Enzyme Models

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Experiment and Theory Reveal the Fundamental Difference between Two-State and Single-State Reactivity Patterns in Nonheme $Fe^{IV}=O$ versus $Ru^{IV}=O$ Oxidants**

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Recent developments in the emerging field of nonheme iron chemistry have provided chemists with a number of synthetic mononuclear nonheme iron(IV) oxo complexes, which have been implicated as the key reactive intermediates in enzymatic and biomimetic oxidation processes.[1] A notable example is the recently synthesized iron(IV) oxo complex bearing a nonheme macrocyclic ligand $[Fe^{IV}(O)(tmc)(NCCH_3)]^{2+}$ (**1**-NCCH$_3$; tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; Figure 1 a).[2] Characterization of the iron oxo species by spectroscopic techniques and X-ray crystallography and studies of their reactivity patterns in various oxidation reactions have created a great opportunity for understanding the chemical and physical properties of these complexes.[2,3]

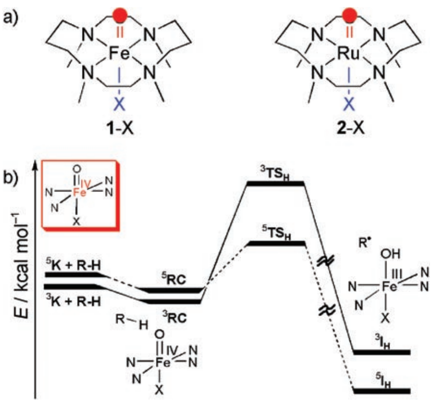

Figure 1. a) The structures of $[Fe^{IV}(O)(tmc)(X)]^{n+}$ (**1**-X) and $[Ru^{IV}(O)(tmc)(X)]^{n+}$ (**2**-X); b) the TSR scenario in H-abstraction reactions by $[Fe^{IV}(O)(tmc)(X)]^{n+}$.

Substitution of the acetonitrile ligand of **1**-NCCH$_3$ with a variety of anionic axial ligands (e.g., $X = CF_3CO_2^-$, N_3^-, or SR^-) made it possible to demonstrate that the reactivity of $[Fe^{IV}(O)(tmc)(X)]^{n+}$ (**1**-X) is significantly affected by the nature of the axial ligands in a manner that depends on the type of reaction.[4,5] Thus, while electron-donating axial ligands diminished the oxidative reactivity of **1**-X in oxo-transfer reactions (towards PPh$_3$, for which the reactivity order is **1**-NCCH$_3$ > **1**-CF$_3$CO$_2$ > **1**-N$_3$ > **1**-SR), they enhanced the reactivity of **1**-X in H-abstraction reactions (from phenol O–H and alkyl aromatic C–H bonds), that is, a reactivity order of **1**′-SR > **1**-N$_3$ > **1**-CF$_3$CO$_2$ > **1**-NCCH$_3$.[5] Theoretical studies proposed that the puzzling reactivity trends arose from the fact that these nonheme iron(IV) oxo reagents have two closely lying spin states, a ground state with a triplet spin state (T) and a low-lying quintet spin state (Q), as shown schematically in Figure 1 b.[6,7] Thus, the triplet state has a high energy barrier, while the quintet state has a much lower barrier that crosses through the larger triplet barrier. Therefore, the H-abstraction reactions proceed on the two energy surfaces, and the resulting blended reactivity is behind the unusual reactivity patterns.[6] Without the two-state blend, the reactivity on any one of the spin-state surfaces was shown to follow the electrophilicity of **1**-X.[6]

How can one test this two-state reactivity (TSR) concept for the dichotomic reactivity pattern in oxo-transfer and H-abstraction processes by $[Fe^{IV}(O)(tmc)(X)]^{n+}$? The most straightforward way to interrogate the TSR hypothesis is to design a family of metal oxo complexes as closely analogous to $[Fe^{IV}(O)(tmc)(X)]^{n+}$ as possible, while replacing only the iron ion with a different metal ion so that the quintet state becomes energetically inaccessible. Theory predicts that such probe complexes will not exhibit dichotomic reactivity trends in oxo-transfer and H-abstraction reactions. To test this prediction, we focused on Ru^{IV} oxo complexes due to their propensity to prefer low-spin states to high-spin states.[8] Accordingly, we synthesized ruthenium(IV) oxo analogues bearing different axial ligands $[Ru^{IV}(O)(tmc)(X)]^{n+}$ (**2**-X; Figure 1 a) and examined their reactivity in oxo-transfer and H-abstraction reactions. Herein we report experimental and theoretical studies on the effects of axial ligands of the Ru^{IV} oxo complexes in oxo-transfer and H-abstraction reactions.

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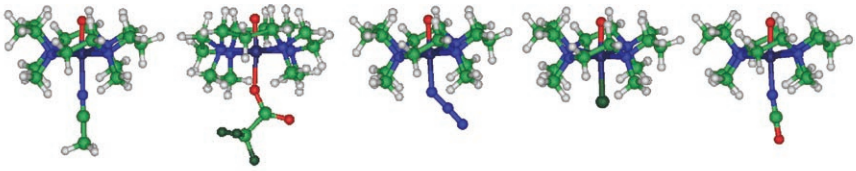
We carried out DFT calculations using three functionals and four basis sets up to triple-zeta valence with diffuse and polarization functions on $[\mathrm{Ru^{IV}(O)(tmc)(X)}]^{n+}$ [X = $\mathrm{NCCH_3}$ (**2**-$\mathrm{NCCH_3}$), $\mathrm{CF_3CO_2^-}$ (**2**-$\mathrm{CF_3CO_2}$), $\mathrm{N_3^-}$ (**2**-$\mathrm{N_3}$), $\mathrm{Cl^-}$ (**2**-Cl), $\mathrm{NCO^-}$ (**2**-NCO)], to compare the axial-ligand effects on the reactivity of $[\mathrm{Ru^{IV}(O)(tmc)(X)}]^{n+}$ and $[\mathrm{Fe^{IV}(O)(tmc)(X)}]^{n+}$ in oxo-transfer and H-abstraction reactions. The results, which are summarized in the Supporting Information, show no sensitivity to either functional or basis set and demonstrate unequivocally that all **2**-X species have a triplet ground state, while the quintet state lies 41–48 kcal mol^{-1} higher in energy. Figure 2 summarizes the key geometric features of the two states for **2**-X (X = $\mathrm{NCCH_3}$, $\mathrm{CF_3CO_2^-}$, $\mathrm{N_3^-}$, $\mathrm{Cl^-}$, and $\mathrm{NCO^-}$) and **1**-X[6] (X = $\mathrm{NCCH_3}$, $\mathrm{CF_3CO_2^-}$, and $\mathrm{N_3^-}$). The figure also compares the corresponding quintet–triplet energy gaps ΔE(Q-T) and the amount of charge Δq_{CT} that the ligand X transfers to the $\mathrm{tmc(X)MO}^{n+}$ moiety at the common computational level (see also the Supporting Information). There are obvious similarities and differences between the ruthenium and iron complexes. The similarities are: 1) For both metals, the ligands X = $\mathrm{NCCH_3}$ and $\mathrm{CF_3CO_2^-}$ transfer the least amount of charge to the reaction center (i.e., the $\mathrm{tmc(X)MO}^{n+}$ moiety), compared to the more powerful donating ligands, $\mathrm{Cl^-}$ and $\mathrm{N_3^-}$. 2) For both metals, ΔE(Q-T) is inversely proportional to Δq_{CT}; the better the electron-donating ability of the ligands, the smaller the ΔE(Q-T) gap. These similarities show that the Ru and Fe exhibit the same trends in their electronic features.



	2-$\mathrm{NCCH_3}$	**2**-$\mathrm{CF_3CO_2}$	**2**-$\mathrm{N_3}$	**2**-Cl	**2**-NCO
r(Ru-O)	1.79 [1.79]	1.81 [1.80]	1.83 [1.82]	1.81 [1.81]	1.82 [1.82]
r(Ru-A)	2.26 [2.25]	2.11 [2.09]	2.10 [2.07]	2.50 [2.46]	2.08 [2.05]
Δq_{CT}	0.22 [0.23]	0.42 [0.44]	0.53 [0.56]	0.69 [0.75]	0.44 [0.44]
ΔE(Q–T)	46.8	45.2	43.2	42.8	43.4
	1-$\mathrm{NCCH_3}$	**1**-$\mathrm{CF_3CO_2}$	**1**-$\mathrm{N_3}$		
r(Fe-O)	1.64 [1.64]	1.65 [1.65]	1.67 [1.67]		
r(Fe-A)	2.12 [2.09]	1.97 [1.93]	1.96 [1.94]		
Δq_{CT}	0.27 [0.27]	0.47 [0.49]	0.57 [0.61]		
ΔE(Q–T)	6.9	5.0	2.7		

Figure 2. Key geometric features of the triplet [quintet] states of $[\mathrm{M^{IV}(O)(tmc)(X)}]^{n+}$ complexes[6] obtained at the B3LYP/LACVP computational level; bond lengths are given in [Å]. "A" is the atom in the axial ligand coordinating to Ru or Fe. Also shown are the corresponding quintet–triplet energy gaps ΔE(Q-T) [kcal mol^{-1}] and the charge-transfer parameters Δq_{CT}. See the Supporting Information for data obtained at higher levels.

The major difference between the iron and ruthenium complexes is quantitative. Thus, the energy gaps for M = Fe are smaller than 10 kcal mol^{-1}, whereas they are larger than 40 kcal mol^{-1} for M = Ru. With the small ΔE(Q-T) gaps for M = Fe, the quintet state is accessible and can mediate the reaction (Figure 1 b). In contrast, with the very large ΔE(Q-T) gaps, larger than the largest barrier measured here, the quintet state is completely inaccessible for reactivity on the ground-state surface (see the Supporting Information), and the reactivity of $[\mathrm{Ru^{IV}(O)(tmc)(X)}]^{n+}$ is expected to be exclusively triplet-state reactivity. As was the case for $[\mathrm{Fe^{IV}(O)(tmc)(X)}]^{n+}$,[6,7d] the reactivity trend on the triplet-state surface is expected to follow the relative electrophilic character of the $[\mathrm{Ru^{IV}(O)(tmc)(X)}]^{n+}$ complexes. Furthermore, since the triplet barriers of the iron complexes are quite high and their moderately high reactivity derives only from the involvement of the quintet state, we might reasonably predict that the $[\mathrm{Ru^{IV}(O)(tmc)(X)}]^{n+}$ will be more sluggish bond activators compared to their iron analogues due to the inaccessibility of the quintet state in **2**-X. We emphasize that previous calculations on C–H activation by iron oxo and ruthenium oxo porphyrin complexes showed that, for a given spin state of the two reagents, the ruthenium oxo complex is the more powerful bond activator.[8a]

We now turn to experimental reactivity studies to verify the theoretical prediction. Ruthenium(IV) oxo complexes $[\mathrm{Ru^{IV}(O)(tmc)(X)}]^{n+}$ [X = $\mathrm{NCCH_3}$ (**2**-$\mathrm{NCCH_3}$), $\mathrm{CF_3CO_2^-}$ (**2**-$\mathrm{CF_3CO_2}$), $\mathrm{Cl^-}$ (**2**-Cl), $\mathrm{NCO^-}$ (**2**-NCO), $\mathrm{N_3^-}$ (**2**-$\mathrm{N_3}$), $\mathrm{NCS^-}$ (**2**-NCS)], were prepared by literature methods (see the Supporting Information for the syntheses and UV/Vis spectra of **2**-X),[9] and the binding of the axial ligands was confirmed by electrospray ionization mass spectra (ESI-MS) of **2**-X. The reactivity of **2**-X were then investigated in the oxidation of $\mathrm{PEt_3}$ and xanthene in $\mathrm{CH_3CN}$ at 35 °C. On addition of $\mathrm{PEt_3}$ to solutions of **2**-X, **2**-$\mathrm{NCCH_3}$ and **2**-$\mathrm{CF_3CO_2}$ were converted to the corresponding $\mathrm{Ru^{II}}$ complexes [Eq. (1); X = $\mathrm{NCCH_3}$, $\mathrm{CF_3CO_2^-}$], with isosbestic points at 282, 337, and 380 nm for **2**-$\mathrm{NCCH_3}$ (Figure 3 a).

$$[\mathrm{Ru^{IV}(tmc)(O)(X)}]^{n+} + \mathrm{Et_3P} \rightarrow [\mathrm{Ru^{II}(tmc)(X)}]^{n+} + \mathrm{Et_3PO} \qquad (1)$$

Pseudo-first-order rate constants increased proportionally with $\mathrm{PEt_3}$ concentration and afforded second-order rate constants of $8.9(8)\times10^{-3}$ and $6.0(5)\times10^{-3}\,\mathrm{M^{-1}s^{-1}}$ for the reactions of **2**-$\mathrm{NCCH_3}$ and **2**-$\mathrm{CF_3CO_2}$, respectively (Figure 3 b). In contrast, other $\mathrm{Ru^{IV}}$ oxo complexes, such as **2**-Cl, **2**-NCO, **2**-$\mathrm{N_3}$, and **2**-NCS, did not show any reactivity with $\mathrm{PEt_3}$ under identical conditions (Figure 3 b). These results indicate that the electron-donating ability of the axial ligands towards the $[\mathrm{Ru^{IV}(O)(tmc)}]^{2+}$ moiety is an important factor in determining the reactivity of **2**-X in O transfer to $\mathrm{PEt_3}$; **2**-X with more electron-donating axial ligands become more electron rich and would be expected to be less reactive in electrophilic oxidation reactions. To verify this, the electron richness of **2**-X was determined by measuring $\mathrm{Ru^{IV/III}}$ reduction potentials $E_{\mathrm{p,c}}$ (vs ferrocene, $\mathrm{Fc^{+/0}}$) of **2**-X. The $E_{\mathrm{p,c}}$ of **2**-$\mathrm{NCCH_3}$ and **2**-$\mathrm{CF_3CO_2}$ is about −0.78 V, and that of **2**-Cl, **2**-NCO, **2**-$\mathrm{N_3}$, and **2**-NCS about −1.3 V (see the

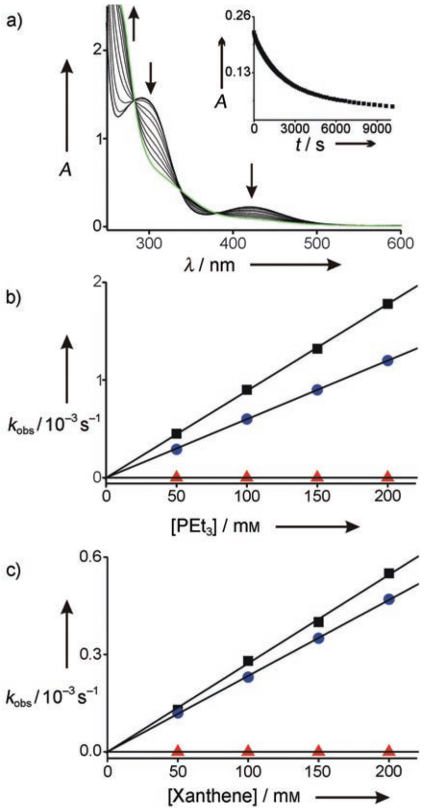


Figure 3. Reactions of **2**-X with PEt$_3$ and xanthene. a) UV/Vis spectral changes of **2**-NCCH$_3$ (1 mM) on addition of PEt$_3$ (50 mM) in CH$_3$CN at 35 °C. The inset shows the time course of the decay of **2**-NCCH$_3$ monitored at 420 nm. b) Plot of k_{obs} against PEt$_3$ concentration to determine second-order rate constants in CH$_3$CN at 35 °C. Black squares: **2**-NCCH$_3$; blue circles: **2**-CF$_3$CO$_2$; red triangles: **2**-Cl, **2**-NCO, **2**-N$_3$, and **2**-NCS. c) Plot of k_{obs} against xanthene concentration to determine second-order rate constants in CH$_3$CN at 35 °C. Black squares: **2**-NCCH$_3$; blue circles: **2**-CF$_3$CO$_2$; red triangles: **2**-Cl, **2**-NCO, **2**-N$_3$, and **2**-NCS.

Supporting Information).[10] These results demonstrate that the latter species are more electron rich than the former, in accord with expectation from DFT calculations. The peak potentials for **2**-CF$_3$CO$_2$ (−0.77 V) and **2**-NCO (−1.3 V) further resolve the ambiguity due to the small computed difference in the Δq_{CT} values (Figure 2) by showing that **2**-NCO is indeed electron richer. It is thus natural that electron-rich Ru^{IV} oxo species are poorer oxidants in electrophilic oxidation reactions.[11]

The effect of the axial ligand on H-abstraction also was investigated in the oxidation of activated C–H bonds by **2**-X. Among the tested substrates having weak C–H bonds, **2**-X reacted with xanthene (75.5 kcal mol^{-1}) but not with 9,10-dihydroanthracene (77 kcal mol^{-1}), 1,4-cyclohexadiene (78 kcal mol^{-1}), and fluorene (80 kcal mol^{-1}),[12,13] that is, H-abstraction from C–H bonds by **2**-X is a rate-determining step. On addition of xanthene to the solutions of **2**-NCCH$_3$ and **2**-CF$_3$CO$_2$, we observed pseudo-first-order decay, as monitored with a UV/Vis spectrophotometer, and the second-order rate constants were determined to be $2.7(3) \times 10^{-3}$ and $2.3(3) \times 10^{-3}$ M^{-1} s^{-1} for the reactions of **2**-NCCH$_3$ and **2**-CF$_3$CO$_2$, respectively (Figure 3c). Product analysis of the reaction solutions with GC and GC-MS revealed the formation of xanthone as sole product (ca. 50% based on the oxidants used). In contrast, **2**-Cl, **2**-NCO, **2**-N$_3$, and **2**-NCS did not react with xanthene at all (Figure 3c). These results indicate that the electrophilicity of the oxidants also governs the H-abstraction reactions. Importantly, these axial ligand effects in the **2**-X series stand in sharp contrast to those observed in the iron analogues [Fe^{IV}(O)(tmc)(X)]$^{n+}$, for which the H-abstraction reactivity behaved in a contrary manner to the electrophilicity of the oxidant, whereas O-transfer reactivity followed the electrophilicity order.[5] In the [Fe^{IV}(O)(tmc)(X)]$^{n+}$ series, it was postulated from DFT calculations[5,6] that the observed reactivity reflected the availability of two closely lying spin states for all **1**-X reagents, that is, the so-called TSR hypothesis (Figure 1 b), whereby the excited quintet state has a much lower reaction barrier than the ground triplet state.[7] Thus, in the iron complexes, increasing the electron-donating character of the axial ligand decreases the triplet–quintet gap and increases participation of the quintet state in C–H bond activation.[6] In contrast, the observation that Ru^{IV} oxo complexes **2**-X show the same reactivity trends in the oxidation of PEt$_3$ and xanthene is in perfect agreement with the DFT results (Figure 2) that the triplet–quintet gap in **2**-X is so large that the quintet state cannot possibly participate in the course of the reaction (see the Supporting Information), and hence the reactivity trend is dominated by the electrophilic power of the reagents and reactions are sluggish compared to the iron complexes. We therefore conclude that the observed experimental reactivity trends for the **2**-X versus **1**-X complexes follow the predictions that, as opposed to the TSR in **1**-X, the reactivity of **2**-X involves a single spin state.

In conclusion, the interplay of experiment and theory in the present paper constitutes a test of the TSR hypothesis. Thus, for Fe^{IV} oxo complexes **1**-X both quintet and triplet states contribute to the reactivity, which results in a counterintuitive trend in H-abstraction reactivity and in moderately fast reactions. By contrast, the inaccessibility of the quintet state in **2**-X results in sluggish reactions compared with **1**-X and relative reactivity that is dominated by the electrophilicity of **2**-X. Since for a given spin state of the two reagents the ruthenium oxo porphyrin was computed before to be more reactive than the corresponding iron oxo complex,[8a] the present opposite observation for **1**-X versus **2**-X provides additional support for the conclusion that the enhanced reactivity of the iron oxo complexes **1**-X reflects the participation of a low-lying quintet state as opposed to the inaccessibility of this state for **2**-X. Thus, this entire contrast between the reactivity patterns of **1**-X and **2**-X is also proof of principle for the operation of TSR in iron(IV) oxo complexes.[5,6]

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