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PII: S0020-1693(16)30348-6
DOI: http://dx.doi.org/10.1016/j.ica.2016.06.038
Reference: ICA 17129

To appear in: *Inorganica Chimica Acta*

Received Date: 3 February 2016
Revised Date: 9 May 2016
Accepted Date: 28 June 2016

Please cite this article as: J.M. Bae, M.M. Lee, S.A. Lee, S.Y. Lee, K.H. Bok, J. Kim, C. Kim, Nonheme iron complex-catalyzed efficient alcohol oxidation by *t*-BuOOH with *N*-hydroxyphthalimide (NHPI) as co-catalyst: Implication of high valent iron-oxo species, *Inorganica Chimica Acta* (2016), doi: http://dx.doi.org/10.1016/j.ica.2016.06.038

Nonheme iron complex-catalyzed efficient alcohol oxidation by *t*-BuOOH with *N*-hydroxyphthalimide (NHPI) as co-catalyst: Implication of high valent iron-oxo species

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Abstract: Two iron catalysts ([Fe(bpc)Cl_2][Et_4N] (**1a**) and [Fe(Me_2bpb)Cl_2][Et_3NH] (**1b**) displayed efficient catalysis in oxidation of various alcohols to the corresponding carbonyl products using *t*-BuOOH as an oxidant in the presence of *N*-hydroxyphthalimide (NHPI) under mild conditions. **1a** having an electron-withdrawing group showed a little better catalytic activity than that of **1b** with an electron-donating group. The mechanistic studies through Hammett plot, deuterium isotope effect, and the use of 2-methyl-1-phenylprop-2-yl hydroperoxide (MPPH) as a mechanistic probe suggested that the reactive oxidants responsible for the alcohol oxidation possibly involved Fe^{IV}=O species, alkoxy radical ($RO^{\cdot}$), and phthalimide *N*-oxyl radical ($PINO^{\cdot}$). On the other hand, the presence of imidazole increased the heterolytic cleavage of Fe-OOR intermediate to form Fe^{V}=O species and accelerated its O-O bond cleavage rate. In particular, the formation of Fe^{V}=O intermediate via the heterolytic cleavage of Fe-OOR species in the presence of imidazole in the catalytic oxidation systems of nonheme iron complexes with *t*-BuOOH was substantialized, for the first time, to the best of our knowledge.

Keywords: nonheme iron complexes, alcohol oxidation, high-valent iron-oxo species, *tert*-butyl hydroperoxide, imidazole, *N*-hydroxyphthalimide.

1. Introduction

Efficient and selective oxidation of alcohols to their corresponding carbonyl compounds is an essential transformation in organic synthesis because the target compounds, which can be gained directly in one-pot sequences, are significant precursors for many chemicals [1]. Most catalytic methods for oxidation of alcohols have been designed utilizing various transition metals such as Pd [2], Cu [3], Co [4], Ru [5], and Au [6]. Unfortunately, these transition metals cause disadvantages, such as expensive reagents, high reagent loadings and generation of a lot of toxic heavy metal waste [7]. To overcome these problems, more efficient, cheaper, and greener oxidation processes have been recently developed in both industry and academia [1g-h,8]. In these processes, iron is an attractive candidate because it is readily available, inexpensive, abundant in nature and less toxic compared to the other transition metals [9]. However, not many reports have been published to-date on alcohol oxidation with iron-based complexes [10]. Moreover, some iron-based catalysts exhibit selectivity and reactivity only toward a few types of substrates. Thus, iron-based catalysts, with high selectivity and efficiency for alcohol oxidation are still in great demand.

Peroxides, such as hydrogen peroxide (H_2O_2) or *tert*-butyl hydroperoxide (*t*-BuOOH) have been preferred more as environmentally friendly oxidation systems due to their non-toxic reaction products [11], than the systems employing toxic oxidants such as MCPBA, PhIO, CrO_3. Additionally, the peroxides are cheaper and readily available [12]. However, *t*-BuOOH is not so much recognized as a promising oxidant, which is possibly because its reaction with nonheme iron complexes affords non-specific products. The non-specific products are formed by Fe^{IV}=O species and *tert*-butoxy radical, which are produced from the homolytic O-O bond cleavage of Fe-OOR species. Therefore, one of the important goals of bioinorganic chemists is to produce Fe^{V}=O species from the reactions of *t*-BuOOH and nonheme iron catalysts, which would show specific hydrocarbon oxidations. To the best of our knowledge, Fe^{V}=O species that is generated from the reaction of nonheme iron(III) complexes with *t*-BuOOH has not been reported until now.

NHPI was first used by Masui as an efficient electron carrier in the electrochemical oxidation of alcohols [13]. Subsequently, Ishii *et al.* found that NHPI can also catalyze efficiently aerobic oxidation of various organic substrates to oxygen-containing compounds under non-electrochemical conditions [13c]. They explained that $PINO^{\cdot}$ radical, which was

derived from NHPI can abstract a hydrogen atom from the C-H bond and improve the reaction rates and selectivities [14].

Meanwhile, we reported epoxidation of olefins in excess by *m*-chloroperbenzoic acid (MCPBA) as terminal oxidant with two amide-based nonheme iron complexes ([Fe(Me_2bpb)(H_2O)] and [Fe(bpc)(H_2O)]) [15]. However, these two iron catalysts were less efficient for alcohol oxidation, because they were not robust enough to carry out the C-H bond activation of alcohols at alcohol to MCPBA ratio of 1:1. In order to improve the efficiency of alcohol oxidation with the above two iron complexes and to observe possible iron-oxo species from the reaction of the nonheme iron complexes with *t*-BuOOH, we planned to replace the strong oxidant MCPBA with a combination of environmentally friendly and mild oxidant *t*-BuOOH and NHPI as a co-catalyst.

In this paper, we report efficient oxidation of alcohols to their corresponding carbonyl compounds with *t*-BuOOH catalyzed by two iron complexes (**1a** and **1b**, see Scheme 1) in the presence of NHPI as a co-catalyst. Moreover, the reaction mechanism for the alcohol oxidation reactions will be discussed based on the product analysis, such as Hammett plot, kinetic isotope effect (KIE) study, and the use of MPPH as a mechanistic probe. Under the same conditions, in particular, the presence of Fe^{V}=O species was proposed in the presence of imidazole, which has not been reported earlier from the reactions of *t*-BuOOH with nonheme iron complexes.

2. Results and Discussion

Optimized conditions for alcohol oxidation: In order to find the optimized conditions for the most efficient alcohol oxidation, we conducted the oxidation of cyclohexanol with *t*-BuOOH using imidazole or/and NHPI as co-catalyst in the presence of iron complexes under various reaction conditions as shown in Table 1. CH_3CN was found to be the best solvent for the reactions. The control experiments indicated that presence of both the iron catalyst and NHPI was absolutely necessary for efficient alcohol oxidation (entries 1-9 in Table 1 and Figure S1). Cyclohexanol was oxidized effectively to the corresponding ketone in the highest yield only in presence of both the iron catalysts and NHPI (87.1% for **1a** and 87.3% for **1b**, entries 6 and 8) under various reaction conditions. Under anaerobic conditions, the yields for cyclohexanol oxidation with catalysts **1a** and **1b** were almost identical to those obtained in

the aerobic systems (entries 6 vs 7 and 8 vs 9), indicating that O_2 was little involved in the alcohol oxidation reaction. Switching to imidazole from NHPI gave worse oxidation results (entries 4 vs 6 and 5 vs 8), although its presence made the reaction time faster from 7 h to 0.17 h. On the other hand, presence of both NHPI and imidazole reduced the product yield to half (compare entries 6 vs 10 and 8 vs 11). Next, we examined the stability of catalysts **1a** and **1b** during the catalytic reactions. In the presence of imidazole, most of **1b**, with electron-donating groups ($-CH_3$), decomposed at the end of the reaction (Figure S2(b)), while **1a**, with the electron-withdrawing groups (-Cl), decomposed to a lesser extent (Figure S2(a)). These observations might be consistent with small amounts of products as shown in entries 4 and 5 of Table 1. In presence of NHPI, **1a** and **1b** seemed to be robust (Figure S3). Therefore, we may observe high yield of the products. On the other hand, in the presence of both NHPI and imidazole, little **1a** and some of **1b** decomposed (Figure S4) and these results seemed to be consistent with the reduced yields of the products that were observed in the reactivity study (entries 10 and 11 in Table 1). Another possibility for the reduced yields of the products in the presence of imidazole is that *t*-BuOOH also acts as a substrate toward a potential oxidant Fe^{V}=O species generated from heterolytic cleavage of Fe-OOR intermediate [16].

Oxidation of various alcohols catalyzed by iron complexes: As the most efficient results for the alcohol oxidation were obtained under the condition of entries 6 and 8 in Table 1, the oxidation reaction of various alcohols with *t*-BuOOH was carried out under those conditions and the results are shown in Table 2. With complex **1a**, cyclic alcohols such as cyclopentanol and cycloheptanol were oxidized to the corresponding ketones showing excellent yields (70.5% and 100%; entries 1 and 2), with conversions ranging from 83.3 to 100%. In the case of benzyl alcohol (entry 3), the benzaldehyde (45.4%) was a major product along with moderate amounts of benzoic acid (22.4%), which was generated from further oxidation of benzaldehyde. Secondary alcohol, *viz. sec*-phenethyl alcohol, produced the corresponding ketone with a good yield (93.5%, entry 4). *cis*-2- and *trans*-2-Methylcyclohexanols were almost quantitatively converted to the corresponding ketones, while *trans*-2-methylcyclohexanol took a longer reaction time (14 h) than *cis*-2-methylcyclohexanol because of steric hindrance (entries 5 and 6). *endo*-Norborneol showed a higher activity than *exo*-norborneol (100% vs 57.9%, entries 7 and 8). A linear aliphatic primary alcohol, 1-

octanol, was converted to the corresponding aldehyde (1.7%, entry 9), which underwent further oxidation to the corresponding carboxylic acid (14.4%). Linear aliphatic secondary alcohols such as 2-hexanol, 3-hexanol and 2-octanol were oxidized smoothly to the corresponding ketones in high yields (entries 10, 11 and 12). Complex **1b** showed a little lower efficiency than **1a** (Table 2). These results demonstrated that the substitution of an electron withdrawing group -Cl on the ligand enhanced its reactivity toward alcohol oxidation than an electron-donating group -CH_3, which was similar to the results observed in the olefin epoxidation systems using [Fe(Me_2bpb)(H_2O)] vs [Fe(bpc)(H_2O)] complexes [15c].

Competitive experiments of *sec*-phenethyl alcohol and *para*-substituted *sec*-phenethyl alcohols for Hammett plot: To further investigate the electronic influence of the substituents on the reaction rate, we carried out the competitive oxidation between *sec*-phenethyl alcohol and equivalent amounts of *para*-substituted *sec*-phenethyl alcohols by iron complexes with *t*-BuOOH in the presence of NHPI. The ρ values were determined to be -0.44 for **1a** (Figure 1) and -0.40 for **1b** (Figure S5). The negative ρ values indicated the electrophilic character of the reactive intermediates responsible for the alcohol oxidation. In addition, the two similar ρ values implied that both **1a** and **1b** possibly catalyzed alcohol oxidation via the same reaction mechanism. These ρ values are smaller than those reported for the oxidation of phenethyl alcohols using P-450 enzymes (-1.19 and -1.41) [17] and iron porphyrin complex [(F_{20}TPP)FeCl] (F_{20}TPP = tetrakis(pentafluorophenyl)porphyrin) (-1.34) [18].

Kinetic isotope effect (KIE) study on competitive oxidation of benzyl alcohol and deuterated benzyl alcohol by *t*-BuOOH in the presence of iron complexes: Since the kinetic isotope effect had been extensively used as a mechanistic probe in alkane hydroxylation by both P-450 enzymes and metalloporphyrin models [18,19], we studied intermolecular competitive alcohol oxidation of benzyl alcohol and benzyl alcohol-d_7 by *t*-BuOOH in presence of the two iron catalysts. These reactions were performed in presence of excess substrate because further oxidation of benzaldehyde, derived from benzyl alcohol, to benzoic acid obstructed the determination of the exact KIE value. Thus, reliable KIEs were obtained from the formation ratio of both benzaldehyde and deuterated benzaldehyde as the only product in these competitive experiments.

Alcohol oxidation by only NHPI without any catalyst showed a k_H/k_D value of 2.3 (yield: less than 10% after 1 day, entry 1, Table 3), indicating a typical radical type of alcohol oxidation by PINO$^{\cdot}$ [20]. The k_H/k_D for benzyl alcohol oxidation by *t*-BuOOH with iron catalysts and without both imidazole and NHPI afforded 5.1 for **1a** and 4.8 for **1b** (entries 2 and 3, Table 3). We assumed that the reactive species under entries 2 and 3 might be Fe^{IV}=O species and *tert*-butoxy radical and will be discussed later. The KIE values for catalysts **1a** and **1b** in the presence of imidazole without NHPI were found to be 3.5 and 3.8, respectively (entry 4 and 5). These values were almost identical to those of a corresponding hydrogen abstraction reaction by the *tert*-butoxy radical (entry 10) and by the combination of an iron(III) porphyrin complex [(F_{20}TPP)FeCl] with MCPBA [18]. The KIE values for catalysts **1a** and **1b** in the presence of NHPI without imidazole were determined to be 6.3 and 5.8, respectively (entries 6 and 7). These results suggested that Fe^{IV}=O, *t*-BuO$^{\cdot}$ radical, and PINO$^{\cdot}$ radical species might be involved in alcohol oxidation and will also be discussed in details later. In the presence of both imidazole and NHPI, the KIE values were 6.7 for **1a** and 6.3 for **1b**, which were the highest among all the reactions tested in this study. Based on these results, it can be concluded that hydrogen atom abstraction from C-H bonds was involved in the rate-determining step, and that the reactive species responsible for the alcohol oxidation under each reaction condition of Table 3 might be different.

Analysis of the O-O bond cleavage products from the alcohol oxidation reactions by MPPH in the presence of iron complexes: Previously, MPPH had been used a mechanistic probe to distinguish between heterolytic and homolytic cleavage of alkyl hydroperoxide O-O bond [21]. As shown in Scheme 2, if the O-O bond of the Fe-alkylperoxo intermediate (Fe^{III}-OOC(O)R, **2**) is heterolytically cleaved, it can generate 2-methyl-1-phenylprop-2-ol (MPPOH (**5**)) as a heterolytic cleavage product and Fe^{V}=O species (**3**, pathway (a) of Scheme 2) responsible for the alcohol oxidation. On the other hand, homolysis of the O-O bond can afford the Fe^{IV}=O intermediate (**4**) and alkoxy radical, which can form benzyl radical and acetone via a fast β-scission cleavage (2.2×10^8 s^{-1}) (pathway (b) of Scheme 2). This benzyl radical is then converted to benzyl alcohol (**6**), benzaldehyde (**7**), and toluene (**8**) [21a,d,22].

We investigated the oxidation of *sec*-phenethyl alcohol with MPPH as a mechanistic probe in the presence of iron catalysts (Table 4). The oxidation results for catalyst **1a**showed

5.7% of MPPOH as a heterolytic cleavage product, whereas 69.6% of benzaldehyde and 11.1% of benzyl alcohol as homolytic cleavage products without imidazole and NHPI (entry 1). The yield of acetophenone as the product was 14%. This result demonstrated that the intermediate Fe-OOR species formed from the reaction of iron(III) complex with MPPH was cleaved as 6.5% heterolysis and 93.5% hemolysis. Before we were confident about the completion of the oxidation reaction, we carried out another control experiment to determine whether MPPH was completely consumed by catalyst **1a** during the reaction period (10 h). Therefore, in the duplicate experiment PPh_3 was added into the reaction mixture after the given reaction time (entry 2), because it is well known that alkyl hydroperoxides react quickly with PPh_3 to give the corresponding alcohols [23]. The product analysis of entries 1 and 2 in Table 4 showed nearly identical product distributions, suggesting that MPPH decomposed completely during the alcohol oxidation reactions within the given reaction time. Next, we carried out the same oxidation reaction of *sec*-phenethyl alcohol with MPPH in the presence of imidazole, and the results showed 12.4% of the heterolytic product, whereas 73.1% and 9.0% of the homolytic products (entry 5), indicating a 13.0% heterolytic and 87.0% homolytic cleavage of Fe-OOR species. These results suggested that a certain amount of heterolytic cleavage product from Fe-OOR species, *viz.* Fe^{V}=O species, could be formed in the presence of imidazole, which was not ever reported from the reactions of *t*-BuOOH with nonheme iron complexes. In the presence of NHPI, 1.2% of MPPOH and 98.2% of benzaldehyde were obtained (entry 9), surprisingly, suggesting that the homolytic cleavage of Fe-OOR species occurred exclusively. In the presence of both imidazole and NHPI, 14.0% of MPPOH and 73.3% of benzaldehyde were formed (entry 13), indicating 16.0% heterolytic and 84.0% homolytic cleavage of the Fe-OOR species. The highest heterolytic cleavage portion was observed under these conditions. These results indicated that the heterolytic cleavage of the iron(III)-alkylperoxo species could occur in the catalytic reactions of nonheme iron(III) complexes with *t*-BuOOH under a certain condition, for example, in the presence of imidazole. Similar results were also obtained for **1b** (entries 3-4, 7-8, 11-12, 15-16, Table 4), indicating that both catalysts **1a** and **1b** possibly catalyze alcohol oxidation via the same reaction mechanism.

Imidazole effect on the alcohol oxidation: Imidazole had been reported as a co-catalyst in hydrocarbon oxidation reactions in literatures dealing with iron and manganese porphyrin

complexes [24-29]. Labeque and Marnett studied the effects of imidazole on olefin epoxidation by heme iron complexes with *t*-BuOOH [30], and found that the presence of imidazole enhanced the yields of epoxide. Based on these results, they proposed that imidazole might act as a general base catalyst to promote heterolytic cleavage of an O-O bond [26-31]. We also investigated the influence of imidazole in our catalytic oxidation of alcohols. As shown in the entries 2 and 3 vs 4 and 5 of Table 1, the presence of imidazole reduced the reaction time from 10 h to 0.17 h with no change in the yield of products. The presence of imidazole with NHPI also reduced the reaction time from 7 h to 1 h (entries 6 and 8 vs 10 and 11), although in this case the product yields were reduced to half. Under the same condition, in Table 4 are shown the alcohol oxidation results due to the effect of imidazole on the cleavage mode of alkyl hydroperoxide O-O bond using MPPH as the oxidant. As shown in entries 1 and 3 vs 5 and 7, imidazole enhanced the heterolytic O-O bond cleavage of Fe-OOR intermediate almost twice that of the one without imidazole. Moreover, the presence of imidazole with NHPI increased the heterolytic O-O bond cleavage percent 5 to 16 times (entries 9 and 11 vs 13 and 15). These results demonstrated that imidazole not only accelerated the O-O bond cleavage rate of Fe-OOR species but also affected the ratio between homolytic and heterolytic O-O bond cleavage. In particular, the enhancement of the heterolytic cleavage of Fe-OOR species by imidazole in the catalytic oxidation systems of nonheme iron complexes with *t*-BuOOH was evidenced, for the first time, to the best of our knowledge.

In order to observe the proposed reactive intermediates Fe^{III}-OOC(O)R, Fe(V)=O, and Fe(IV)=O, we used the spectroscopic instruments such as EPR and ESI-mass. As shown in Table 1, all the reaction times are so long from 0.17 to 10 h. Therefore, we assumed that it was not easy to trap the reactive intermediates directly by utilizing the spectroscopic instruments, because the sufficient amounts of the intermediates could not be accumulated. These observations led us to concentrate only on the fastest reaction (entries 10 and 11 in Table 1) under the conditions which the iron complexes are stable to some degree during the catalytic reaction. First, we carried out EPR experiments to trap the proposed reactive intermediates, but could not observe any reactive species. Next, we used ESI-mass instrument, and was able to observe a possible Fe(V)=O species in the presence of both NHPI and imidazole (under entry 10 condition in Table 1), as shown in Fig. S6. The negative-ion mass

spectrum indicated that the peak at m/z = 598.87 was assignable to [(bpc)Fe(V)=O + OH^- + 3 solvents]$^-$ [calcd, 598.98] intermediate.

Mechanism: Based on all of our results, the most plausible mechanisms for the alcohol oxidation reaction by nonheme iron complexes **1a** and **1b** with alkyl hydroperoxides are illustrated in Scheme 3. The iron(III) complex reacted with alkyl hydroperoxides to form iron(III)-alkylperoxide intermediate **2**, which underwent a homolytic O-O bond cleavage almost exclusively to produce Fe^{IV}=O species **4** and *t*-butoxy radical (pathway a). These two reactive species might not be efficient for alcohol oxidation, because the ketones obtained under the reaction conditions were in low yields. Interestingly, the presence of imidazole increased the heterolytic O-O bond cleavage of Fe-OOR intermediate twice, although the yields of the ketone remained almost unchanged (pathway b). We assumed that the low ketone yield might be due to self-destruction of the iron complexes by Fe^{V}=O species **3** formed from the heterolytic O-O bond cleavage of Fe-OOR intermediate in the presence of imidazole (Figure S2). Instead of imidazole, the presence of NHPI caused homolysis cleavage exclusively of the O-O bond in Fe-OOR to achieve efficient alcohol oxidation (pathway c). These results led us to propose that both Fe^{IV}=O species **4** and alkoxy radical generated from the homolytic O-O bond cleavage of the intermediate Fe-OOR **2** oxidized NHPI to PINO$^{\cdot}$ radical via hydrogen abstraction reaction (Scheme 4). The resulting PINO$^{\cdot}$ radical then abstracted the hydrogen atom of the C-H bond of cyclohexanol to produce the cyclohexanol radical. Finally, Fe^{IV}=O, alkoxy radical and PINO$^{\cdot}$ radical oxidized the cyclohexanol radical to the corresponding cyclohexanone (Scheme 5).

Therefore, the Fe^{IV}=O, alkoxy radical and PINO$^{\cdot}$ radical probably acted as key reactive intermediates responsible for alcohol oxidation under this condition. Lastly, the presence of both imidazole and NHPI enhanced the heterolysis (up to 16%) of the O-O bond in Fe-OOR intermediate, with reduced yields of ketone products (pathway d in Scheme 3). We presumed that the reduced ketone products might be attributed to some self- destruction of the iron complexes by Fe^{V}=O intermediate (Figure S4). Nevertheless, some iron complexes were still alive, which afforded half amounts of yields.

3. Conclusion

We have conducted efficient oxidations of a variety of alcohols catalyzed by the iron complexes and *t*-BuOOH as environmentally friendly terminal oxidant in the presence of NHPI. Various alcohols were converted to the corresponding ketones efficiently under our catalytic system. **1a** was found to be a little better catalyst for alcohol oxidation than **1b**. The active oxidants in these systems were proposed to be Fe^{IV}=O, alkoxy radical and PINO· radical, as indicated by KIE (k_H/k_D) and Hammett study, as well as the use of MPPH as an oxidant. On the other hand, imidazole not only accelerated the O-O bond cleavage rate of Fe-OOR species but also affected the ratio between the homolytic and heterolytic O-O bond cleavage. Therefore, it was proposed that an Fe^{V}=O might exist in the presence of imidazole in the catalytic oxidation systems of nonheme iron complexes with *t*-BuOOH. Our future work will focus on (1) further exploring the biologically relevant reactivity of the iron (III) complex/*t*-BuOOH systems, and (2) obtaining further spectroscopic evidence for the Fe^{V}=O species described herein.

4. Experimental Section

General: Alcohols, ketones, carboxylic acids, anhydrous acetonitrile, dodecane, *t*-BuOOH, imidazole and NHPI were purchased from Aldrich Chemical Co. and were used without further purification. MPPH was synthesized according to the literature method [21a]. [Fe(bpc)Cl_2][Et_4N] (**1a**) and [Fe(Me_2bpb)Cl_2][Et_3NH] (**1b**) were obtained from the previous study [15].

Instruments: Product analyses for alcohol oxidation and MPPH experiment were conducted by using a DS6200 gas chromatograph equipped with a FID detector of Donam instrument Co. and a 30 m capillary column (Hewlett-Packard, DB-5 or HP-FFAP).

Catalytic alcohol oxidations by *t*-BuOOH in the presence of iron complexes: *t*-BuOOH (0.075 mmol) was added to a mixture of substrate (0.05 mmol), iron complex ($1.0x10^{-3}$ mmol), imidazole (0.01 mmol), NHPI (0.02 mmol), and solvent (CH_3CN; 1 mL). The mixture was stirred for the given time at 50 ^{o}C. Each reaction was monitored by GC/MS analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. Dodecane was used as an internal standard to quantify the yields of products and conversions of substrates.

All reactions were run at least in triplicate, and the average conversions and product yields have been presented. Conversions and product yields were calculated with respect to substrates.

Competitive reactions of *sec*-phenethyl alcohol and *para*-substituted *sec*-phenethyl alcohols for Hammett plot: To a mixture of *sec*-phenethyl alcohol (0.025 mmol), *para*(X)-substituted phenethyl alcohol (X = -OCH_3, -F, -Br and -CF_3, 0.025 mmol), NHPI (0.02 mmol), catalysts **1a** or **1b** (1.0 x 10^{-3} mmol), and solvent (CH_3CN, 1 mL) was added *t*-BuOOH (0.04 mmol). The mixture was stirred for 7 h at 50 ^oC. The amounts of *sec*-phenethyl alcohols before and after the reactions were measured by GC/MS analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. The relative reactivities were calculated using the following equation: $k_x/k_y = \log(X_f/X_i)/\log(Y_f/Y_i)$ where X_i and X_f are each initial and final concentration of *para*-substituted *sec*-phenethyl alcohols and Y_i and Y_f are each initial and final concentration of *sec*-phenethyl alcohol [18].

KIE study on competitive oxidation of benzyl alcohol and deuterated benzyl alcohol by *t*-BuOOH in the presence of iron complexes: This reaction was performed in presence of excess substrate to avoid further oxidation of the benzaldehyde, derived from benzyl alcohol, to benzoic acid which inhibits the determination of the exact KIE value. Moreover, in order to improve the accuracy in measuring the amount of deuterated benzyl alcohol product, a 1:6 mixture of benzyl alcohol and deuterated benzyl alcohol was used. The reaction procedure: *t*-BuOOH (0.075 mmol) was added to a mixture of benzyl alcohol (0.1 mmol) and benzyl-d_7-alcohol (0.6 mmol), imidazole (0.01 mmol), NHPI (0.02 mmol), catalysts **1a** or **1b** (1.0x10^{-3} mmol), and solvent (CH_3CN, 1 mL). The mixture was stirred for the given time at 50 ^oC. Reaction conversion was monitored by GC/MS analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All the reactions were run at least in triplicate and the average KIE values have been presented.

Analysis of the O–O bond cleavage products from the oxidation reactions of substrates by MPPH in the presence of iron complexes: MPPH (0.02 mmol) was added to a mixture of substrate (0.05 mmol), imidazole (0.01 mmol), NHPI (0.02 mmol), catalysts **1a** or **1b** (1.0x10^{-3} mmol), and solvent (anhydrous CH_3CN, 1 mL). The mixture was stirred for the

given time at 50 ^{o}C. In order to check whether MPPH was decomposed completely within a given reaction time, PPh_3 in the duplicate experiment was added into the reaction mixture after the given reaction time. Each reaction was monitored by GC/MS analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least in triplicate, and the average conversions and product yields have been presented. Conversions and product yields were based on MPPH.

Acknowledgements

Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2014R1A2A1A11051794 and NRF-2015R1A2A2A09001301) are gratefully acknowledged.

Supplementary data

Supplementary data related to this article can be found at http: //

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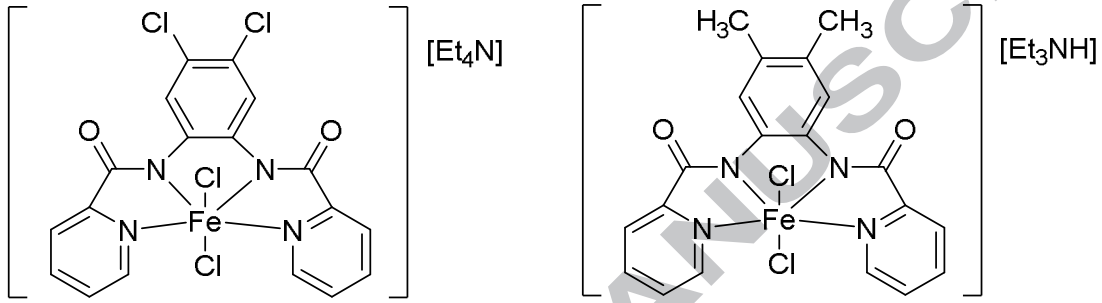
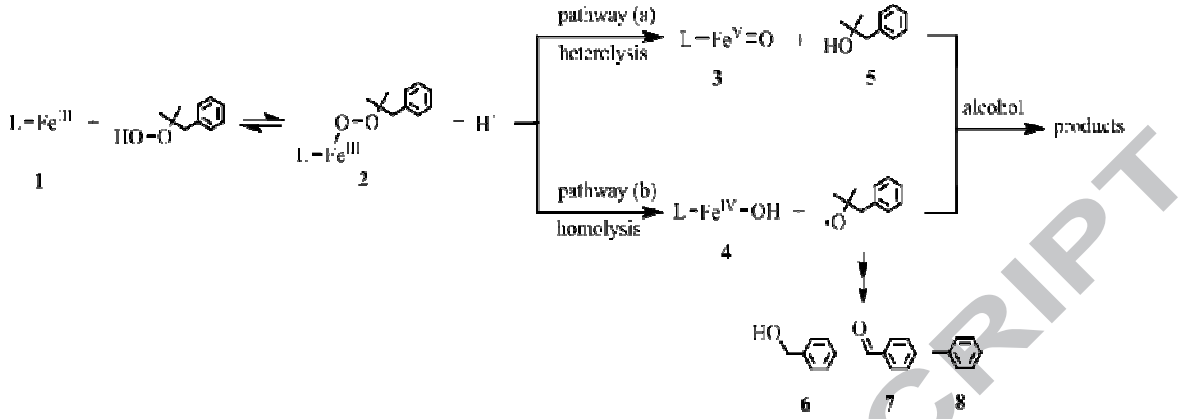


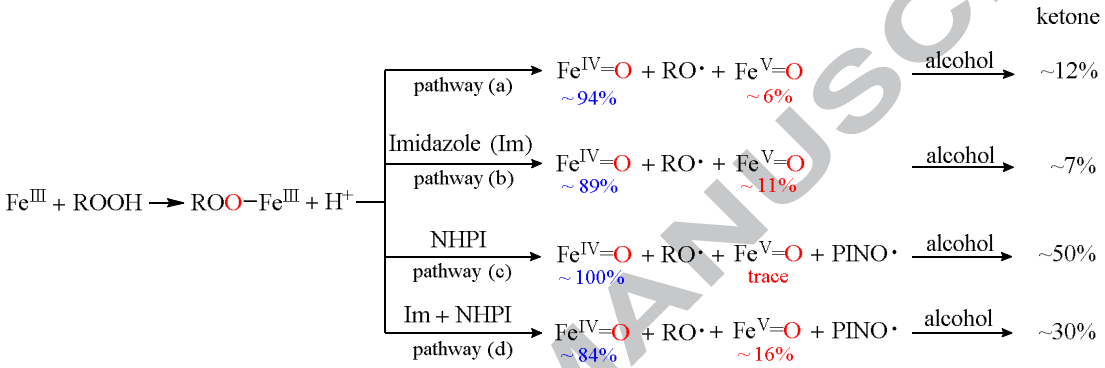
1a
$[Fe(bpc)Cl_2][Et_4N]$

1b
$[Fe(Me_2bpb)Cl_2][Et_3NH]$

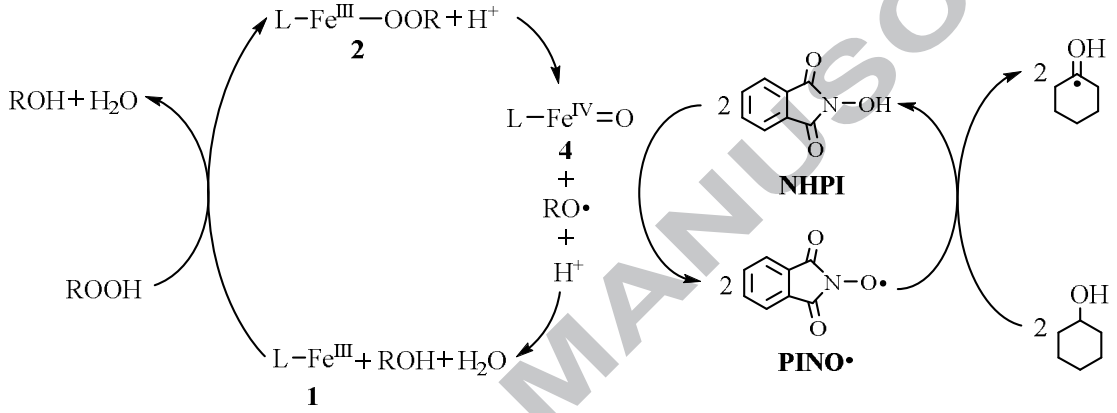
Scheme 1. Structures of iron(III) complexes.



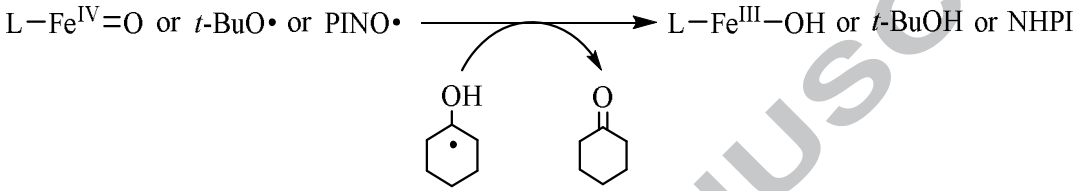
Scheme 2. Possible degradation pathways of MPPH by iron complexes.



Scheme 3. Plausible mechanisms for the alcohol oxidation by iron complexes with MPPH (Based on Table 4).



Scheme 4. Possible alcohol oxidation mechanism for the pathway (c) in Scheme 3.



Scheme 5. Termination of the cyclohexanol radical by the active oxidants.

Table 1. Oxidation of cyclohexanol catalyzed by iron complexes **1a** and **1b** with *t*-BuOOH in the absence or/and presence of imidazole and NHPI at 50 °C.[a]

Entry	Catalyst	Reaction time (h)	imidazole	NHPI	Cyclohexanol[b]	
					Conversion (%)	Yield (%)
1	No	24	No	Yes	1.3 ±1.2	trace
2	**1a**	10	No	No	10.2±1.6	9.5±0.3
3	**1b**	10	No	No	14.6±2.8	13.7±0.4
4	**1a**	0.17	Yes	No	12.1±1.7	10.2±0.1
5	**1b**	0.17	Yes	No	14.1±0.3	10.8±0.3
6	**1a**	7	No	Yes	89.5±2.2	87.1±4.6
7	**1a**[c]	7	No	Yes	90.4±3.9	89.4±2.2
8	**1b**	7	No	Yes	91.3±2.1	87.3±4.6
9	**1b**[c]	7	No	Yes	90.4±4.3	89.0±5.3
10	**1a**	1	Yes	Yes	57.5±0.7	46.4±3.2
11	**1b**	1	Yes	Yes	55.2±1.4	52.9±2.0

[a] Reaction conditions: cyclohexanol (0.05 mmol), catalyst (1.0×10^{-3} mmol), imidazole (0.01 mmol), NHPI (0.01mmol), *t*-BuOOH (0.075 mmol), and solvent (1 mL, CH_3CN). [b] Based on substrate. [c] Under anaerobic conditions with N_2 atmosphere.

Table 2. Oxidation reaction of various alcohols catalyzed by iron complexes **1a** and **1b** with *t*-BuOOH in the presence of NHPI at 50 °C.[a]

Entry	Substrate	Product	1a [b]		1b [b]	
			Conversion (%)	Yield (%)	Conversion (%)	Yield (%)
1	cyclopentanol	cyclopentanone	83.3	70.5	82.8	68.3
2	cycloheptanol	cycloheptanone	100	100	100	89.0
3	benzyl alcohol	benzaldehyde	96.2	45.4	75.8	53.6
		benzoic acid		22.4 (44.8) [c]		8.2 (16.4) [c]
4	*sec*-phenethyl alcohol	acetophenone	100	93.5	100	87.2
5	*cis*-2-methylcyclohexanol	2-methylcyclohexanone	98.7	85.3	87.4	76.7
6	*trans*-2-methylcyclohexanol	2-methylcyclohexanone	91.8	80.5	90.5	80.0
7	*endo*-norborneol	norcamphor	100	100	96.9	94.5
8	*exo*-norborneol	norcamphor	61.4	57.9	54.0	51.5
9	1-octanol	octanal	55.4	1.7	53.6	1.9
		octanoic acid		14.4 (28.8) [c]		10.9 (21.8) [c]
10	2-hexanol	2-hexanone	89.3	86.8	87.7	86.8
11	3-hexanol	3-hexanone	94.4	91.0	92.2	90.3
12	2-octanol	2-octanone	88.4	85.8	85.9	85.2

[a] Reaction conditions: alcohols (0.05 mmol), catalyst (1.0×10^{-3} mmol), NHPI (0.01 mmol), *t*-BuOOH (0.075 mmol), and solvent (1 mL, CH_3CN). Reaction time was 7 h. [b] Based on substrate. [c] Yields in parenthesis are considered the further oxidation of the first oxidation aldehyde to the corresponding carboxylic acids.

Table 3. Kinetic isotope effects on oxidation of benzyl alcohol/benzyl-d_7 alcohol by iron complexes **1a** and **1b** with *t*-BuOOH at 50 °C.[a]

Entry	Catalyst	Reaction time (h)	Imidazole	NHPI	k_H/k_D	Reference
1	No	24	No	Yes	2.3±0.2	this work
2	**1a**	10	No	No	5.08 ± 0.3	this work
3	**1b**	10	No	No	4.78 ± 0.0	this work
4	**1a**	0.17	Yes	No	3.49 ± 0.2	this work
5	**1b**	0.17	Yes	No	3.75 ± 0.0	this work
6	**1a**	7	No	Yes	6.26 ± 0.0	this work
7	**1b**	7	No	Yes	5.72 ± 0.0	this work
8	**1a**	1	Yes	Yes	6.67 ± 0.1	this work
9	**1b**	1	Yes	Yes	6.31 ± 0.2	this work
10	*t*-butoxy radical		-	-	3.6	19c

[a] Reaction conditions: benzyl alcohol (0.1 mmol), benzyl-d_7 alcohol (0.6 mmol), catalyst (1.0×10^{-3} mmol), imidazole (0.01 mmol), NHPI (0.01 mmol), *t*-BuOOH (0.075 mmol), and solvent (1 mL, CH_3CN).

Table 4. Yield of products derived from 2-methyl-1-phenylprop-2-yl hydroperoxide (MPPH) mediated by iron complexes **1a** and **1b** in the presence of *sec*-phenethyl alcohol at 50 °C.[a]

Entry	Catalyst	Reaction time (h)	Im[b]	NHPI	PPh_3 (mM)[c]	Hetero/Homo	Heterolysis[d,e]	Homolysis[d,e]		Yield[d] (%)
							MPPOH	aldehyde	ol	acetophenone
1	**1a**	10	No	No	0	**0.07** (6.5/93.5)	5.7±0.7	69.6±3.3	11.1±3.3	14.1±0.2
2		10	No	No	100	**0.10** (9.1/90.9)	8.3±0.8	69.6±1.6	10.8±0.7	15.6±0.2
3	**1b**	10	No	No	0	**0.07** (6.5/93.5)	6.3±0.2	80.3±4.1	7.7±0.1	11.0±1.2
4		10	No	No	100	**0.08** (7.4/92.6)	6.9±0.3	79.3±2.8	6.2±0.4	9.5±0.5
5	**1a**	0.3	Yes	No	0	**0.15** (13.0/87.0)	12.4±0.1	73.1±2.1	9.0±0.5	4.3±0.2
6		0.3	Yes	No	100	**0.16** (13.8/86.2)	12.4±0.6	68.1±0.2	8.1±1.3	3.9±0.1
7	**1b**	2	Yes	No	0	**0.10** (9.1/90.9)	6.8±0.7	67.8±2.6	1.2±1.2	8.9±0.1
8		2	Yes	No	100	**0.12** (10.7/89.3)	7.8±1.0	63.2±1.1	0.0	8.1±0.9
9	**1a**	7	No	Yes	0	**0.01** (1.0/99.0)	1.2±0.9	98.2±1.3	0.0	52.7±0.9
10		7	No	Yes	100	**0.02** (2.0/98.0)	2.4±0.3	98.4±1.4	0.0	55.0±0.2
11	**1b**	7	No	Yes	0	**0.03** (3.0/97.0)	3.0±0.4	93.5±0.3	4.5±0.7	53.5±0.6
12		7	No	Yes	100	**0.04** (4.0/96.0)	4.1±0.7	91.3±0.8	3.2±2.1	51.7±0.3
13	**1a**	4	Yes	Yes	0	**0.19** (16.0/84.0)	14.0±0.2	73.3±5.9	0.0	28.0±0.5
14		4	Yes	Yes	100	**0.23** (18.7/81.3)	16.7±0.6	72.1±4.4	0.0	27.5±0.4
15	**1b**	4	Yes	Yes	0	**0.18** (15.3/84.7)	14.1±0.2	77.4±1.5	0.0	33.2±4.0
16		4	Yes	Yes	100	**0.20** (16.7/83.3)	15.3±1.4	76.4±3.0	0.0	36.5±2.4

[a] Reaction conditions: *sec*-phenethyl alcohol (0.05 mmol), catalyst ($1.0x10^{-3}$ mmol), imidazole (0.01 mmol), NHPI (0.01 mmol), MPPH (0.02 mmol), and solvent (1 mL, CH_3CN). [b] Im = imidazole. [c] In order to confirm whether MPPH was completely consumed or not, PPh3 was added into the reaction solution after the reaction finished. [d] Based on MPPH. [e] MPPOH, aldehyde, and ol indicate 2-methyl-1-phenyl-2-propanol, benzaldehyde, and benzyl alcohol, respectively.

Figure Caption

Figure 1. Hammett plot for selective reactivities of *sec*-phenethyl alcohol to *para*-substituted *sec*-phenethyl alcohols by **1a** with *t*-BuOOH in the presence of NHPI.

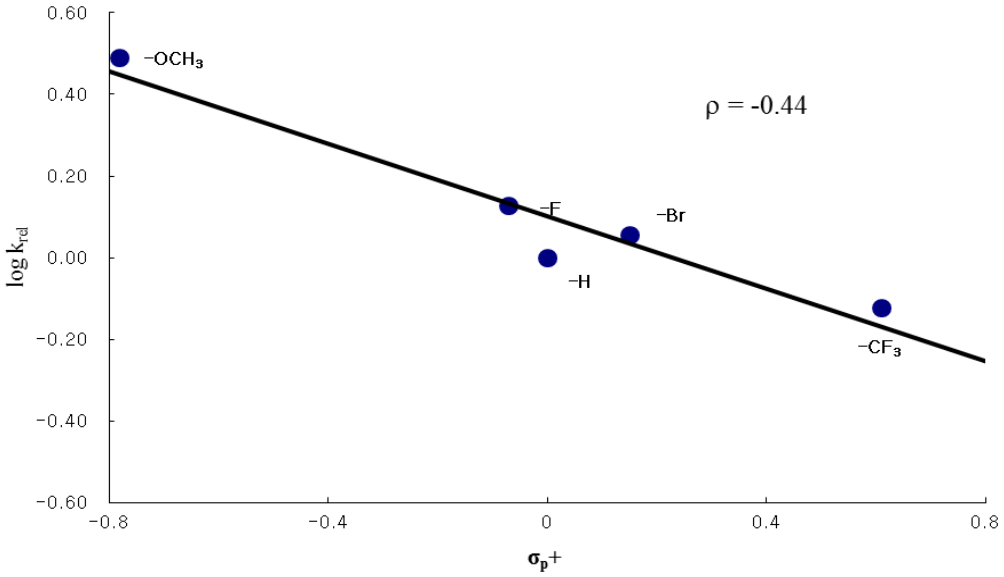
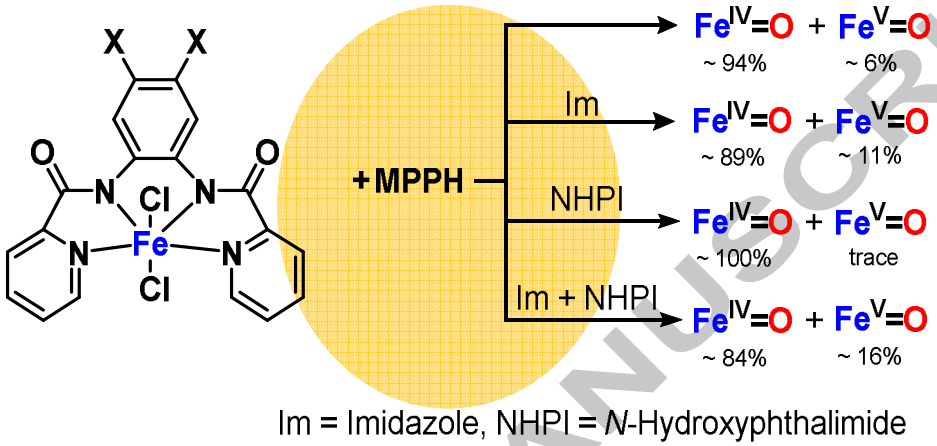


Figure 1.

Graphical Abstract



Graphical Abstract

Two iron catalysts ([Fe(bpc)Cl_2][Et_4N] (**1a**) and [Fe(Me_2bpb)Cl_2][Et_3NH] (**1b**) displayed efficient catalysis in oxidation of various alcohols to the corresponding carbonyl products using *t*-BuOOH as an oxidant in the presence of *N*-hydroxyphthalimide (NHPI) under mild conditions. The mechanistic studies through Hammett plot, deuterium isotope effect, and the use of 2-methyl-1-phenylprop-2-yl hydroperoxide (MPPH) as a mechanistic probe suggested that the reactive oxidants responsible for the alcohol oxidation possibly involved Fe^{IV}=O species, alkoxy radical ($RO^{\cdot}$), and phthalimide *N*-oxyl radical ($PINO^{\cdot}$).

Highlights

1. Two iron catalysts displayed efficient catalysis in oxidation of various alcohols.

2. Reactive oxidants are Fe^{IV}=O species, alkoxy radical ($RO^{\cdot}$), and $PINO^{\cdot}$.

3. Presence of imidazole increases formation of Fe^{V}=O intermediate.