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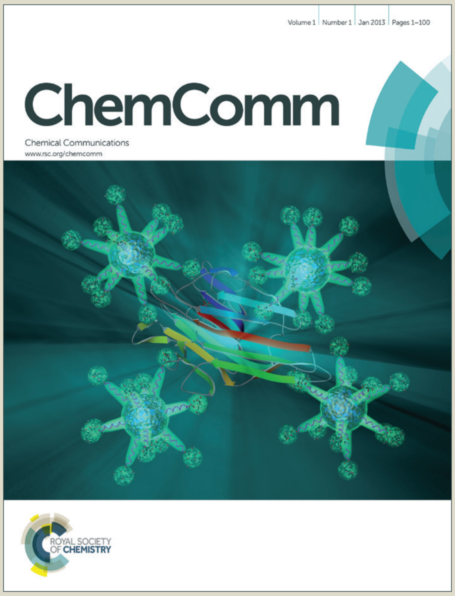

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Mechanistic Elucidation of C–H Oxidation by Electron Rich Non-heme Iron(IV)-oxo at Room Temperature

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th June 2015,
Accepted 00th June 2015

DOI: 10.1039/x0xx00000x

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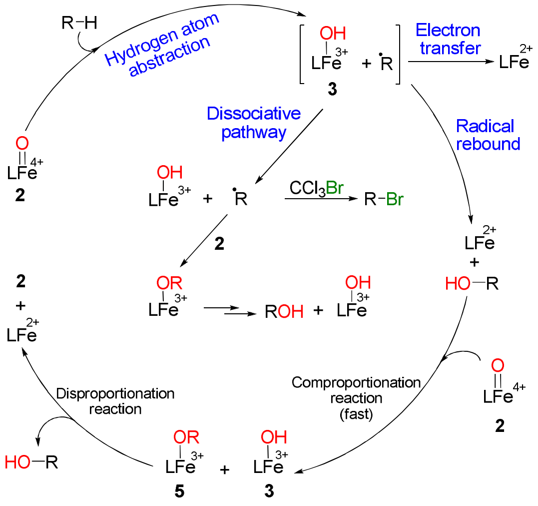
Non-heme iron(IV)-oxo species form iron(III) intermediates during hydrogen atom abstraction (HAA) from C–H bond. By synthesizing a room temperature stable, electron rich, non-heme iron(IV)-oxo compound, we obtained iron(III)-hydroxide, iron(III)-alkoxide and hydroxylated-substrate-bound iron(II) as the detectable intermediates. Present study revealed that a radical rebound pathway was operative for benzylic C–H oxidation of ethylbenzene and cumene. A dissociative pathway for cyclohexane oxidation was established based on UV-vis and radical trap experiments. Interestingly, experimental evidences including O-18 labeling and mechanistic study suggested an electron transfer mechanism to be operative during C–H oxidation of alcohols (e.g. benzyl alcohol and cyclobutanol). The present report, therefore, unveils non-heme iron(IV)-oxo promoted substrate-dependent C–H oxidation pathways of synthetic as well as biological significance.

High-valent iron-oxo species are responsible for C–H oxidations in numerous biological and chemical transformations for both heme and non-heme enzymes.[1] Heme enzymes like cytochrome P450 carry out alkane hydroxylation, olefin epoxidation and sulfoxidation involving iron(IV)-oxo porphyrin π-cation radical.[2] Non-heme enzymes such as Rieske oxygenase, *α*-ketoglutarate dependent dioxygenases, TauD-*J,* routinely perform biochemical oxidative transformations involving iron(IV)-oxo intermediate. Intense experimental work has been devoted for mimicking the chemistry of heme/non-heme enzymes.[3]

Non-heme iron(IV/V)-oxo complexes abstract hydrogen atom from C–H bonds in the rate determining step to form iron (III) hydroxide and radical species ($R^{\bullet}$).[4] These active species, depending on their properties, can pursue a radical rebound, radical non-rebound or an electron transfer mechanism to form the respective C–H oxidation products (Scheme 1).[4l, 5] Following radical rebound pathway, the *in situ* formed iron(II)-species and alcohol can undergo comproportionation reaction in presence of another equivalent of iron(IV)-oxo (Scheme 1).[3b] In case of dissociative pathway, iron(III)-hydroxide and substrate radical (generated upon HAA) becomes separated from solvent cage resulting in subsequent radical trapped products and other side reactions of iron(III)-hydroxides. Such pathway is well accepted for iron(IV/V)-oxo and manganese (IV)-oxo complexes.[5-6]

Although radical rebound pathway has been established for ruthenium(IV)-oxo,[7] gathering concrete evidences for the same in case of iron(IV)-oxo requires further study. We thought to synthesize a modified N4Py ligand scaffold (L) with electron rich substituents at picolyl moiety. We were particularly intrigued by the DFT data of Fe-(N4Py) complex which showed greater HOMO contribution by two picolyl moieties that resulted in shorter Fe-N(picolyl) distance in Fe-(N4Py) complex.[8] We rationalized that introduction of electron donating group (such as 4-OMe) in picolyl unit will further shorten the Fe-(N4Py) distance and will increase HOMO contribution (Figure 1).[8] Consequently it will produce more reactive reaction intermediates, which may be verified by detailed mechanistic studies.[3d-f, 4a, 4b]



Scheme 1. C–H oxidations by non-heme iron (IV)-oxo

The non-heme iron complex $[(N4Py)^{OMe,Me}Fe^{II}(CH_3CN)](OTf)_2$ (**1**) was synthesized by reacting $Fe(OTf)_2.2CH_3CN$ with an electronically enriched and substituted $N4Py^{OMe,Me}$ ligand.[5] Complex **1** was also characterized by X-ray (Figure 1), ESI-MS (*m*/*z*, 688.150), UV-vis spectroscopy (maximum at 459 nm due to

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LMCT).[9] NMR (0-10 ppm, ^{1}H- and 0-200 ppm, ^{13}C-) and EPR (silent) studies indicated the diamagnetic character of **1**.[10],[11] Electrochemical study of complex **1** showed lower Fe^{III}/Fe^{II} reduction potential ($E_{1/2}$ ~ 0.84 V *vs* SCE) compared to that of unsubstituted N4Py iron(II) complex ($E_{1/2}$ ~ 1.01 V *vs* SCE).[8],[12] This further suggested that iron(III) species for **1** is more stable compared to unsubstituted N4Py iron(III) complex. The corresponding iron (IV)-oxo species, $[(N4Py)^{OMe,Me}Fe^{IV}(O)]^{2+}$ (**2**) was synthesized by reacting **1** with iodosyl benzene in acetonitrile at room temperature. Characteristic UV-vis maximum at 692 nm (ϵ ~ 432 $M^{-1}cm^{-1}$) due to ligand field transitions (d-d transition) was also observed.[4a, 13] Complex **2** showed slightly more negative Fe^{IV}/Fe^{III} reduction potential ($E_{p,c}$ ~ -0.19 V *vs* SCE) compared to that of unsubstituted $[(N4Py)Fe^{IV}(O)]^{2+}$ ($E_{p,c}$ ~ -0.15 V *vs* SCE). Notably, **2** was found to be stable at room temperature for few days ($t_{1/2}$ ~50 h at 30 °C in air).[8] The ESI-MS characterization of complex **2** revealed major isotopic peak at 704.145 due to $[(N4Py)^{OMe,Me}Fe^{IV}(O)](OTf)^+$ which was shifted to 706.150 upon O-18 labeling with $H_2{}^{18}O$ (~95% O-18 incorporation, *vide infra*).[14] The ^{1}H NMR spectrum (–20 to 50 ppm) along with EPR silent behaviour at 77 K suggested paramagnetic character of **2** (likely in the S=1 spin state).[10, 15]

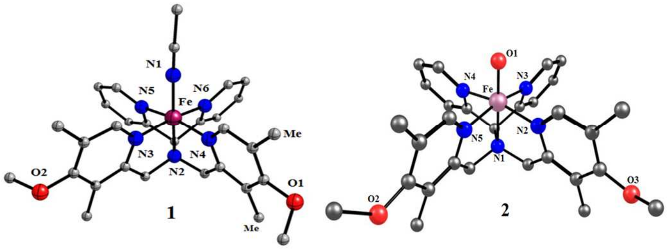
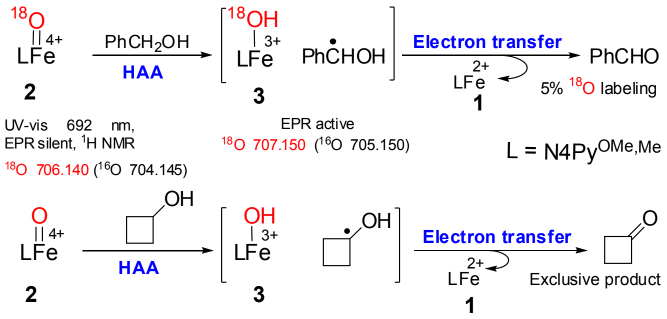
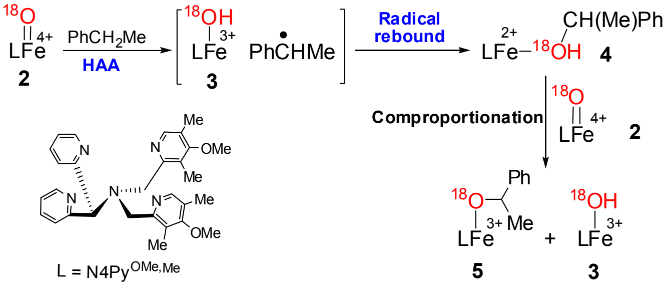


Figure 1. ORTEP diagram of complex **1** (CCDC, 1051845) and DFT optimized geometry of **2** using B3LYP/LANL2DZ with $N4Py^{OMe,Me}$ ligand



Scheme 2. Alcohol oxidations by $[(N4Py)^{OMe,Me}Fe^{IV}(O)]^{2+}$ (**2**)

Oxidation of benzyl alcohol by **2** provided benzaldehyde as the sole product (yield, 86%). Labeling study showed 5% O-18 incorporation in benzaldehyde. Furthermore, C–H oxidation of $PhCH_2OH$ and $PhCD_2OH$ (~95%, D enriched) provided kinetic isotope effect value, 11 which suggests that the initial hydrogen atom abstraction is the rate determining step.[8] [16] [3b] Cyclobutanol as mechanistic probe provided cyclobutanone exclusively ($2e^-$ oxidation product) (ring open product 4-hydroxybutanal was not detected) without any O-18 labeling (Scheme 2). These observations suggested that following HAA, an electron transfer mechanism is operational during C–H oxidation of benzyl alcohol.[16-17] Subsequently, we have studied C–H oxidation chemistry of **2** using ethylbenzene (Scheme 3), cumene and cyclohexane.[8] Cyclohexane produced cyclohexanol (~15% yield, 52% O-18 enriched) whereas ethyl benzene gave 1-phenyl ethanol (yield, 22%; 60% O-18 labeled).



Scheme 3. Intermediates during reaction of **2** and ethylbenzene

The ESI-MS data obtained upon addition of ethylbenzene to **2** suggested formation of iron(III)-hydroxide (**3**, *m/z*, 705.150), 1-phenylethanol bound intermediate, $[(N4Py)^{OMe,Me}Fe^{II}(HO(Me)CHPh)](OTf)^+$ (**4**) (*m/z*, 810.22; Figure 2g) and iron(III)-alkoxide, $[(N4Py)^{OMe,Me}Fe^{III}(O(Me) CHPh)](OTf)^+$ (**5**, *m/z*, 809.215; Figures 2b and 2e) (Scheme 3). Most interestingly, 1-phenylethanol bound intermediate $[(N4Py)^{OMe,Me}Fe^{II}(HO(Me)CHPh)](OTf)^+$ (**4**) formed as a consequence of radical rebound step was rapidly oxidized by **2** to produce **3** and **5**.[7] Formation of **5** occurred *via* comproportionation reaction of **1** and **2** in presence of 1-phenyl ethanol. This was further verified by adding 1-phenyl ethanol to a solution of **2** in acetonitrile where both **3** and **5** were simultaneously detected.

Furthermore, the formation of iron(III) complex was confirmed from rhombic signal at $g_1 = 1.94$, $g_2 = 2.11$, $g_3 = 2.10$ and axial signal at $g_1 = 4.17$, $g_2 = 5.98$ by EPR experiment of a solution of **2** and ethyl benzene (or cumene) (Figure 3a and 3b).[5, 15, 18] Replacing ethyl benzene by cumene also showed formation of iron(III)-hydroxide (**3**) and iron(III)-alkoxide species, $[(N4Py)^{OMe,Me}Fe^{III}O(Me)_2CPh)](OTf)^+$ (**5a**, *m/z*, 823.21; Scheme 4), which upon ^{18}O labeling shifted by two mass unit (*m/z*, 825.21; Figures 4a and 4b) along with 70% O-18 enriched cumyl alcohol.

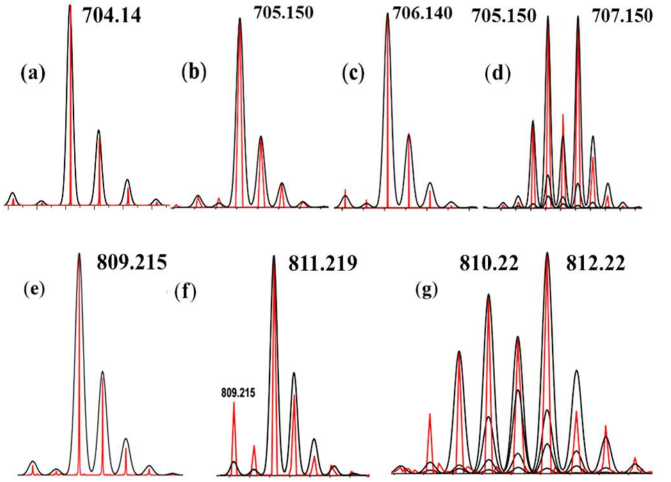


Figure 2. ESI-MS of the intermediates during reaction of **2** and ethylbenzene (red line, experimental and black line, simulated, spectra were recorded after 5 min of addition). ESI-MS of **2** (2a), **3** (2b), 18-O-**2** (2c), 18-O-**3** (2d), **5** (2e), 18-O-**5** (2f), **4** and 18-O-**4** (2g).[8]

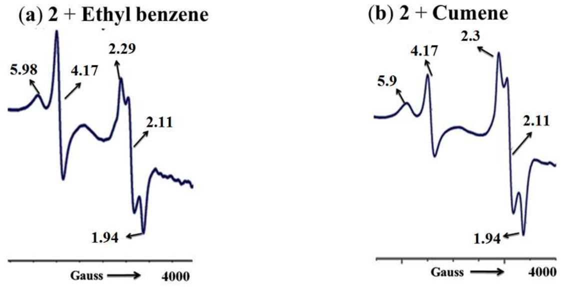
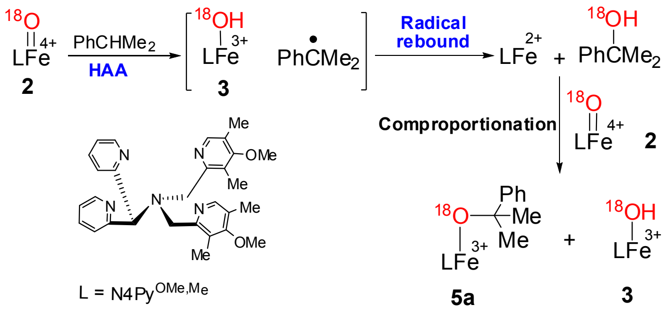


Figure 3. EPR spectra (acetonitrile, 77 K) obtained from reaction between **2** and (a) ethylbenzene (b) cumene

The formation of **5a** was presumed to occur *via* comproportionation reaction. This was verified when 2-phenyl-2-propanol was added to a solution of **2**, trace amount of **3** and **5a** were observed after 30 min. Notably, a significant amount of these compounds was formed after 16 h. Complex **2** decayed with time to form **1**, which in presence of 2-phenyl-2-propanol and **2** underwent comproportionation reaction to form **3** and **5a**. Expectedly, formation of **3** and **5a** (Scheme 4) were observed within 10 minutes *via* comproportionation reaction when 2-phenyl-2-propanol was added to a mixture of **1** and **2**.



Scheme 4. Radical rebound pathway for C–H oxidation of cumene

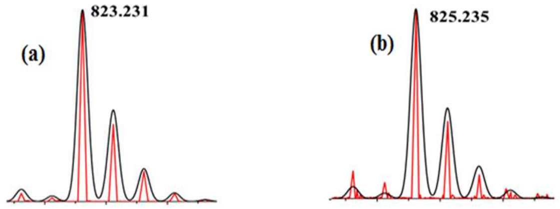


Figure 4. ESI-MS of the intermediates, **5a** (4a) and 18-O labeled **5a** (4b) during reaction of **2** and cumene (red line, experimental and black line, simulated)

In presence of ethylbenzene (or cumene), the absorbance *vs* time plot for complex **2** (decay profile at 692 nm) was fitted with the pseudo-first order reaction profile (rate constant, k_1; Figure **5**).[3b, 4a, 5] A straight line was obtained by plotting the different values of k_1 against concentration of the substrate. The slope of this plot yielded the second order rate constant (k_2, Figure 5).[8] During C–H oxidation reaction by **2**, cumene reacted slightly faster ($k_2 \sim 0.01\ M^{-1}s^{-1}$) compared to ethylbenzene ($k_2 \sim 0.0021\ M^{-1}s^{-1}$) due to higher benzylic C–H bond strength.[19] Reaction of cumene and complex **2** occurred with a slightly faster rate (~5 times, $k_2 \sim 0.01\ M^{-1}s^{-1}$ *vs* $k_2 = 0.002\ M^{-1}s^{-1}$ for Fe-N4Py-oxo)[4a] compared to that for unsubstituted Fe-N4Py-(oxo) complex. However, reaction rate of **2** with ethylbenzene is similar to its unsubstituted analogue ($0.0021\ M^{-1}s^{-1}$ *vs* $0.0031\ M^{-1}s^{-1}$ or $0.008\ M^{-1}s^{-1}$).[4a, 5] Notably, during the C–H oxidation reactions of **2** with ethylbenzene, cumene, triphenyl methane, benzyl alcohol and cyclobutanol (500 *equiv.*) iron(II) was regenerated. Initially after 1-2 hour of the reaction, 40-60% of iron(II) species was regenerated. After 48 hours of the reaction, iron(II) was obtained quantitatively (~95%). On the contrary, unsubstituted $[Fe^{II}(N4Py)(O)]^{2+}$ complex generated ~95% of iron(III) species *via* dissociative pathway after completion of the reaction with ethyl benzene, cumene and triphenyl methane.[5]

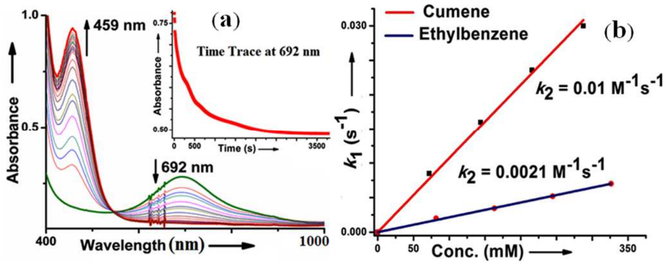


Figure 5. (a) UV-vis change at 692 nm for **2**, in presence of cumene, (b) kinetics plot for cumene and ethylbenzene

Cyclohexane oxidation by **2** produced major amount of iron(III) (~90%) and minor amount of iron(II) species (10%). Moreover, cyclohexyl radical was trapped in the form of cyclohexyl bromide on adding CCl_3Br (or CBr_4) during cyclohexane oxidation by **2**.[8],[11] These experimental evidences suggested that cyclohexane oxidation was likely following a dissociative pathway.

No radical trapped or brominated product was found during the reaction of **2** with ethylbenzene or cumene.[11],[20] Therefore, the substrate based organic radicals failed to escape from solvent cage for ethylbenzene and cumene.[20c] Although radicals formed *via* dissociative pathway have been trapped as per the prescient knowledge from reported literature for non-heme iron(IV)-oxo, our experimental observations suggested that following HAA, the iron(III)-hydroxide and the exogenous substrate based radical may not undergo dissociation (*e.g.* in case of ethylbenzene and cumene).[21] The reaction followed a radical rebound pathway and produced an iron(II)-alcohol coordinated product that was subsequently oxidized by **2**.[20c]

In summary we have synthesized an electron rich, room temperature stable and reactive non-heme iron(IV)-oxo species $[(N4Py)^{OMe,Me}Fe^{IV}(O)](OTf)^{+}$ (**2**). The iron(IV)-oxo derived intermediates like iron(III)-hydroxide (**3**), iron(III)-alkoxide (**5**) and substrate-bound iron(II) species (**4**) were detected from the reaction mixture. The mechanistic switch during C–H oxidation by non-heme iron(IV)-oxo complex **2** mainly depends on the stability of the radical generated after HAA. More stable radical preferred electron transfer pathway (Scheme 2), whereas moderately stable radical underwent radical rebound pathway (Schemes 3 and 4). Least stable radical of all (*e.g.* in case of cyclohexane) underwent dissociative pathway.

Notes and references

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DOI: 10.1039/C5CC04803F

This activity is supported by SERB, India. Financial support received from CSIR-India (fellowships to S. R.) is gratefully acknowledged. DM sincerely thanks Dr. Sayam Sen Gupta (NCL Pune), Dr. Tapan K. Paine (IACS Kolkata) and their group members for stimulating scientific discussions and constant support to conduct a number of experiments in their laboratories.

Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

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