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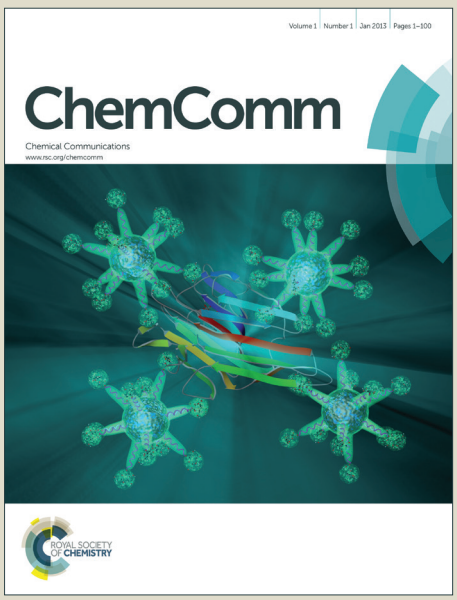

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Mechanistic Elucidation of C–H Oxidation by Electron Rich Non-heme Iron(IV)-oxo at Room Temperature

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Sujoy Rana, Aniruddha Dey and Debabrata Maiti*

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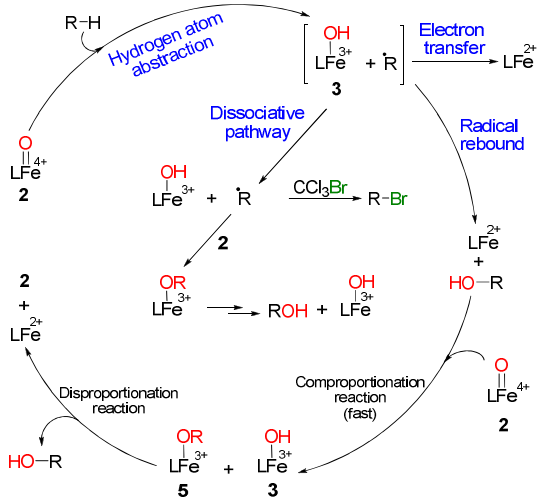
Non-heme iron(IV)-oxo species form iron(III) intermediates during hydrogen atom abstraction (HAA) from C–H bond. By synthesizing a room temperature stable, electron rich, non-heme iron(IV)-oxo compound, we obtained iron(III)-hydroxide, iron(III)-alkoxide and hydroxylated-substrate-bound iron(II) as the 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$_3$CN)] (OTf)$_2$ (**1**) was synthesized by reacting Fe(OTf)$_2$.2CH$_3$CN 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

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]

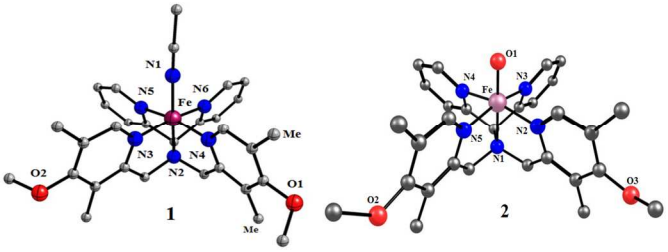
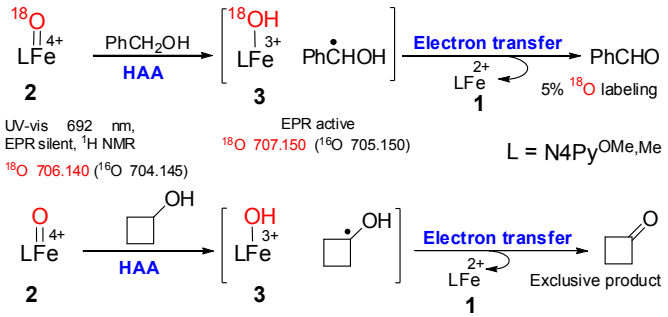
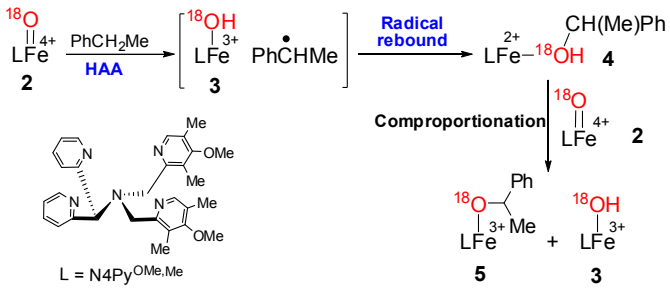


Figure 1. ORTEP diagram of complex **1** (CCDC, 1051845) and DFT optimized geometry of **2** using B3LYP/LANL2DZ with $N4Py^{OMe,Me}$ ligand



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.

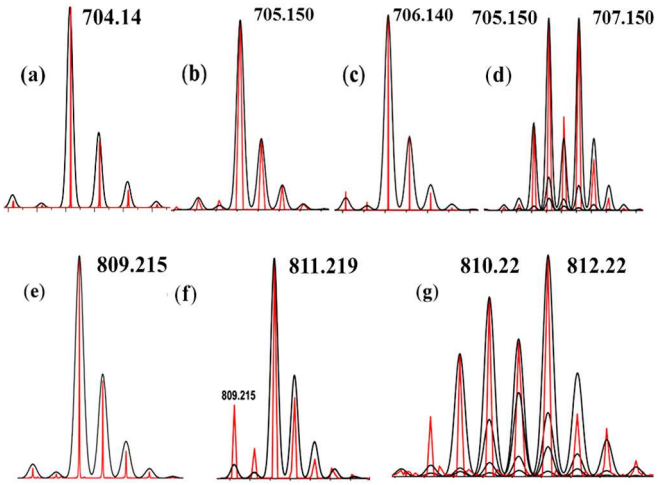


Figure 2. ESI-MS of the intermediates during reaction of **2** and ethylbenzene (red line, experimental and black line, simulated, spectra were recorded after 5 min of addition). ESI-MS of **2** (2a), **3** (2b), 18-O-**2** (2c), 18-O-**3** (2d), **5** (2e), 18-O-**5** (2f), **4** and 18-O-**4** (2g).[8]

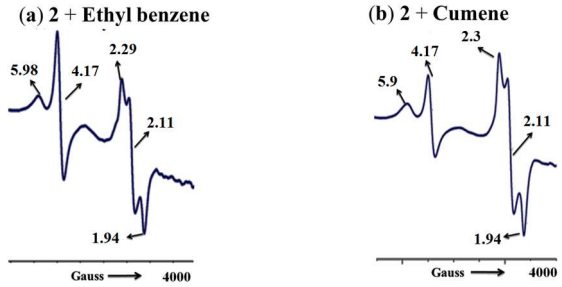
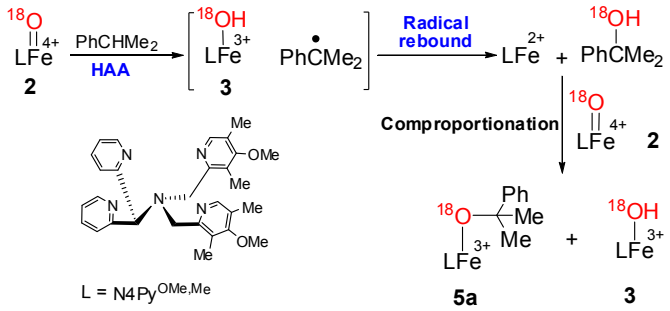


Figure 3. EPR spectra (acetonitrile, 77 K) obtained from reaction between **2** and (a) ethylbenzene (b) cumene

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

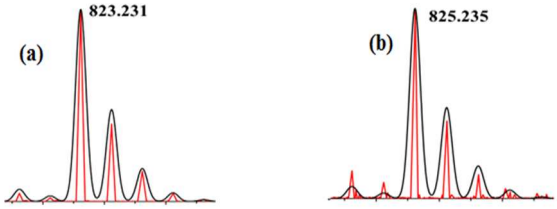


Figure 4. ESI-MS of the intermediates, **5a** (4a) and 18-O labeled **5a** (4b) during reaction of **2** and cumene (red line, experimental and black line, simulated)

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 ~ 0.01 $M^{-1}s^{-1}$) compared to ethylbenzene (k_2 ~ 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 ~ 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]

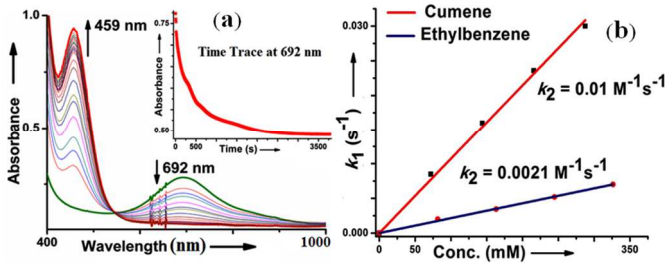


Figure 5. (a) UV-vis change at 692 nm for **2**, in presence of cumene, (b) kinetics plot for cumene and ethylbenzene

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

†Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

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