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Reactive Intermediates in Oxygenation Reactions by Mononuclear Non-Heme Iron Catalysts**

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Mononuclear non-heme iron oxygenases catalyze a diverse array of important metabolic transformations that require the binding and activation of dioxygen.[1] In the catalytic cycles of the non-heme iron enzymes, several intermediates, such as iron(III)-hydroperoxo, iron(IV)-oxo, and iron(V)-oxo species, have been proposed as active oxidants that effect the oxygenation of organic substrates.[2] Among the proposed intermediates, synthetic non-heme iron(III)-hydroperoxo species were shown to be a sluggish oxidant that cannot oxygenate organic substrates, such as alkanes and olefins.[3]

The first non-heme iron(IV)-oxo complex was characterized spectroscopically by Wieghardt and co-workers.[4] Subsequently, a crystal structure of a non-heme iron(IV)-oxo complex was reported by Münck, Nam, Que, and their co-workers.[5] Since then, a handful of

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iron(IV)-oxo complexes have been synthesized and investigated in various oxidation reactions.[6,7] Thus, it has been well demonstrated that non-heme iron(IV)-oxo species are capable of oxygenating organic substrates, such as alkanes, alkenes, alcohols, and sulfides.

Iron(V)-oxo species have also been inferred as active oxidants in the oxygenation of organic substrates by non-heme iron catalysts.[8] Although such an iron(V)-oxo intermediate was synthesized and characterized with various spectroscopic techniques,[9] evidence for the involvement of iron(V)-oxo species as active oxidants in catalytic oxygenation reactions was indirect and mainly from product analysis, such as a selectivity of alcohol over ketone in alkane hydroxylation, a KIE value of >4, and the incorporation of ^{18}O from H_2^{18}O into products in labeled water experiments.[8] However, iron(IV)-oxo complexes have also shown very large KIE values[7] and the oxygen exchange with H_2^{18}O .[10] Therefore, it is difficult to distinguish the nature of intermediate(s) (i.e., iron(IV)-oxo vs iron(V)-oxo species) in catalytic oxygenation reactions.

In this work, we have generated a new non-heme iron(IV)-oxo complex, $[\text{Fe}(\text{IV})(\text{O})(\text{BQEN})]^{2+}$ (**1**) (BQEN = *N,N'*-dimethyl-*N,N'*-bis(8-quinolyl)ethane-1,2-diamine) (see Figure 1), that shows a high reactivity in the oxidation of alkanes and alcohols. Reactivity studies revealed that the alkane and alcohol oxidations occur via a hydrogen-atom (H-atom) abstraction mechanism. We have also obtained strong evidence that an intermediate different from the iron(IV)-oxo species is involved in the catalytic oxidation of alkanes and alcohols by an iron catalyst and a terminal oxidant.

The reaction of $\text{Fe}(\text{II})(\text{BQEN})(\text{CF}_3\text{SO}_3)_2$ [11] with $\text{CH}_3\text{CO}_3\text{H}$ in CH_3CN at 0 °C produced a green intermediate **1** with λ_{max} at 740 nm (Figure 2a). This chromophore resembles those associated with $S = 1$ non-heme iron(IV)-oxo complexes.[4–7,12] The EPR spectrum of **1** appeared silent, as observed in other iron(IV)-oxo species.[5–7] The electrospray ionization mass spectrum (ESI-MS) of **1** exhibits a prominent ion peak at $m/z = 563.0$ (Figure 2b), which upshifts to $m/z = 565.0$ upon introduction of H_2^{18}O into the solution of **1** (Supporting Information (SI), Figure S1 for mass spectral changes of **1** at different incubation times), indicating that **1** contains an iron-oxo group which exchanges its oxygen with H_2^{18}O at a slow rate.[10] These ESI-MS data are consistent with the formulation of **1** as $[\text{Fe}(\text{IV})(\text{O})(\text{BQEN})(\text{CF}_3\text{SO}_3)]^+$ (calculated m/z of 563.1).

The formation of an Fe(IV)-oxo species in the reaction of $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and $\text{CH}_3\text{CO}_3\text{H}$ was further confirmed by X-ray absorption spectroscopy (XAS) (Figure 3a). The Fe K XAS pre-edge and edge of intermediate **1** show an increase in energy of ~2 eV relative to the starting material, as well as a notable increase in pre-edge intensity, from ~7 to ~21 units. The edge shift and increase in pre-edge intensity are a result of greater Z_{eff} and distortion from centrosymmetry, indicating the presence of a short Fe(IV)=O bond.[12c,13] EXAFS data for $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and **1** show a notable intensity decrease upon oxidation as well as a sharpening of the first shell feature in the Fourier transform (Figure 3b; also see SI for detailed discussion). The best EXAFS fits to $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ (fit 3) and **1** (fit 4) are given in SI, Table S2. The EXAFS data of $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ fits to a 6-coordinate first shell of light atoms (nitrogen/carbon) at 1.97 Å, whereas a short 1.67 Å Fe(IV)=O bond is required to accurately fit the EXAFS data for **1**. The decrease in EXAFS amplitude and Fourier transform intensity could be a result of the combination of the formation of a short Fe(IV)=O and by the presence of a mixture due to incomplete conversion to **1**. The short Fe=O bond causes a lengthening of the *trans* Fe-N bond (see SI on XAS Results and Analysis: DFT), resulting in a less ordered first shell. Sharpening of the Fourier transform over the first shell might be a result of the EXAFS wave contribution from the short Fe(IV)=O bond, as the short EXAFS wave overlaps with the main first shell feature, creating destructive interference at high and low k or from interference from the signals of

the starting material. A more detailed analysis of both the pre-edge and EXAFS fits is given in the Supporting Information.

The intermediate **1** has a significant lifetime ($t_{1/2} \sim 0.5$ h) at 0 °C, but decayed at a fast rate upon addition of substrates, such as triphenylmethane, indan, tetralin, cumene, ethylbenzene, and benzyl alcohol. Pseudo-first-order fitting of the kinetic data allowed us to determine k_{obs} values, and the pseudo-first-order rate constants increased linearly with the increase of substrate concentration (SI, Figure S4); the second-order rate constants, k_2 , at 0 °C were $2.4 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for triphenylmethane, $4.5 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for indan, $4.3 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for tetralin, $2.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for cumene, $2.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for ethylbenzene, and $6.7 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for benzyl alcohol. When the $\log k_2'$ values were plotted against the C-H bond dissociation energy (BDE) of the substrates (triphenylmethane, 81 kcal mol⁻¹; indan, 82 kcal mol⁻¹; tetralin, 82 kcal mol⁻¹; cumene, 85 kcal mol⁻¹; ethylbenzene, 87 kcal mol⁻¹), [14] we have obtained a linear correlation between the reaction rates and the C-H BDE of substrates (Figure 4). The observation that the rate constants decrease with the increase of the C-H BDE of substrates implicates an H-atom abstraction as the rate-determining step for the oxidation.[15] Further evidence for the H-atom abstraction mechanism was obtained from a measurement of KIE values in the oxidation of cumene, ethylbenzene, and benzyl alcohol; KIE values of 25(2) for benzyl alcohol, >11 for cumene, and >10 for ethylbenzene are consistent with C-H bond cleavage being the rate-determining step (SI, Table S3).[16] It is worth noting that large KIE values of 30 – 50 were reported in the oxidation of ethylbenzene and benzyl alcohol by $[\text{Fe}^{\text{IV}}(\text{O})(\text{N4Py})]^{2+}$ (N4Py = *N,N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine)[7a,b] and in the cleavage of the target C-H bond of taurine by the $\text{Fe}^{\text{IV}}=\text{O}$ intermediate of TauD.[17] The good correlation between reaction rates and BDE of substrates and large KIE values in the C-H bond oxidation of alkanes and alcohol support the notion that the oxidation of alkanes and alcohols by **1** occurs via an H-atom abstraction mechanism.[7,17]

Interestingly, when $\text{CH}_3\text{CO}_3\text{H}$ was added to a reaction solution containing $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and indan at 0 °C, the formation of **1** was not observed (SI, Figure S5a). Considering the reaction rate of **1** with indan at 0 °C (SI, Figure S5b), this result implies that a highly reactive intermediate **2** was generated in the reaction of $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and $\text{CH}_3\text{CO}_3\text{H}$ and then reacted fast with indan. If **1** is the sole intermediate generated in the reaction of $[\text{Fe}(\text{BQEN})]^{2+}$ and $\text{CH}_3\text{CO}_3\text{H}$, we should observe the formation of **1** even in the presence of indan and then the decay of **1** due to the reaction with the substrate as shown in SI, Figure S5b.

The following observations further support the involvement of **2** as an active species in the reaction of $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and $\text{CH}_3\text{CO}_3\text{H}$ under catalytic conditions. When the oxidation of benzyl alcohol by $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and $\text{CH}_3\text{CO}_3\text{H}$ was carried out at 0 °C, a deep green color developed within 60 s ($\lambda_{\text{max}} = 660$ nm) (SI, Figure S6a). The ESI-MS of the green species **3** exhibits a prominent peak at $m/z = 520.1$ (calculated m/z of 520.2) (SI, Figure S6b), whose mass and isotope distribution pattern corresponds to $[\text{Fe}(\text{III})(\text{BQEN})(\text{OCH}_2(\text{C}_6\text{H}_4)\text{O})]^+$ (see the proposed structure **3** in Scheme 1). The EPR spectrum of **3** shows a strong signal at $g = 4.3$, typical of a high-spin ($S = 5/2$) Fe^{III} species (SI, Figure S6c). The spectroscopic observations indicate that the aromatic ring hydroxylation of benzyl alcohol took place at the *ortho* position, affording an iron(III) complex bearing a 2-hydroxybenzyl alcohol ligand (Scheme 1, pathway E).[18] This proposal is based on the recent reports that reactions of non-heme iron(II) complexes bearing two *cis*-labile sites, such as $[\text{Fe}(\text{TPA})]^{2+}$ (TPA = tris(2-pyridylmethyl)amine) and $[\text{Fe}(\text{BPMEN})]^{2+}$ (BPMEN = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine), react with perbenzoic acids or benzoic acid plus H_2O_2 , affording iron(III)-salicylate complexes as products.[19] We therefore propose that the aromatic ring hydroxylation is a preferred pathway in the

oxidation of benzyl alcohol by the intermediate **2**. In contrast, the formation of **3** was not observed in the reaction of **1** and benzyl alcohol, demonstrating that **1** does not hydroxylate the aromatic ring of benzyl alcohol but oxidizes benzyl alcohol to benzaldehyde (Scheme 1, pathway D).

By carrying out labeled water experiments, the intermediate **2** was found to contain an iron-oxo group exchangeable with H_2^{18}O at a fast rate. We have shown above that the iron-oxo group of **1** exchanges with H_2^{18}O at a slow rate (e.g., ~50% ^{18}O -exchange after 20 min incubation; see SI, Figure S1) (Scheme 1, pathway F). Interestingly, when **1** was generated in the presence of H_2^{18}O in the reaction of $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and $\text{CH}_3\text{CO}_3\text{H}$ and analyzed immediately (e.g., less than 30 s) by ESI-MS, we found that **1** contained ~63% ^{18}O derived from H_2^{18}O (Figure 2b, inset). These results imply that **2** exchanges its oxygen with H_2^{18}O at a fast rate (Scheme 1, pathway G), followed by the conversion of **2** to **1** (Scheme 1, pathway H). The present results further indicate that the proposed iron(V)-oxo species exchanges its oxygen with H_2^{18}O much faster than the corresponding iron(IV)-oxo species. This speculation is of interest since the dependence of the oxygen exchange of metal-oxo species on the oxidation states of metal ions has never been explored previously,[20] and we are currently investigating the effect of the metal oxidation states on the oxygen exchange between high-valent metal-oxo complexes and H_2^{18}O under the identical conditions (e.g., the same ligand structure and solvent systems).

Finally, we propose the mechanism for the formation of **1** and **2** in the reaction of $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and $\text{CH}_3\text{CO}_3\text{H}$ as follows: $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ is oxidized to $[\text{Fe}(\text{III})(\text{BQEN})]^{3+}$ by $\text{CH}_3\text{CO}_3\text{H}$. [21] Then, $[\text{Fe}(\text{III})(\text{BQEN})(\text{OO}(\text{O})\text{CCH}_3)]^{2+}$ is generated by the reaction of $[\text{Fe}(\text{III})(\text{BQEN})]^{3+}$ and $\text{CH}_3\text{CO}_3\text{H}$. The O-O bond heterolysis of $[\text{Fe}(\text{III})(\text{BQEN})(\text{OO}(\text{O})\text{CCH}_3)]^{2+}$ produces **2**, followed by one e^- reduction of the unstable **2** that leads to the formation of **1**. [22] Nonetheless, other high-valent iron-oxo species, such as $[\text{Fe}(\text{IV})(\text{OH})_2(\text{BQEN})]^{2+}$ and a high-spin ($S = 2$) $[\text{Fe}(\text{IV})(\text{O})(\text{BQEN})]^{2+}$, [23] can be considered as plausible structures for **2**.

In conclusion, we have reported the synthesis, characterization, and reactivities of a mononuclear non-heme iron(IV)-oxo complex, $[\text{Fe}(\text{IV})(\text{O})(\text{BQEN})]^{2+}$ (**1**). We have also provided strong evidence that an intermediate different from **1**, possibly an iron(V)-oxo species (**2**), is involved as an active oxidant in the catalytic oxidation of alkanes and alcohols by $[\text{Fe}(\text{II})(\text{BQEN})]^{2+}$ and peracetic acid. The reactivity of **2** is greater than that of **1**, the product distributions observed in the reactions of **1** and **2** are different, and **2** exchanges its oxygen with H_2^{18}O much faster than **1**. Future studies will focus on attempts to characterize the intermediate **2** and understand the reactivity of **2** in various oxygenation reactions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Schematic representation of the BQEN ligand (left) and $[\text{Fe(IV)}(\text{O})(\text{BQEN})]^{2+}$ (**1**) (right).

Figure 2.

(a) UV-vis spectral changes showing the formation of **1** (red-colored bold line) in the reaction of Fe(II)(BQEN)(CF₃SO₃)₂ (2 mM) (black-colored bold line) and CH₃CO₃H (6 mM) in CH₃CN at 0 °C. (b) ESI-MS of **1**. The ion peak at $m/z = 227.4$ corresponds to [Fe(IV)(O)(BQEN)(CH₃CN)]²⁺. Inset shows observed isotope distribution patterns for **1**-¹⁶O (left) and for a mixture of **1**-¹⁶O (37%) and **1**-¹⁸O (63%) (right). The latter ESI-MS spectrum was obtained by generating **1** in the reaction of Fe(II)(BQEN)(CF₃SO₃)₂ (2 mM) and CH₃CO₃H (6 mM) in the presence of H₂¹⁸O (20 μL) in CH₃CN at 0 °C.

Figure 3.

(a) Fe X-ray absorption spectra showing the intensity normalized pre-edge (inset), edge, and XANES. (b) Overlay of the Fourier transform ($k = 2\text{--}13 \text{ \AA}^{-1}$) and EXAFS data (inset). $[\text{Fe(II)(BQEN)}]^{2+}$ (blue) and $[\text{Fe(IV)(O)(BQEN)}]^{2+}$ (**1**) (red).

Figure 4.

Plot of $\log k_2'$ of **1** against C-H BDE of substrates. Second-order rate constants, k_2 , were determined at 0 °C and then adjusted for reaction stoichiometry to yield k_2' based on the number of equivalent target C-H bonds of substrates (e.g., 1 for triphenylmethane and cumene, 2 for ethylbenzene, and 4 for indan and tetralin).

Scheme 1.

Reactions of an in situ-generated iron(IV)-oxo (1) and a proposed iron(V)-oxo (2) under stoichiometric and catalytic conditions, respectively.