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Formation of a Room Temperature Stable $Fe^{V}(O)$ Complex: Reactivity Toward Unactivated C−H Bonds

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Supporting Information

ABSTRACT: An $Fe^{V}(O)$ complex has been synthesized from equimolar solutions of $(Et_4N)_2[Fe^{III}(Cl)$(biuret-amide)] and *m*CPBA in CH_3CN at room temperature. The $Fe^{V}(O)$ complex has been characterized by UV−vis, EPR, Mössbauer, and HRMS and shown to be capable of oxidizing a series of alkanes having C−H bond dissociation energies ranging from 99.3 kcal mol^{-1} (cyclohexane) to 84.5 kcal mol^{-1} (cumene). Linearity in the Bell−Evans−Polayni graph and the finding of a large kinetic isotope effect suggest that hydrogen abstraction is engaged the rate-determining step.

High valent iron-oxo intermediates play key roles in enzymatic oxidations.[1−5] For example, in the cytochrome P450 enzymes, the high valent $Fe^{IV}(O)$(porphyrin−radical−cation), isoelectronic with $Fe^{V}(O)$, has been shown to be the reactive intermediate in the selective hydroxylation of camphor.[2,6] In the Rieske dioxygenase enzyme family,[1] an $Fe^{V}(O)$ active intermediate has been proposed.[7,8] Several functional models of both heme[9] and nonheme[10−13] iron-dependent monooxygenase enzymes have been synthesized[15−18] including the TAML system, which has provided fully functional, small molecule replicas of the peroxidase and short-circuited P450 enzymes.[12,13] For nonheme iron catalyzed oxidations, Fe^{IV}═O active intermediates have been isolated and structurally characterized and their reactivity toward C—H bond hydroxylation has been studied in detail.[9,14−16] Synthetic functional models of Rieske dioxygenase family of enzymes have been postulated to engage an $Fe^{V}(O)$ reactive species in C—H and C═C bond oxidations.[17,18] Several complexes having $Fe^{V}(O)$ have been reported, and they are thermally not stable above −40 °C.[19,20] Que et al. has described the formation of an $Fe^{V}(O)$ complex from $[Fe^{IV}(O)(TMC)(MeCN)]^{2+}$ at −44 °C ($t_{1/2}$ = 60 min).[21] Recently, Costas et al. has reported formation of a purported $Fe^{V}(O)$ at −60 °C (characterized using mass spectroscopy) and studied its reactivity.[18] Collins et al. first produced a nonheme $Fe^{V}(O)$ complex by oxidation of an Fe^{III}-TAML complex at −60 °C using *m*-chloroperbenzoic acid (*m*CPBA); this was thoroughly characterized by UV−vis, ESI−MS, EPR, EXAFS, and Mössbauer spectroscopies.[22] The $Fe^{V}(O)$ intermediate was shown to be reactive toward sulfoxidation and epoxidation in the −40 to −60 °C range in nitrile solvents.[22,23] However, to date it has not been possible to characterize and explore the ambient conditions for the reactivity of an $Fe^{V}(O)$ complex because no system has been stable enough to permit this. The availability of an $Fe^{V}(O)$ complex that is both stable and reactive at ambient to physiological temperatures would have the potential to advance insight into enzymatic oxidation processes and especially oxidations of the C−H bonds of unactivated alkanes, which are among the most difficult of all oxdiation processes to carry out in a controlled fashion.

We have recently reported the first preparation and initial studies of an Fe^{III} complex of a biuret-amide based macrocyclic ligand, **1**,[24a] a member of the broad suite of catalysts called TAML activators that were invented by Collins in the mid-1990s.[24b] Complex **1** is the first member of a fifth generation of TAML activators—generation numbers mark the order of preparation of sets of TAML activators with distinctive structural motifs. Activator **1** differs from the prototypical first generation TAML activator by substitution of the CMe_2 moiety in the six-membered macrocylic subring[25] with an −NMe group (Figure 1). The planar six-membered ring allows

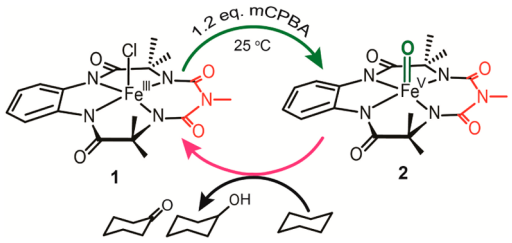

Figure 1. Schematic presentation of $Fe^{V}(O)$ formation and reaction toward cyclohexane.

electron donation from −NMe group and subsequent delocalization of the electron density throughout the ring.[26] This is evident in electrochemical studies where the Fe^{IV}/Fe^{III} couple of **1** is 230 mV higher[24a] than the corresponding Fe-TAML. This in addition to the fact that the −NMe group is situated far away from the Fe center made us to believe that $Fe^{V}(O)$ complex (**2**) should have stability at temperatures higher than −40 °C.[22,23] In this article, we report the formation and characterization of the $Fe^{V}(O)$ complex **2** from **1**.

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Remarkably, **2** is sufficiently stable that it can be produced quantitatively and its reactivity can be examined at room temperature. We also demonstrate that **2** readily cleaves the unactivated alkane C−H bond of cyclohexane; studies of the kinetics lead to the conclusion that H atom abstraction by $Fe^{V}(O)$ is the rate determining step (r.d.s) in the resulting hydroxylation process (Figure 1).

Complex **2** was prepared at 25 °C from the parent TAML activator, $(Et_4N)_2[Fe^{III}(Cl)(\text{biuret-amide})]$ **1**, in CH_3CN by adding equimolar amounts of *m*CPBA.[22] Addition of 0.5 equivalent of *m*CPBA (5×10^{-5} M) to **1** (10^{-4} M) at RT in CH_3CN with exclusion of O_2 afforded a violet-colored solution. Addition of a second half equivalent of *m*CPBA to this violet solution resulted in the formation of a green solution with distinct absorption maxima at 441 nm ($\varepsilon = 4.35 \times 10^3$ M^{-1} cm^{-1}) and 613 nm ($\varepsilon = 3.42 \times 10^3$ M^{-1} cm^{-1}) (Figure 2A).

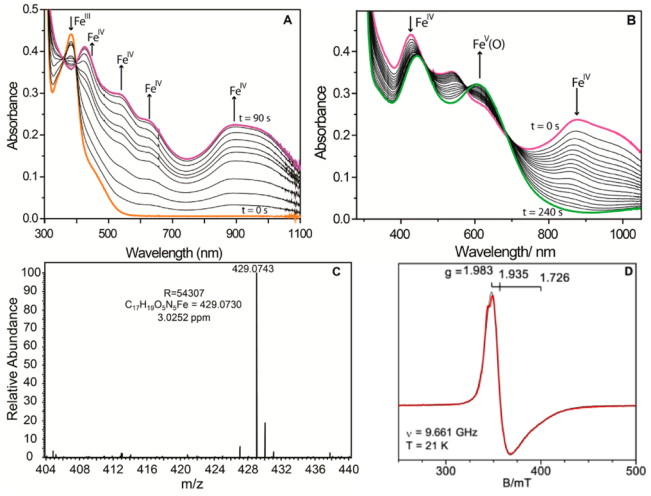

Figure 2. (A) UV−vis spectral changes upon addition of 0.5 equiv of *m*CPBA (5×10^{-5} M) to **1** (10^{-4} M). Orange = spectrum of **1**, violet = proposed $(Fe^{IV})_2O$ dimeric product. (B) UV−vis spectral changes upon addition of 0.5 equiv *m*CPBA (5×10^{-5} M) to the preformed $(Fe^{IV})_2O$. Green = spectrum of $Fe^{V}(O)$. (C) HRMS spectra of green $Fe^{V}(O)$. (D) EPR spectra. Red = $Fe^{V}(O)$, Blue = simulated spectrum.

The green solution was examined by mass, EPR, and Mössbauer spectroscopies. A sample of the green solution was split and frozen in liquid nitrogen and then analyzed with EPR and Mössbauer spectroscopies. The X-band EPR spectrum at 21 K showed a rhombic $S = 1/2$ species with **g** = 1.983, 1.935, 1.726 (Figure 2D). Spin quantification indicated quantitative conversion of the starting Fe^{III} complex (**1**) to the corresponding $Fe^{V}(O)$ (**2**). The Mössbauer spectrum of ^{57}Fe enriched **2** at 4 K showed a doublet with an isomer shift of $\Delta = -0.44$ mm/s and quadrupole splitting of $\Delta Eq = 4.27$ mm/s (Supporting Information Figure SI 1). A paramagnetic pattern is not observed, and the doublet is broad due to intermediate relaxation of the spin system. The intermediate relaxation and broad EPR signal suggest molecular aggregation. The **g**-values and Mössbauer parameters are close to those of the $Fe^{V}(O)$ complex reported previously.[22] Both the EPR and Mössbauer spectral analyses suggest quantitative conversion (≥95%) of the starting **1** to **2** (Figure 2 and Supporting Information Figure SI 1). This is in contrast to the $Fe^{V}(O)$ prototype TAML, where only 70% of Fe^{V} was produced from the starting Fe^{III} complexes at −40 °C (by Mössbauer spectroscopy).[22] HRMS examination of **2** in CH_3CN revealed one prominent ion at a mass-to-charge ratio of 429.0745 (calculated m/z 429.0730); the isotopic distribution pattern corresponded to that expected for **2** (Figure 2C). HRMS analysis of a solution prepared by introduction of $H_2{}^{18}O$ (0.5 μL) into the solvent media during the synthesis of **2** showed 70% formation of $Fe^{V}(^{18}O)$ (m/z 431.078, Supporting Information Figure SI 2).

Addition of 1 equiv of **1** to **2** also resulted in formation of a violet solution, the UV−vis spectrum (Figure 2A) of which was identical to the solution formed by addition of 0.5 equiv of *m*CPBA to **1**. This common UV−vis spectrum with its conspicuous features at long wavelengths was very similar to the known UV−vis spectra of μ-oxo-$(Fe^{IV})_2$ species of established Fe-TAML complexes.[23,27] Moreover, the violet solution was found to be EPR silent. Because they were diamagnetic, their ^{1}H NMR spectra was recorded (Supporting Information Figure SI 3), which again reproduced the behavior of the parent $(Fe^{IV})_2O$ TAML complexes.[27] The rate of comproportionation between **1** and **2** was determined to be 1.00×10^5 M^{-1} s^{-1}, twice the rate of the corresponding process for the prototype TAML (NMe replaced by CMe_2, Supporting Information Figure SI 4), consistent with the less sterically encumbered nature of the biuret system.[23] A detailed study to elucidate the nature of this Fe^{IV} is currently underway.

The spontaneous reduction of Fe^{V} to Fe^{IV}/Fe^{III} was studied using UV−vis spectroscopy by monitoring the decrease characteristic 613 nm band of **2**. The initial rate of the decay was found to be first order with respect to **2** and the first order rate constants for the decay ($k_{5/4,3}$) were determined from the slope of the straight lines at three different temperatures of 25, 10, and 4 °C (Supporting Information Figure SI 5). The $k_{5/4,3}$ value at 25 °C (4.45×10^{-5} s^{-1}) was similar to the $Fe^{V}(O)$ prototype TAML reported at −40 °C,[23] showing that the biuret-substituted TAML ligand leads to a much more stable $Fe^{V}(O)$ complex. In fact, **2** is the first example of an $Fe^{V}(O)$ complex that is stable at room temperature. The stability of the Fe^{IV} species (generated by reaction of **1** with 0.5 equivalent of *m*CPBA) was determined by monitoring the decrease of a characteristic band at 428 nm. Over time, this proposed $(Fe^{IV})_2O$ slowly converted to **1**.

The unprecedented high stability of **2** has allowed us to examine its room temperature reactivity. Activation of C−H bonds by **2** at room temperature were studied for a range of hydrocarbons with bond dissociation energies (BDE), spanning 85−100 kcal mol^{-1}.[28] Excess cyclohexane (1000 equiv) was added to a solution of **2** (10^{-4} M) in CH_3CN at 25 °C with exclusion of O_2, and the reaction was monitored by UV−vis spectroscopy. Upon addition of cyclohexane, spectral scans showed the rapid formation of a mixture of Fe^{IV} and Fe^{III} species, which then slowly converted to **1** (ESI−MS, UV−vis confirmation, Figure 3). GC and GC−MS analysis indicated cyclohexanol and cyclohexanone as products (Table 1), showing **2** is capable of effective oxygen atom insertion into an unactivated C−H bond. Based on the concentration of **2**, the yield of the reaction was determined to be 42% with an alcohol to ketone ratio of 9:1 (Table 1, Supporting Information Figures SI 6 and SI 7). Reactions of **2** with substrates having stronger and weaker C−H bonds than cyclohexane were also studied. Addition of benzene (BDE of C−H ~110 kcal mol^{-1}) to a solution of **2** showed no additional change in the UV−vis spectrum and no product was observed by GC−MS. In contrast, substrates having lower BDE like cumene, ethylbenzene, toluene, and 2,3-dimethylbutane (DMB) reacted more rapidly with **2** than with cyclohexane. In the case of

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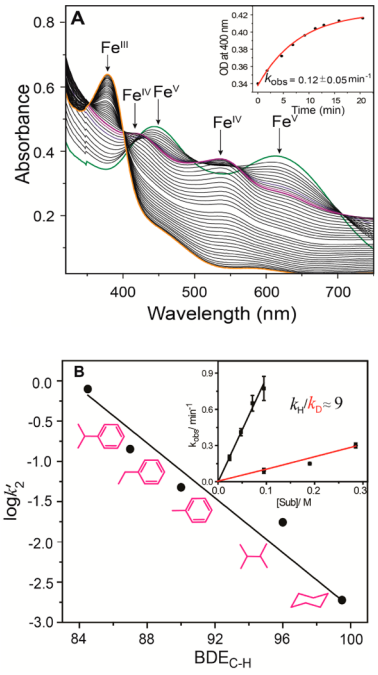

Figure 3. (A) UV−vis spectral changes upon reaction of **2** (1×10^{-4} M) with cyclohexane (0.093 M). (Inset) the absorbance vs time plot at 400 nm (■ indicates experimental data point; the red line is the first order fit according to the equation $[(A_t = A_\alpha - (A_\alpha - A_o)e^{(-k_{obs}t)}]$. (B) log k_2' vs BDE_{C-H} of various hydrocarbons for the reactions with **2** at 25 °C. (Inset) Plot of k_{obs}/min^{-1} vs [toluene] (black line) and [toluene-d_8] (red line) showing a pronounced KIE at 25 °C.

DMB, **2** selectively hydroxylated the tertiary C−H bond (BDE ~96 kcal mol^{-1}, Table 1) in preference to the primary C−H bond (BDE ~99 kcal mol^{-1}), leading exclusively to the formation of 2,3-dimethyl-2-butanol.

To confirm, if part of the product obtained was due to the reaction with the Fe^{IV} species, which is initially formed upon addition of substrate to **2**, the reactivity of the Fe^{IV} species (generated by the reaction of complex **1** with 0.5 equiv of *m*CPBA) toward C−H activation was also explored. It was found from UV−vis, GC, and GC−MS studies that the reaction of cyclohexane with Fe^{IV} species did not lead any product formation on the time scale (≥6 h) of the experiments.

Extensive kinetic studies were performed to ascertain the nature of the hydroxylations by **2** using UV−vis spectroscopy at the isosbestic points for Fe^{III} and Fe^{IV} interconversions (353 and 400 nm) under pseudo-first-order conditions. The pseudo-first-order rate constant (k_{obs}) calculated from the absorbance vs time traces at both wavelengths were obtained from nonlinear curve fitting $[(A_t = A_\alpha - (A_\alpha - A_o)e^{(-k_{obs}t)}]$ (Supporting Information Figures SI 8 and 9) and exhibited good agreement in rate constant values within 5% error. The k_{obs} values thus obtained correlated linearly with the substrate concentration to provide the second order rate constant k_2 (Supporting Information Figure SI 9), and it was observed that the rate constant decreased with an increase in the BDE of C−H bonds in the substrates. Linearity in Bell−Evans−Polanyi (BEP) relation was found from the plot of log k_2' (k_2/the number of equivalent H atoms) vs BDE (Figure 3)[28] for all the substrates from cyclohexane to cumene (slope of −0.17). This linearity supports hydrogen abstraction ($H^\bullet$) from a C−H bond by $Fe^V(O)$ group of **2** in the r.d.s as has been previously reported for $[Fe^{IV}(O)(N_4Py)(CH_3CN)]$ complexes.[29] A significant kinetic isotope effect (KIE) of 9 was observed for toluene/toluene-d_8 at 25 °C, supporting the conclusion that the r.d.s entails abstraction of an H atom from the C−H bond by the $Fe^V(O)$ (Figure 3, inset); KIEs of 2.1 and 6.5 have been found for typical porphyrin π-radical cation $[(4\text{-TMPyP})^{\bullet+}\ Fe^{IV}(O)]^+$ and $[(TMP)^{\bullet+}\ Fe^{IV}(O)(p\text{-}CH_3\text{−}PyO)]^+$ with xanthene and xanthene-d_2, respectively.[9,29,30] Oxygen incorporation from $Fe^V(O)$ into the cyclohexane was followed by using 55% O^{18} labeled Fe^V, which resulted 35% O^{18} enriched product, supporting a rebound mechanism. (Supporting Information Figure SI 7).

Thus, the data supports the conclusion that the mechanism of C−H activation by **2** involves initial abstraction of an H atom from the hydrocarbon substrate by $Fe^V(O)$ followed by rebound to yield the oxidized product together with the regeneration of the parent Fe^{III} complex **1** (see Figure 3A and Supporting Information Figure SI 10 for pictorial representations of the proposed mechanism). The Fe^{III} complex **1** thus formed undergoes rapid comproportionation (Supporting Information Figure SI 4) with **2** to form the observed μ-oxo-$(Fe^{IV})_2$ product (UV−vis, ^1H NMR). Kinetic studies of the comproportionation reaction between **2** and **1** show that the second order rate constant ($1.00 \times 10^5\ M^{-1}s^{-1}$; see Supporting Information Figure SI 4) is at least 10^5-fold faster than the rate for C−H activation. Because this comproportionation reaction is extremely fast, the direct conversion of **2** to **1** is not observed in initial spectral scans. This is also corroborated by the observation that the product formation in all the reactions is less than 50% for all the substrates. Similar observations have been reported for sulfide oxidation by the parent $Fe^V(O)$ TAML activator. However, in this system, the likely $(Fe^{IV})_2O$ product formed by reacting **2** and **1** undergoes further slow reduction to finally yield **1**. The faster self-reduction of our Fe^{IV} species is in contrast to the prototype Fe-TAML system, where the μ-oxo-$(Fe^{IV})_2$ is extremely stable and does not undergo reduction. Because the Fe^{IV} species is not reactive toward oxidation of alkanes, the formation of the oxidized product in the reaction is solely due to the reaction of alkanes with **2**. Preliminary experiments performed in the presence of O_2 show high amounts of ketone formation in respect to the corresponding alcohol, indicating that the radical formed after C−H abstraction is capable of reacting with O_2, as has been proposed before.[30]

Table 1. Summary of Data for the Oxidation of Different Hydrocarbon by $Fe^V(O)$

alkane (no. of equivalent H atom)	BDE_{C-H} (kcal mol^{-1})	k_2 ($M^{-1}\ s^{-1}$)	products (equiv/Fe)	conversion
$PhCH(CH_3)_2$ (1)	84.5	$(7.91 \pm 0.09) \times 10^{-1}$	$PhC(OH)(CH_3)_2$ (0.49); $PhC(O)CH_3$ (0.07)	56%
PhEt (2)	87	$(2.84 \pm 0.21) \times 10^{-1}$	$PhCH(OH)CH_3$ (0.3); $PhC(O)CH_3$ (0.22)	52%
$PhCH_3$ (3)	90	$(1.36 \pm 0.16) \times 10^{-1}$	PhCHO (0.30)	30%
2,3-dimethylbutane (2)	96.5	$(3.50 \pm 0.10) \times 10^{-2}$	2,3-dimethyl-2-butanol (0.46)	46%
Cyclohexane (12)	99.3	$(2.26 \pm 0.10) \times 10^{-2}$	$C_6H_{11}OH$ (0.4); $C_6H_{10}O$ (0.02)	42%

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In conclusion, we have successfully synthesized an $Fe^{V}(O)$ complex of a biuret-containing TAML activator at room temperature. EPR and Mössbauer spectroscopic studies show quantitative conversion of Fe^{III} (**1**) to the $Fe^{V}(O)$ complex. This complex displays remarkably higher stability at room temperature than any previously reported Fe^{V}-oxo complex. This higher stability has allowed us to study oxidation reactions with alkanes having strong C−H bond, such as that in cyclohexane (BDE_{C-H} = 99.3 kcal mol^{-1}), at room temperature. This is the first report of a well-defined $Fe^{V}(O)$ species that has been shown to react with strong C−H bonds. It was observed that **2** oxidizes cyclohexane to cyclohexanol and cyclohexanone with high reaction rates, k_2 at 25 °C is $(2.26 \pm 0.10) \times 10^{-2}$ M^{-1} s^{-1} (Supporting Information Figure SI 9).[31] It is possible that the subsequent oxygen atom incorporation may proceed by either rebound mechanism or a dissociative mechanism or a combination of both, as has been recently proposed.[32] Studies aimed at further understanding the complete reaction mechanism including efforts to crystallographically characterize **2** are underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization data, details of kinetic studies and proposed mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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