Experiment and Theory Reveal the Fundamental Difference between Two-State and Single-State Reactivity Patterns in Nonheme Fe\textsuperscript{IV}=O versus Ru\textsuperscript{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\textsuperscript{IV}(O)(tmc)-tetraazacyclotetradecane; Figure 1 a).[2] Characterization of these complexes.[2, 3] Accordingly, we synthesized ruthenium(IV) oxo analogues bearing different axial ligands [Ru\textsuperscript{IV}(O)(tmc)(X)]\textsuperscript{n-} (1-X) and [Ru\textsuperscript{IV}(O)(tmc)(X)]\textsuperscript{n+} (2-X; Figure 1 a) and examined their reactivity 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 [RuIV(O)(tmc)(X)]\(^{1+}\) [X = NCCH\(_3\), N\(_3\), CF\(_2\)CO\(_2\), CF\(_2\)CF\(_2\), Cl\(^-\), N\(_{2}\)\(^-\), CF\(_3\)CO\(_2\)], C\(\equiv\)O\(^-\), NCO\(^-\)]. We compared the axial-ligand effects on the reactivity of [RuIV(O)(tmc)(X)]\(^{1+}\) and [FeIV(O)(tmc)(X)]\(^{1+}\) 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 ground-state surfaces (see the Supporting Information), and the reactivity of [RuIV(O)(tmc)(X)]\(^{1+}\) is expected to be exclusively triplet-state reactivity. As was the case for [FeIV(O)(tmc)(X)]\(^{1+}\), the reactivity trend on the triplet-state surface is expected to follow the relative electrophilic character of the [RuIV(O)(tmc)(X)]\(^{1+}\) 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 [RuIV(O)(tmc)(X)]\(^{1+}\) 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 o xo and ruthenium o xo porphyrin complexes showed that, for a given spin state of the two reagents, the ruthenium o xo complex is the more powerful bond activator.\(^{[a]}\)

We now turn to experimental reactivity studies to verify the theoretical prediction. Ruthenium(IV) oxo complexes [RuIV(O)(tmc)(X)]\(^{1+}\) [X = NCCH\(_3\), N\(_3\), CF\(_2\)CO\(_2\), CF\(_2\)CF\(_2\), Cl\(^-\), N\(_{2}\)\(^-\), NCO\(^-\), CF\(_3\)CO\(_2\)] 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 PEt\(_3\) and xanthene in CH\(_3\)CN at 35 °C. On addition of PEt\(_3\) to solutions of 2-X, 2-NCCCH\(_3\), and 2-CF\(_2\)CO\(_2\) were converted to the corresponding Ru\(^{II}\) complexes [Eq. (1); X = NCCH\(_3\), CF\(_2\)CO\(_2\)] with isosbestic points at 282, 337, and 380 nm for 2-NCCCH\(_3\) (Figure 3 a).

\[
{[\text{RuIV}(\text{tmc})(\text{O})(\text{X})]^{1+} + \text{Et}_3\text{P} \rightarrow [\text{RuIV}(\text{tmc})(\text{X})]^{1+} + \text{Et}_3\text{PO}} \tag{1}
\]

Pseudo-first-order rate constants increased proportionally with PEt\(_3\) concentration and afforded second-order rate constants of \(8.9(8) \times 10^{-3}\) and \(6.0(5) \times 10^{-3}\) m\(^{-1}\)s\(^{-1}\) for the reactions of 2-NCCCH\(_3\) and 2-CF\(_2\)CO\(_2\), respectively (Figure 3b). In contrast, other Ru\(^{IV}\) oxo complexes, such as 2-Cl, 2-NCO, 2-N\(_3\), and 2-NCS, did not show any reactivity with PEt\(_3\) under identical conditions (Figure 3b). These results indicate that the electron-donating ability of the axial ligands towards the [RuIV(O)(tmc)]\(^{1+}\) moiety is an important factor in determining the reactivity of 2-X in O transfer to 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 Ru\(^{IV}\) reduction potentials \(E_{p,1}\) (vs ferrocene, Fc\(^{0}\)) of 2-X. The \(E_{p,1}\) of 2-NCCCH\(_3\) and 2-CF\(_2\)CO\(_2\) is about −0.78 V, and that of 2-Cl, 2-NCO, 2-N\(_3\), and 2-NCS about −1.3 V (see the
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Supporting Information. 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 $\Delta q$CT values (Figure 2) by showing that $2$-NCO is indeed electron richer. It is thus natural that electron-rich Ru$^\text{IV}$ oxo species are poorer oxidants in electrophilic oxidation reactions.$^{[10]}$

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$_3$, $2$-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$_2$, 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 1b), 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.$^{[8]}$ 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,$^{[9a]}$ 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.$^{[5,4]}$

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