conversion with 3°/2° ratio of 11.4.

It is interesting to compare the catalytic behavior of the synthesized non-heme diiron(III) complexes with those of reported catalysts toward oxidation of saturated hydrocarbons. The selectivity for cyclohexane oxidation (A/K) and regioselectivity  $(3^{\circ}/2^{\circ})$  in the case of adamantane oxidation has been found to be higher in comparison to Gif family of catalysts [33]. Catalysts such as  $[Fe_2O(OAc)_2(bpy)_2]Cl_2$  [34],  $[Fe_2O(OAc)_2(tmima)_2](ClO_4)_3$  [17] and  $[Fe_2O(bpy)_4(H_2O)_2]$  ( $ClO_4)_4$  [35] exhibit A/K values around 1. With adamantane as substrate, the selectivity for the oxidation at the tertiary position  $(3^{\circ}/2^{\circ})$  higher than the published results with diiron complexes has also been observed [22, 34–36]. The selectivity with A/K ratio of 1.8-2.4 in the oxidation of cyclohexane and cyclooctane and regioselectivity with  $3^{\circ}/2^{\circ}$  ratio of 11.1–11.4 in adamantane oxidation catalyzed by the

Entry	Substrate	Catalyst	Conversion (%)	Product yield (?	%) <sup>a</sup>		Remarks <sup>b</sup>
Cyclohexane oxidation				Cyclohexanol		Cyclohexanone	A/K
1	$\bigcirc$	1	22	14		8	1.8
2	$\checkmark$	2	17	11		6	1.8
Cyclooctane oxidation				Cyclooctanol		Cyclooctanone	A/K
3	$\bigcirc$	1	23	16		7	2.3
4		2	17	12		5	2.4
Adamantane oxidation				1-ol	2-ol	2-one	$3^{\circ}/2^{\circ}$
5	D	1	33	26	5	2	11.1
6		2	24	19	3	2	11.4

Table 1 The results of oxidation of alkanes by diiron(III) complexes 1 and 2 with  $H_2O_2$ 

Reaction conditions: Alkane (700 mM), catalyst (0.7 mM), H<sub>2</sub>O<sub>2</sub> (7 mM), CH<sub>3</sub>CN (2 ml), RT, 3 h

<sup>a</sup>Yields are determined by GC analysis with internal standard based on the oxidant used

<sup>b</sup>A/K = alcohol/ketone,  $3^{\circ}/2^{\circ} = (1 - ol \times 3)/(2 - ol + 2 - one)$ 

synthesized oxo-bridged non-heme diiron complexes with  $H_2O_2$  convey a hint of the presence of metal-based oxidant



Scheme 2 Possible products obtained in the oxidation of adamantane

[37, 38]. Also no change in the product selectivity and yield was observed upon performing the hydroxylation reaction under nitrogen atmosphere, which ruled out the formation of cyclohexylperoxide species. This is also supported the involvement of metal-based oxidant in the catalytic oxyfunctionlization of saturated hydrocarbons [39].

# Role of acetic acid in the catalytic oxidation of alkanes

The catalytic activities of the diiron(III) complexes **1** and **2** toward oxidation of saturated hydrocarbons have also been studied with  $H_2O_2$  in the presence of acetic acid (AcOH). Both the complexes displayed efficient hydroxylation of cyclohexane, cyclooctane and adamantane with an excellent selectivity in the presence of  $H_2O_2$ /AcOH. The obtained catalytic results are summarized in Table 2.

Cyclohexane oxidation catalyzed by  $1/H_2O_2$  in the presence of acetic acid provided 26% of CyOH and 7% of CyO with an A/K ratio of 3.7. However, complex 2 as catalyst afforded lower yield of oxygenates with 24% conversion based on oxidant (Table 2, entry 2). Similarly, oxyfunctionalization of cyclooctane by oxo-bridged diiron(III) catalysts produced cyclooctanol with yields 32% and 24% along with minor amount of cyclooctanone (5-7%) while the corresponding A/K ratio was found to be 4.6 and 4.8 respectively (Table 2, entries 3–4). In both the cases, amount of ketone formed remains the same as that obtained in the absence of AcOH. On the other hand, exclusive hydroxylation has been achieved with  $H_2O_2$  in the presence of acetic acid and not even a trace amount of subsequent oxidation product 2-adamantanone was detected (Table 2, entries 5 and 6). A total conversion of 48% for 1 and 35% for 2 by H<sub>2</sub>O<sub>2</sub>/AcOH with  $3^{\circ}/2^{\circ}$  of 17.6–18.0 was obtained.

The data presented in Table 2 indicated that the use of AcOH as an additive in non-heme diiron(III) catalyzed alkane oxidation resulted in an increase in both catalytic activity and selectivity toward hydroxylation as compared with the reactivity in the absence of acetic acid (Table 1). Moreover, addition of AcOH to 1 or 2 in the presence of  $H_2O_2$  also resulted in an increase in the oxidation rate; the reaction time reduced to 1 h as compared to 3 h in the absence of AcOH. Here also, the involvement of metal-based oxidants in the C–H hydroxylation of cyclohexane,

Entry	Substrate	Catalyst	Conversion (%)	Product Yield (%	6) <sup>a</sup>		Remarks <sup>b</sup>
Cyclohexane oxidation				Cyclohexanol		Cyclohexanone	A/K
1	$\bigcirc$	1	33	26		7	3.7
2	$\checkmark$	2	24	19		5	3.8
Cyclooctane oxidation				Cyclooctanol		Cyclooctanone	A/K
3	$\bigcirc$	1	39	32		7	4.6
4		2	29	24		5	4.8
Adamantane oxidation				1-ol	2-ol	2-one	3°/2°
5	D	1	48	41	7	_	17.6
6		2	35	30	5	-	18.0

Table 2 Product distributions for the oxidation of alkanes with H<sub>2</sub>O<sub>2</sub> in the presence of AcOH

Reaction conditions: Alkane (700 mM), catalyst (0.7 mM), H<sub>2</sub>O<sub>2</sub> (7 mM), AcOH (50 µM), CH<sub>3</sub>CN (2 ml), RT, 1 h

<sup>a</sup>Yields are determined by GC analysis with internal standard based on the oxidant used

<sup>b</sup>A/K = alcohol/ketone,  $3^{\circ}/2^{\circ} = (1 \text{-ol } x 3)/(2 \text{-ol} + 2 \text{-one})$ 

cyclooctane and adamantane has been suggested as indicated by A/K and  $3^{\circ}/2^{\circ}$  ratio.

To explore the effect of AcOH in alkane oxidation by  $H_2O_2$ , it has been proposed that in the first step of the reaction, the binding of the oxidant  $H_2O_2$  to the dinuclear complex results in the formation of Fe<sup>III</sup>–OOH intermediate, which play a key role in the catalytic cycle of alkane hydroxylation. On the basis of literature reports [40, 41], it has been suggested that the addition of AcOH promoted the heterolytic cleavage of the O–O bond to generate high-valent iron-oxo species (active oxidizing intermediate), which on subsequent reaction with alkane results in hydroxylation. The involvement of this high-valent iron-oxo species leads to hydrocarbon oxidation with significant chemo- and regioselectivity.

## Conclusion

In summary,  $\mu$ -oxo-bridged diiron(III) complexes (1 and 2) containing tetradentate *N*,*N*'-bis(2-pyridylmethyl)-diamine ligand framework have been synthesized and characterized. The synthesized complexes efficiently catalyze the oxidation of alkanes at room temperature with environmentally friendly H<sub>2</sub>O<sub>2</sub> as oxidant. The catalytic experimental results (A/K and 3°/2° ratio) suggest that the oxidation of saturated hydrocarbons by H<sub>2</sub>O<sub>2</sub> occurs via a mechanism involving metal-based oxidant. The preference for hydroxylation toward hydrocarbon oxidation has been amplified in the presence of acetic acid. It has been found that catalytic

oxidation of cyclohexane and cyclooctane provide mainly alcohol along with very little amount of ketone with H<sub>2</sub>O<sub>2</sub>/ AcOH. On the other hand, it is remarkable that only the hydroxylation products 1-adamantanol and 2-adamantanol with no subsequent oxidation product 2-adamantanone have been detected in the presence of acetic acid during adamantane oxidation. Both the product yield and selectivity toward hydroxylation of saturated hydrocarbons have been drastically improved by the synthesized non-heme oxo-bridged diiron complexes with the exchangeable coordination sites using  $H_2O_2$  as oxidant in the presence of acetic acid. Thus, the addition of acetic acid in the presence of  $H_2O_2$  can be a good strategy to design efficient and synthetically useful systems for hydroxylation of saturated hydrocarbons. Further studies on detailed mechanism of the reactions are currently in progress. This work also explores the opportunity to investigate the effect of acetic acid in the presence of H<sub>2</sub>O<sub>2</sub> toward olefin epoxidation catalyzed by non-heme diiron complexes.

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