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Thermodynamics of Hydrogen Atom Transfer to a High-Valent Iron Imido Complex

Ismael Nieto,[†] Feizhi Ding,[†] Ranko P. Bontchev,[‡] Haobin Wang,[†] and Jeremy M. Smith^{*,†}

Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces New Mexico 88003, and Cabot Corporation, 5401 Venice Ave. N.E., Albuquerque, New Mexico 87113

Received October 5, 2007; E-mail: jesmith@nmsu.edu

Non-heme iron dioxygenases and their model complexes hydroxylate saturated hydrocarbons via high-valent iron oxo intermediates.¹ Initial C–H bond cleavage by hydrogen atom transfer (HAT) to the reactive Fe^{IV}=O species is proposed as the first step of these hydroxylation mechanisms.² High-valent iron imidos³ may be anticipated to participate in analogous amination reactions that involve initial HAT to the imido ligand⁴ (known N–H bondforming reactions of iron imidos include hydrogenation⁵ and NIH shift following electrophilic arene attack).⁶

Considering the thermodynamics of HAT in terms of its component steps, i.e., electron and proton transfer,⁷ can provide insight into the forces that drive the reaction. For example, these considerations have led to the proposal that the thermodynamic driving force for HAT in cytochrome P450 is provided by a highly basic reduced ferryl intermediate, allowing the enzyme to oxygenate hydrocarbons at potentials low enough to be tolerated by the protein matrix.⁸

In this contribution we report the preparation of a stable highvalent iron imido complex that is supported by a bulky tris(carbene)borate ligand. The thermal stability of this complex has allowed us to undertake studies relevant to HAT to the imido ligand. These investigations determine the propensity for HAT and show that the high basicity of the reduced imido complex provides the thermodynamic driving force.

The iron imido complex, $L^{Mes}Fe \equiv NAd$ ($L^{Mes} =$ phenyltris(1mesitylimidazol-2-ylidene)borate), is prepared by a similar synthetic route to other iron(III) imido complexes (Scheme 1).^{9,10} The fourcoordinate complex $L^{Mes}FeCl$, prepared from " $L^{Mes}Li$ "¹¹ and FeCl₂-(THF)_{1.5}, is reduced in the presence of cyclooctene to form the low-valent complex $L^{Mes}Fe(\eta^2-C_8H_{14})$. Reaction of this complex with one equivalent of azidoadamantane results in nitrene transfer to form dark-red $L^{Mes}Fe \equiv NAd$. All of these complexes have been spectroscopically and crystallographically characterized, see Supporting Information (SI) for details.

Oxidation of L^{Mes}Fe≡NAd by [Cp₂Fe]OTf results in formation of the high-valent imido complex [L^{Mes}Fe≡NAd]OTf. The metrical parameters of this complex (characterized as the BPh₄⁻ salt) are very similar to those of its precursor (Figure 1). The Fe−N bond distance in L^{Mes}Fe≡NAd⁺ (1.618(3) Å) is also comparable to other crystallographically characterized four-coordinate iron(IV) imido complexes.^{3a,b} The ¹H NMR spectrum of [L^{Mes}Fe≡NAd]OTf is consistent with the X-ray crystal structure, and distinct from that of L^{Mes}Fe≡NAd. The magnetic moment, determined by the Evans method ($\mu_{eff} = 2.7(3)$ BM), is consistent with S = 1 Fe(IV).

Air-stable [L^{Mes}Fe \equiv NAd]OTf can be heated for days at 100 °C with no evidence of decomposition. This unusual thermal stability has allowed us to undertake thermodynamic investigations relevant to HAT. In particular, we have determined the barriers toward





 a Conditions and reagents: (i) cyclooctene, KC₈, THF, 81%; (ii) N₃Ad, THF, 79%; (iii) [Cp₂Fe]OTf, THF, 60%.



Figure 1. X-ray crystal structures of $L^{Mes}Fe \equiv NAd$ and $[L^{Mes}Fe \equiv NAd]$ -BPh₄. Thermal ellipsoids are shown at 50% probability; hydrogen atoms and most of the tris(carbene)borate ligand have been omitted for clarity.

electron and proton transfer, allowing the thermodynamic barrier to HAT to be calculated.

Electron transfer from $[L^{\text{Mes}}\text{Fe}\equiv\text{NAd}]\text{OTf}$ is reversible. The cyclic voltammogram of $[L^{\text{Mes}}\text{Fe}\equiv\text{NAd}]\text{OTf}$ (MeCN, 0.10 M NBu₄-PF₆) reveals a wave at $E_{1/2} = -0.98$ V relative to Cp₂Fe⁺/Cp₂Fe, which we have assigned to the Fe^{IV}/Fe^{III} couple.¹² Consistent with this low barrier toward electron transfer, weak oxidants, such as I₂, cleanly oxidize $L^{\text{Mes}}\text{Fe}\equiv\text{NAd}$ to $[L^{\text{Mes}}\text{Fe}\equiv\text{NAd}]^+$. Therefore, $[L^{\text{Mes}}\text{Fe}\equiv\text{NAd}]\text{OTf}$ is a weak oxidant.

The two imido complexes, L^{Mes}Fe≡NAd and [L^{Mes}Fe≡NAd]-OTf, undergo rapid electron transfer on the ¹H NMR time scale. Line-shape analysis¹³ of a mixture of the two complexes in THF d_8 has allowed us to determine the second-order rate constant for self-exchange to be $k_2 = 7.6(5) \times 10^7$ M⁻¹ s⁻¹ at 308 K. This

[†] New Mexico State University. [‡] Cabot Corporation.





^a All energies in kcal/mol. ^bRelative to Cp₂Fe^{+/0}. ^cFrom ref 16.

large rate constant is consistent with the low reorganizational barrier that would be expected on the basis of the structural similarity of the two complexes. The rate constant is similar to that for electron transfer between Cp*₂Fe and Cp*₂Fe⁺ ($k_2 = 5.5(5) \times 10^7 \text{ M}^{-1}$ s⁻¹, CD₃CN, 308 K).^{13d}

We have been unable to directly measure the thermodynamic barrier toward proton transfer to L^{Mes}Fe≡NAd. Addition of acids to L^{Mes}Fe≡NAd, even in stoichiometric amounts, results in the formation of 1-adamantylamine (characterized by ¹H NMR and ESI-MS), along with unidentified iron product(s). We suspect that the anticipated product, LMesFe-N(H)Ad+, is unstable under the reaction conditions. The barrier toward proton transfer has therefore been estimated by reaction of L^{Mes}Fe≡NAd with a series of acids that differ in their pK_a . 1-Adamantylamine formation occurs with the weak acid CF₃CH₂OH ($pK_a = 33(2)$ in MeCN),¹⁴ but not with acetone ($pK_a = 38(2)$). This provides an upper limit for the pK_a of $L^{Mes}Fe-N(H)Ad^+$ in acetonitrile.

The difficulty in experimentally determining the thermodynamic barrier toward proton transfer has led us to calculate it using density functional theory with hybrid functional B3LYP and basis set SDD. The central quantity in the theoretical investigation is the pK_a of L^{Mes}Fe-N(H)Ad⁺ in MeCN. This is derived by considering the generic acid-base reaction $L^{Mes}Fe-N(H)Ad^+ + A^- \rightarrow L^{Mes}Fe \equiv$ NAd + HA, where HA is a weak acid. Acetonitrile solvent was implicitly modeled for the bulky iron complexes using the polarizable continuum model, and explicitly modeled for some smaller acids. A series of weak acids have been chosen to span a proper range of pK_a values that is estimated to be either slightly above or below that of LMesFe-N(H)Ad+. The theoretically derived value of pK_a for $L^{Mes}Fe-N(H)Ad^+$ in MeCN is 37(3),¹⁵ which is consistent with the experimental data.

The N-H BDFE (free energy) of L^{Mes}Fe-N(H)Ad⁺ is therefore 88(5) kcal/mol (Scheme 2).¹⁶ Consistent with this value, [L^{Mes}Fe≡ NAd]OTf reacts with 9,10-dihydroanthracene (BDE = 78(1) kcal/ mol)¹⁷ at 100 °C to form anthracene in 25 \pm 6% yield.¹⁸

In summary, the driving force for HAT by L^{Mes}Fe=NAd⁺ is the high basicity of the reduced imido complex, L^{Mes}Fe≡NAd. The N-H BDFE is comparable to that of the O-H bond formed by HAT to some non-heme iron(IV) oxo complexes (84 \pm 1 kcal/ mol).19

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Supporting Information Available: Complete experimental and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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