Sizing up a supercharged ferryl
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Terminal transition metal-oxo (oxo = O\(^{2-}\)) intermediates enjoy storied status in inorganic chemistry. The elucidation of the vanadyl (VO\(^{2+}\)) electronic structure by Ballhausen and Gray (1) helped usher in the era of molecular orbital depictions of bonding in transition metal chemistry. Since then, metal-oxo species have been implicated in vital roles throughout biological catalysis, with key examples including the ferryl-porphyrin radical intermediate, compound I (2) used by cytochrome P450 enzymes to hydroxylate C–H bonds and high-valent Mn-oxo species postulated to participate in O–O bond formation by the oxygen-evolving complex of photosystem II (3, 4). These natural examples have inspired considerable synthetic efforts: The past few decades have witnessed the syntheses of numerous examples of terminal metal-oxo complexes capable of activating moderately strong bonds (5–7). The ubiquity of reactive terminal metal-oxos has also reached the field of heterogeneous catalysis. Recently, Solomon and coworkers (8) characterized a potent zeolite-supported ferryl (FeO\(^{2+}\)) species capable of hydroxylating methane at room temperature. Now, in PNAS, Synder et al. (9) extend characterization of this species, using synchrotron-based spectroscopies to access valuable bonding parameters essential to defining the electronic structure underpinning the reactivity of this ferryl.

The capacity for Fe-doped zeolites to effect methane hydroxylation under mild conditions has been known for decades (10). However, identifying the “active ingredient” in materials with low (ca. 0.3 wt%) Fe loading required adopting a “bioinorganic approach” of site-selective spectroscopies (8). Variable-temperature/variable-field magnetic circular dichroism (VTVH-MCD) allowed direct focus on the paramagnetic Fe\(^{2+}\) active site (α-Fe) and its methane-hydroxylating oxygenated derivative (α-O). VTVH-MCD intensifies transitions between d-d (ligand-field) excited states as a function of temperature and applied magnetic field, and the resulting magnetization curves may be fit to yield two parameters: \(g_{\text{eff}}\) (effective g value) and \(\delta\) (rhombic zero field splitting) (11). Extracted parameters indicated that both α-Fe and α-O are mononuclear high-spin (\(S = 2\)) species; α-Fe is an oxygen-coordinated, square-planar Fe\(^{2+}\), and α-O is a tetragonal ferryl. These findings distinguished α-O from binuclear “intermediate Q,” which is the methane-hydroxylating active species formed by the enzyme-soluble methane monoxygenase (12, 13). Although the methane-oxidizing intermediate had a face at this point, mystery persisted. High-spin ferryls have been reported and characterized previously (14, 15), but without such oxidative alacrity as exhibited by α-O.

The structural characterization of α-Fe and α-O reported in PNAS (9) offers a rationale for the oxidative potency. Using Fe K-edge X-ray absorption spectroscopy

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**Note:** The text includes a figure and a table, which are not transcribed here. The figure is titled “Blueprints afforded by Synder et al. (9) for a potent methane hydroxylation intermediate.” The table is not provided. The article also references a figure (Fig. 1) and a table (Table 1). The figure and table are not included in the transcription. The article includes references to previous work by Ballhausen and Gray (1), Solomon and coworkers (8), and others. The synthetic efforts and characterization of terminal metal-oxo complexes are highlighted, with a focus on the work by Solomon et al. (8) and Synder et al. (9) on a ferryl species supported by zeolites.

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and extended X-ray absorption fine structure (EXAFS) data obtained at the Stanford Synchrotron Radiation Lightsource, Synder et al. (9) established the inner-sphere metrical parameters of α-Fe: four inner-sphere zeolite O ligands at 2.02 ± 0.03 Å. For α-O, a 1.63 ± 0.03 Å Fe=O scatterer completes the inner coordination sphere. Further support for a five-coordinate ferryl came from the particularly intense 1s → 3d pre-edge excitation reflective of a high degree of 3d/4p mixing due to diminished site centrosymmetry. However, ambiguities intrinsic to EXAFS analysis, particularly the inability to distinguish neighboring elements on the periodic table at similar distances (16), necessitated additional recourse to completing the local structural description, including disposition of Si and Al about the Fe active site.

For this, the investigators used $^{57}$Fe nuclear resonance vibrational spectroscopy (NRVS). This technique measures vibrational fine structure proximal to the $^{57}$Fe nuclear excitation that reports directly on vibrational modes involving Fe (17). These modes are sensitive not only to the nature of the inner coordination sphere but also to the placement of Al and Si in the β-type six-membered ring (β-6MR) housing the active Fe. Using normal mode analysis, Synder et al. (9) could exclude all but a β-6MR, where Al centers bridge Fe-coordinating zeolite O-donors.

The final, key experimental data furnished by this work concern the nature of the Fe=O bond. The 1.63 ± 0.03 Å Fe=O bond in α-O is typical for both S = 1 and S = 2 ferryls, and thus affords no clues concerning reactivity (18). However, NRVS directly afforded a stretching frequency, 885 cm$^{-1}$, for $\nu_{Fe=O}$, where $\nu$ is vibration. This stretching frequency, which is over 50 cm$^{-1}$ greater than the next reported value for a nonheme ferryl (19), reveals α-O to have a considerably stronger Fe=O interaction. Density functional theory calculations were carried out that effectively reproduce the experimental spectra features of α-O. Further examination of these experimentally validated electronic structure calculations reveal that the Fe=O interaction is highly covalent, manifesting an electron-deficient oxo primed for facile H-atom abstraction.

All told, the structural and spectroscopic characterization of α-O affords a blueprint for a “hot” ferryl capable of activating E-H bonds as recalcitrant as the 104 kcal-mol$^{-1}$ C–H bond of methane (Fig. 1). The active ingredients contributing to the reactivity of α-O manifest from the well-defined, constrained environment afforded by its host zeolite lattice. Not unlike how a protein defines the inner- and outer-sphere coordination about a metal to imbue reactivity properties, the present study shows that the “enigmatic” effect (20–22) is alive and well in a heterogeneous catalyst. These crucial, synergistic features of α-O include (i) low coordination number, (ii) a set of weak inner-sphere donors, and (iii) a highly covalent Fe=O interaction. Together, these attributes impart high driving force for a low activation barrier to E−H bond activation. The weak field imparted by the four inner-sphere zeolite O-donors favors the high-spin configuration, a feature implicated in bolstering in the reactivity of metal oxos (23). What makes α-O truly special is the high Fe=O covalency, which manifests in an electron-deficient oxo with a large driving force for O−H bond formation. Metal-ligand covalency, recognized early on as essential to properly describing bonding in coordination compounds (24), is once again seen as a vital contributor to reactivity, and thus should influence the design of future transition metal catalysts and reagents (25).

Opportunity abounds to push the limits of ferryl reactivity: Judicious ligand design or material choice could afford a three-coordinate Fe that, upon receipt of an O-atom, imposes even heavier electronic demands on the oxo ligand. Thus, the race is on to leverage the insights afforded in this article by Synder et al. (9) toward the design of new catalysts, be they homogeneous or heterogeneous, for hydroxylation of strong bonds. Such systems would find welcome use in pharmaceutical synthesis, hydrocarbon valorization, and other applications.

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