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Electrochemically Generated cis-Carboxylato-Coordinated Iron(IV) Oxo Acid–Base Congeners as Promiscuous Oxidants of Water Pollutants

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Supporting Information

ABSTRACT: The nonheme iron(IV) oxo complex \([\text{Fe}^{\text{IV}}(\text{O})-(\text{tpena})_2]^{2+}\) and its conjugate base \([\text{Fe}^{\text{IV}}(\text{O})(\text{tpena})]^+\) \(\text{tpena}^- = N,N,N',N'-\text{tris}(2\text{-pyridylmethyl})\text{ethylenediamine}-N'-\text{acetate}\) have been prepared electrochemically in water by bulk electrolysis of solutions prepared from \([\text{Fe}^{\text{III}}(\mu-\text{O})(\text{tpena})_2]^{4-}\) \((\text{ClO}_4)_2\) at potentials over 1.3 V (vs NHE) using inexpensive and commercially available carbon-based electrodes. Once generated, these iron(IV) oxo complexes persist at room temperature for minutes to half an hour over a wide range of pH values. They are capable of rapidly decomposing aliphatic and aromatic alcohols, alkanes, formic acid, phenols, and the xanthene dye rhodamine B. The oxidation of formic acid to carbon dioxide demonstrates the capacity for total mineralization of organic compounds. A radical hydrogen-atom-abstraction mechanism is proposed with a reactivity profile for the series that is reminiscent of oxidations by the hydroxyl radical. Facile regeneration of \([\text{Fe}^{\text{IV}}(\text{O})(\text{tpena})]^+\) and catalytic turnover in the oxidation of cyclohexanol under continuous electrolysis demonstrates the potential of the application of \([\text{Fe}^{\text{III}}(\text{tpena})]^{2+}\) as an electrocatalyst. The promiscuity of the electrochemically generated iron(IV) oxo complexes, in terms of the broad range of substrates examined, represents an important step toward the goal of cost-effective electrocatalytic water purification.

INTRODUCTION

According to the World Health Organization, never before have so many people been without clean drinking water.\(^1\) Not only is the threat to freshwater supplies a concern for developing countries, but it is also becoming an increasing issue in the western world where pesticides, persistent pharmaceuticals, plasticizers, textile dyes, fluorinated coatings, fire retardants, organic solvents, and natural and artificial hormones are contaminating freshwater reservoirs. The pressure for the reuse of treated wastewaters, potentially containing residual amounts of these contaminants, is intensifying.\(^2,3\) Chemically contaminated natural waters have been linked to hormonal disruptions in terrestrial and marine life\(^4\) and a decrease in human male fertility\(^5\) and are also a risk factor in cancerous and congenital disorders.\(^6\) The destruction of persistent organic pollutants from waters for environmental remediation and drinking water production is challenging because low biodegradability means that these contaminants are likely to be unaffected by conventional biological treatment processes\(^7\) and potentially difficult to remove by standard physicochemical processes. Some progress has been achieved through the use of advanced oxidation processes for degrading pollutants in which reactive hydroxyl radicals (\(\text{HO}^*\)) are generated from terminal chemical oxidants such as hydrogen peroxide (\(\text{H}_2\text{O}_2\)), ozone, or persulfate.\(^8\) One of the most common pathways by which \(\text{HO}^*\) is produced is via Fenton reactions, whereby \(\text{H}_2\text{O}_2\) reacts with \([\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}\) to produce \(\text{HO}^*\) and aquted and/or hydroxylated ferric species such as \([\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}\) and \([\text{Fe}^{\text{II}}(\text{OH})(\text{H}_2\text{O})_5]^{3+}\). The reaction is catalytic under acidic conditions because the iron(III) species can be reduced back to the iron(II) state by reaction with a second equiv of \(\text{H}_2\text{O}_2\).\(^9,10\) When the pH is raised, however, \(\text{HO}^*\) is no longer formed,\(^11\) and iron precipitates as a ferric oxide sludge, which itself must be disposed of.\(^12\) Complexation with polyaminecarboxylato ligands such as ethylenediaminetetraacetic acid (EDTA) and related ligands\(^13\) can prevent iron oxide precipitation and allow \(\text{HO}^*\) production at circumneutral \(\text{pH}\).\(^6\) However, the resultant \(\text{Fe}^{\text{III}}\)-EDTA complexes are not readily reduced back to the active form.
iron(II) form, in effect rendering them stoichiometric oxidants only. The discovery of new ligand systems for promoting transient generation of catalytically competent high-valent iron-based oxidants in sustainable redox cycles is therefore of prime importance. Electrochemical activation, rather than terminal chemical oxidant activation, of iron catalysts to form a high-valent species is an alternative but as yet unexploited approach for the production of iron-based oxidants. In water, potent iron(IV) oxo species could be produced by such a potentially more environmentally benign method (using renewable electricity sources). It would present a significant advancement over chemical activation using excess amounts of atom-uneconomical and logistically difficult terminal oxidants, and cleaner methodologies for the oxidation of organic substrates would be opened up.

The ability to activate chemical oxidants in water with the production of high-valent iron complexes is a good starting point in the search for the appropriate electrocatalysts for achieving this goal. Several ligand classes have been demonstrated to support high-valent iron. These include porphyrin, thio-carbamato, amido, and aminopolypyridyl ligands. Of particular note is the work of Collins and co-workers on the iron complexes of tetraanionic tetraamido macrocyclic ligands (abbreviated generally as TAMLs) to activate H2O2. These reactions are proposed to produce mononuclear high-valent oxo complexes [FeIV(O)(TAML)]2+/+ and [FeIV(μ-O)(TAML)]2+/+ and not HO•. The structure of a mononuclear iron(IV) oxo complex with the prototype TAML ligand 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1H-1,4,7,10-benzotetraazaclorotridecane-2,5,7,10-(6H,11H)tetron (H3B•+) is shown in Scheme 1. These H2O2-activating systems have been applied to water remediation. The prototype shown functions optimally around pH 9; however, since this initial work, the Fe-TAML system has evolved through scaffold modification to be capable of the oxidative degradation of a range of compounds in aqueous solution including azo- and phthalocyanine dyes,11 the antidepressant sertraline,12 organophosphorus pesticides,13 nitrophenols,14 and chlorinated phenols and metaldehyde,15 at lower pH values approaching 7. Electroactivation and consequent water oxidation was reported for a carbon-immobilized Fe-TAML.16 This result raises the issue of selectivity of the high-valent iron oxidants toward the oxidation of C–H and CO–H bonds of organic micropollutants over the O–H bonds of water. If water is the medium, it is likely to outcompete micropollutant mineralization, with the result that too much energy will be consumed. Fine-tuning the design of the ligand scaffold supporting molecular iron catalyst design is crucial.

In parallel to the development of Fe-TAML systems, an understanding of the nature and reactivity of molecular nonheme iron(IV) oxo complexes based on aminopolypyridyl ligands has developed. Examples of this class of ligand are the pentadentate systems, parent to the system used in the work described below; i.e., N′-benzyl-N,N,N′-tris(2-pyridylmethyl)ethylenediamine (bztpen)17 and N,N′-bis(2-pyridylmethyl)-N,N′-bis(2-pyridylmethyl)amine (N4Py)c18 as depicted in Scheme 1. The neutrality of these ligands means that their high-valent iron oxo complexes should inherently be more electrophilic relative to the Fe-TAML systems. Unfortunately, these systems are typically incompatible with aqueous chemistry often because of the formation of chemically unreactive stable oxo-bridged iron(III) systems as thermodynamic sinks. They are synthesized in organic solvents from the reaction of iron(II) precursors with hypervalent iodine reagents or alkyl peroxides, in two-electron reactions. Under nonaqueous conditions they have been shown to stoichiometrically oxidize alkanes, alkenes, sulfides, ketones and alcohols.19–22 Oxygen-atom-transfer (OAT) and/or hydrogen-atom-transfer (HAT) mechanisms have been proposed. The ability to target the oxidation of specific substrates is often limited, and overoxidation beyond the intended scope occurs. While this may not be ideal for selective catalysis, such promiscuous reactivity is ideal for applications where oxidative power, and not selectivity, is desired, such as in wastewater treatment.

We have shown that, in contrast to the nitrogen-atom-donor-only poly(pyridyl)-supported systems, the iron(IV) oxo species [FeIV(O)(tpenaH)]2+ [tpena− = N,N,N′-tris(2-pyridylmethyl)-ethylenediamine-N′-acetate; Scheme 1] can be generated in water by oxidizing solutions of [FeIII(μ-O)(tpenaH)]2+ by the reaction with cerium(IV) ammonium nitrate.23 In fact, [FeIV(O)(tpenaH)]2+ cannot be spectroscopically observed in organic solvents, presumably because of its spontaneous decay as the result of it oxidizing these solvents. In comparison, it is relatively stable in water with a half-life of around 2 h. The chemical generation of an iron(IV) oxo complex by one-electron oxidation of an iron(III) precursor contrasts with the two-electron OAT methods used for the preparation of the aforementioned iron(IV) oxo aminopolypyridyl complexes, like those based on bztpen and N4Py, from their resting iron(II) states. We therefore speculated that [FeIII(μ-O)(tpenaH)]2+ might be an interesting candidate complex for the investigation of its electrooxidation in water to form the iron(IV) oxo species. Aside from the salient stability of the 3+ state over the 2+ oxidation state, an important feature afforded by the Fe-tpena complexes is the unique presence of a carboxylate donor along with flexible ligand denticity. When fully coordinated, the tpena ligand is hexadentate, as verified by the structurally characterized homoleptic [MIII(tpena)]2+ complexes (M = Cr24, Co25, and Fe26). Interestingly, the iron complex can be isolated only in the absence of water. Even if trace water is present hemi- and monohydrates, [FeIII(μ-O)(tpenaH)]2+ and [FeIII(OH)(tpenaH)]2+, respectively, are formed. In these, a pyridine arm is decoordinated and protonated. It is noteworthy, with respect to the lability of the iron complex toward nucleophiles including water and thus pertinent to the work described below, that these [MIII(tpena)]2+ complexes...
show irregular octahedral geometries due to the small bite of the ethylenediamine backbone. The distortion from 90° for the chromium(III) complex is exceptional, compared to typical Werner-type complexes (one cis-N–Cr–N angle is 115°). The strain can be relieved by 7-coordination, as seen in the crystal structures of the high-spin d⁸ systems ([Fe₃⁺(tpena)(OIPh)]²⁺ and [Mn⁴⁺(tpena)(H₂O)]⁴⁺) or by decoordination of a pendant arm, as observed in [V⁴⁺(O)(tpenaH)]²⁺ and the hemihydrate [Fe³⁺₂(μ-O)(tpenaH)₂]⁴⁺.²⁶ When the latter occurs, tpena is pentadentate and the decoordinated methylpyridyl group protonated. [Fe⁴⁺(O)(tpenaH)]²⁺ is isovalent with the iron-based oxidant [Fe⁴⁺(O)(tpenaH)]²⁺ and models its structure. Protonation on the dangling pyridine of [Fe⁴⁺(O)(tpenaH)]²⁺ (rather than formation of an Fe⁴⁺OH species) is supported by the reproduction of the Mössbauer spectrum by density functional theory calculations.²⁶ The proximity of an uncoordinated pyridinium/pyridine group is reminiscent of the natural second coordination sphere bases histidine and lysine. Together with the carboxylato donor and a coordination sphere completed by neutral nitrogen-atom donors, this makes [Fe⁴⁺(O)(tpenaH)]²⁺ one of the most germane nonheme iron(IV) oxo enzyme mimics reported to date.

Electrooxidation is envisaged to be kinetically demanding, and the Fe-tpena system has the same advantage as the Fe-TAML systems in that a one-electron-only process is requisite to reach the iron(IV) state from aqueous solution resting states. The fact that [Fe⁴⁺(O)(tpenaH)]²⁺ appears to be a promiscuous oxidant that can be chemically generated using one-electron chemistry from stable aqueous solution iron(III) resting states using an easily accessible solid-state precursor and water as the oxygen-atom donor has prompted us to investigate the potential for its generation in water using electrochemical methods. We describe here success in this approach, along with the first systematic study of the reactivity of aqueous electrochemically generated nonheme iron(IV) oxo complexes. We show that the acid–base congeners [Fe⁴⁺(O)(tpenaH)]²⁺ and [Fe⁴⁺(O)(tpena)]⁺ are active toward the oxidation and mineralization of a wide range of organic pollutants under both stoichiometric and electrocatalytic conditions.

Figure 1. (A) Schematics of the pH-dependent iron(III) speciation of [Fe₃⁺₂(μ-O)(tpenaH)₂][ClO₄]₄ dissolved in water. (B) Selected CVs recorded for aqueous solutions of [Fe₃⁺(tpenaH)]⁴⁺ (0.8 mM per Fe; 0.1 M NaClO₄) at various pH values. Scan rate = 100 mV s⁻¹. The full series and assignments are provided in the Supporting Information. (C) Pourbaix (potential–pH) diagram for the Fe⁴⁺(tpena) system (L = tpena). Open red squares (□) denote anodic peak potentials for the oxidation of [Fe⁴⁺(OH₂)(tpenaH)]²⁻ to [Fe⁴⁺(O)(tpenaH)]²⁺ (2H⁺/1e⁻ and Eₚ = 1.25 V). Open blue squares (■) denote the oxidation of [Fe²⁺(OH₂)(tpenaH)]²⁻ to [Fe³⁺(OH)(tpenaH)]²⁻ (1H⁺/1e⁻ and Eₚ = 0.84 V). Open circles (○) denote the cathodic peak potentials for unassigned {Fe²⁺(O)} reductions (Eₚ ∼ 0.35–0.07 V).

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14938
RESULTS AND DISCUSSION

Speciation of the FeIII-tpena Complexes in Water. The structurally characterized [FeII(μ-O)(tpenaH)2](ClO4)3 is the solid-state starting material for all experiments. [FeII(μ-O)(tpenaH)2]4+ is formally a hemihydrate of [FeII(μ-O)(tpena)]2+ with the water equivalent divided between the oxygen atom of the oxo bridge and the two protons on the dangling pyridyls of each tpena. When dissolved in water, a series of pH-dependent and pH-independent protonation/deprotonation and hydrolysis/dehydration reactions give rise to the mono- and dinuclear species shown in Figure 1A. The structures of these compounds are proposed on the basis of the geometries observed in the crystal structures of iron(III), vanadium(IV), manganese(II), cobalt(III), and chromium(III) complexes, vide supra, and from parallel electron paramagnetic resonance (EPR), UV/visible, and previously reported Mössbauer spectroscopic data. Solution-state EPR spectroscopy can be used to monitor the concentration of the mononuclear species (Figure S2). At pH ≤2.5, the spin content suggests that the iron(III) species are distributed as ~50% low-spin (S = 1/2) and ~10% high-spin (S = 5/2) species. The remaining ~40% is EPR-silent, consistent with the presence of the strongly magnetically coupled oxo-bridged complex [FeII(μ-O)(tpenaH)2]4+, with this assignment corroborated by the Mössbauer spectrum recorded in aqueous solution at pH 4 (Mössbauer signature: δ = 0.47 mm s−1 and ΔEQ = 1.60 mm s−1). The low-spin species is the monohydrate of [FeII(μ-O)(tpena)]2+, namely, [FeII(μ-OH)- (tpenaH)2]4+ (Mössbauer signature: δ = 0.16 mm s−1 and ΔEQ = 2.19 mm s−1)3, shown in Figure 1A, where the water equivalent is divided between the hydroxo ligand and the protonated pyridyl. The high-spin species is proposed to be a protonated derivative, [FeII(μ-OH)(tpenaH)]3+ (or, alternatively, [FeII(OH)(tpenaH)2]3+, not shown in Figure 1A). At pH >5, a high-spin species, [FeII(OH)(tpena)]+, develops, with this evidenced by its signature in the Mössbauer spectrum (δ = 0.46 mm s−1 and ΔEQ = 0.71 mm s−1).3 Additional support for the speciation profile is gleaned from electrospray ionization mass spectrometry (ESI-MS), where the dominant ions produced from [FeII(μ-O)(tpenaH)2]4+ are [FeII(OH)(tpena)]+ (m/z 463.13), [FeII(μ-O)(tpenaH)]2+ (m/z 454.14), and [FeII(tpena)]+ (m/z 464.13).26 The latter gas-phase ferrous complex [FeII(tpena)]+ is not derived from the aqueous solution but is produced during ionization by dehydration and reduction of [FeII(OH)(tpenaH)]2+.34

Electrochemical Generation of [FeIV(O)(tpenaH)]2+. Bulk electrolysis of aqueous solutions containing dissolved [FeII(μ-O)(tpenaH)2](ClO4)4 (native pH ~3.6) using graphite felt or reticulated vitreous carbon electrodes produces [FeII(O)(tpena)]2+ within ~30 min at potentials above +1.3 V vs NHE. Charge-transfer curves indicate an approximately 90% conversion. The electrolysis is accompanied by a color change from yellow-brown to pale-blush-green, with UV/visible spectra showing the formation of a weak near-IR absorption band at λmax = 730 nm (ε ~ 260 M−1 cm−1). This band is characteristic for d–d transitions of nonheme iron(IV) oxo complexes,5,34,35 with the spectrum identical with that for [FeIV(O)(tpena)]2+ produced by chemical oxidation using cerium(IV) in water.26 The extent of conversion and time required is dependent on the amount of iron(III) to be electrolyzed, the potential or current applied, and the size of the working electrode (WE; Figure 2). During [FeIV(O)(tpenaH)]2+ formation, a drop in the pH from ~3.6 to 2.8 is observed, along with slow gas (H2) evolution at the cathode. The applied voltage is higher than the theoretical value for water oxidation (1.03 V at pH 3); thus, it is possible that some water oxidation accompanies the reaction, potentially catalyzed by the complex. However, because [FeIV(O)(tpenaH)]2+ is spectroscopically observable, this competing reaction must be significantly slower than [FeIV(O)(tpenaH)]2+ formation.

pH Dependence of the Reduction and Oxidation of the tpena Complexes of Iron(III). Cyclic voltammograms (CVs) of solutions containing [FeII(μ-O)(tpenaH)2](ClO4)4 were recorded over a pH window of 1.6–9.5. As can be seen from Figure 1B, FeIII → FeIV waves coexist. The wave at E1/2 = 1.36 V shows a pH dependence of −67 mV pH−1, suggesting a one-proton/one-electron oxidation process. This is consistent with [FeIV(O)(tpenaH)]2+ being generated by the oxidation of [FeII(O)(tpena)(OH)]3+. The FeIII → FeIV wave at E1/2 = 1.36 V shows a pH dependence of −67 mV pH−1, suggesting a one-proton/one-electron oxidation, and is assigned to the oxidation of [FeIV(tpena)(OH)]2+ to [FeIV(O)(tpenaH)]2+. The change in the slope of the FeIII → FeIV peak potential at pH 3.5 suggests a change in the protonation state of either [FeII(tpenaH)(OH)]2+ or [FeIV(O)(tpenaH)]2+. At intermediate pH (pH 4–7), the
higher potential Fe\textsuperscript{III} → Fe\textsuperscript{IV} wave shows no pH dependence, with this result consistent with the oxidation of [Fe\textsuperscript{III}(OH)-(tpena)]\textsuperscript{+} to [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+}. Over the same pH range, there is a shift in the pH dependence of the reversible Fe\textsuperscript{III}/Fe\textsuperscript{II} couple from $E_{1/2} = 0.63$ to 0.47 V, which suggests a change in the protonation state of the species involved in this reaction (e.g., [Fe\textsuperscript{II}(tpena)(OH\textsubscript{3})]\textsuperscript{+} to [Fe\textsuperscript{II}(OH)(tpena)]) with a pK\textsubscript{a} value of 5.3. Under alkaline conditions (pH >7), the Fe\textsuperscript{III} → Fe\textsuperscript{IV} peak again becomes pH-dependent with a slope of −54 mV pH\textsuperscript{−1}. This can be rationalized by [Fe\textsuperscript{III}(OH)(tpena)]\textsuperscript{−} being oxidized to [Fe\textsuperscript{IV}(O)(tpena)]\textsuperscript{3+}. A pK\textsubscript{a} value of 6.7 for [Fe\textsuperscript{IV}(O)(tpena\textsuperscript{H})\textsuperscript{2+}] assigned to deprotonation of the pendant protonated pyridyl arm to give the conjugate base [Fe\textsuperscript{IV}(O)(tpena)]\textsuperscript{−}.

The potential for protonation of the electrochemically generated [Fe\textsuperscript{IV}(O)(tpena\textsuperscript{H})\textsuperscript{2+}] was explored by pH manipulation (using HClO\textsubscript{4} or NaOH) in the pH range of 1.6−2.4. The absence of any changes in the UV/visible spectra or decay rate suggests that protonation of the oxo ligand to give an iron(IV) hydroxide complex, e.g., [Fe\textsuperscript{IV}(O)(tpena\textsuperscript{H})\textsuperscript{2+}] \textsuperscript{−} (bpH 4), does not occur. Similarly, Borovik and co-workers have failed to find any evidence for protonation of the oxo ligand in [Fe\textsuperscript{IV}(O)-(H\textsubscript{2}buea)]\textsuperscript{−} (buea = tris[2-(N,N-dimethylamino)ethyl]- aminato).\textsuperscript{35} The intensity of the Fe\textsuperscript{III} → Fe\textsuperscript{IV} wave correlates with the amount of conversion that takes place during bulk electrolysis at a given pH; the highest concentrations of iron(IV) oxo species are generated when the initial pH is around ~2−3. Above this and up to neutral pH, lower concentrations of iron(IV) oxo species are produced. If the pH is adjusted to above 7, no observable amounts of iron(IV) oxo species are generated by bulk electrolysis. At first glance, this is surprising because CVs at these pH values show relatively intense Fe\textsuperscript{III} → Fe\textsuperscript{IV} waves. This effect can, however, be rationalized by considering that observable iron(IV) oxo species are a balance of both the electrochemical formation rate and subsequent decay, which, in the absence of substrates, presumably occurs due to water oxidation. The decay of the iron(IV) oxo species was followed by the generation of [Fe\textsuperscript{III}(O)(tpena\textsuperscript{H})\textsuperscript{2+}] at pH 3−4 and then monitoring of the loss of absorbance at $\lambda_{max} \sim 730$ nm after adjustment of the pH.

At pH 3−4, the half-life of [Fe\textsuperscript{IV}(O)(tpena\textsuperscript{H})\textsuperscript{2+}] is around $\tau_{1/2} \sim 30$ min; as the pH is increased, the decay rate also increases, with the half-life at pH 6−7 being shorter than $\tau_{1/2} \sim 5$ min. The inability to accumulate the iron(IV) oxo species at higher pH is thus presumably due to the fact that [Fe\textsuperscript{IV}(O)-(tpena)]\textsuperscript{2+} is more reactive than its acid congener, [Fe\textsuperscript{IV}(O)-(tpena)]\textsuperscript{2+}. The rate constants for water oxidation of ~1.2 × 10\textsuperscript{−3} and 4 × 10\textsuperscript{−4} M\textsuperscript{−1} s\textsuperscript{−1} were deduced, respectively, at pH 6−7 and 3−4. The assignment of the rate constant for the reaction of [Fe\textsuperscript{III}(O)(tpena)]\textsuperscript{2+} with H\textsubscript{2}O is, however, uncertain because the observed self-decay rate of the iron(IV) oxo species increases markedly at pH >8 because of much more rapid oxidation of OH\textsuperscript{−} than H\textsubscript{2}O, with a rate constant for the reaction of [Fe\textsuperscript{III}(O)(tpena)]\textsuperscript{2+} with OH\textsuperscript{−} determined to be 3 × 10\textsuperscript{5} M\textsuperscript{−1} s\textsuperscript{−1}, i.e., over 5 orders of magnitude greater than the rate for H\textsubscript{2}O oxidation (detailed derivation available in the Supporting Information).

Scope of Substrate Oxidation by Electrochemically Generated [Fe\textsuperscript{IV}(O)(tpena\textsuperscript{H})\textsuperscript{2+}] and [Fe\textsuperscript{IV}(O)(tpena)]\textsuperscript{2+}. When water-soluble organic compounds are added to solutions of electrochemically generated [Fe\textsuperscript{IV}(O)(tpena\textsuperscript{H})\textsuperscript{2+}] and [Fe\textsuperscript{IV}(O)(tpena)]\textsuperscript{2+}, the decay is accelerated by several orders of magnitude. Figure 3A shows the disappearance of the 730 nm absorption before and after the addition of isopropyl alcohol at pH 4. The decay is substantially faster (τ\textsubscript{1/2} < 5 s) when phenol or 4-chlorophenol is added (Figure S4), suggesting that it is a C−H bond in the aliphatic alcohols and a O−H bond in the aromatic alcohols, respectively, that are targeted by the iron(IV) oxidant, with this result consistent with their relative bond dissociation enthalpies (BDEs). Gas chromatography (GC) analyses show that the stoichiometric reactions with both aliphatic and aromatic alcohols produce the derivative ketones as the main products (Figures S5−S9) with the second-order rate constants summarized in Figure 3B and Table 1. Solutions were buffered with acetate or phosphate buffers at pH 4 and 7, respectively. The oxidation of tetrahydrofuran (THF) and cyclohexanol are also relatively fast with rate constants of 2.7 × 10\textsuperscript{−2} M\textsuperscript{−1} s\textsuperscript{−1} and 4.7 × 10\textsuperscript{−2}, respectively. Given that the BDE of the weakest C−H bond in THF is 92.0 versus 92.8 kcal mol\textsuperscript{−1} for cyclohexanol,\textsuperscript{36} it is surprising that the oxidation of cyclohexanol is almost twice as fast as the oxidation of THF. One rationalization for this is a difference in the kinetic barriers. The presence of a hydroxyl group in a substrate might mean that a transition-state ion oxidant−substrate supramolecular adduct for cyclohexanol might be more easily accessed than one for THF. The rates for oxidation of the simple alcohols−isopropyl alcohol (i-ProOH; 1.6 × 10\textsuperscript{−2} M\textsuperscript{−1} s\textsuperscript{−1}), ethanol (EtOH; 5.5 × 10\textsuperscript{−3} M\textsuperscript{−1} s\textsuperscript{−1}), and methanol (MeOH; 7.1 × 10\textsuperscript{−4} M\textsuperscript{−1} s\textsuperscript{−1}) at pH 4−7 follow the order predicted from their BDEs.\textsuperscript{36} The spread in the magnitude of the rate constants is larger than what is expected from the Bell−Evan−Polanyi (BEP) relationship. Corroborating the increase in the decay rate at higher pH, in the absence of substrates, the oxidative power of [Fe\textsuperscript{IV}(O)-(tpena)]\textsuperscript{2+} is also enhanced at higher pH. Thus, the rate of methanol oxidation at pH 7 triples from that at pH 4 to $k_2 = 2.0 \times 10\textsuperscript{−3}$ M\textsuperscript{−1} s\textsuperscript{−1}.

Changes to the protonation state of the substrate also influence the reactivity, with the rate constant for the oxidation of formate/formic acid to carbon dioxide (CO\textsubscript{2}; Figure 3C) observed to increase from 0.30 M\textsuperscript{−1} s\textsuperscript{−1} at pH 3 to 1.2 M\textsuperscript{−1} s\textsuperscript{−1} at pH 5.5. The pH dependence is quantitatively consistent with a higher reactivity of HCOO\textsuperscript{−} compared to HCOOH (pK\textsubscript{a} = 3.75). We speculate that the positive charge of [Fe\textsuperscript{III}(O)-(tpena)]\textsuperscript{2+} and the hydrogen-bonding potential are advantageous for enhanced reactivity toward negatively charged HCOO\textsuperscript{−} over neutral HCOOH. The energetics of the electron-transfer process are likely to be similar; however, a higher outer-sphere association constant for the 2+/1− ion pair would be expected relative to the 2+/neutral case.\textsuperscript{45} Formation of CO\textsubscript{2} as a result of formate oxidation was confirmed by using \textsuperscript{14}C-labeled formate, with the generated \textsuperscript{14}CO\textsubscript{2} recovered in a NaOH trap and quantified by scintillation counting, unambiguously proving that the CO\textsubscript{2} evolved derives from the substrate and not from lignin breakdown.

Mechanism. While we observe a tendency for faster rates for the oxidation of substrates with weaker BDEs by [Fe\textsuperscript{IV}(O)(tpena\textsuperscript{H})\textsuperscript{2+}]/[Fe\textsuperscript{IV}(O)(tpena)]\textsuperscript{2+}, as mentioned...
above, a BEP correlation does not apply. This outcome contrasts with the BEP relationships that have been reported for hydrocarbon and alcohol oxidations by iron(IV) oxo complexes in nonaqueous solutions.\textsuperscript{46-49} The BEP relationship builds on the assumption that the entropic contributions to the activation barriers, for a series of reactions using closely related substrates, can be ignored. This assumption may be inappropriate for the Fe-tpena system. The mechanistic alternative to a HAT pathway, a proton-coupled electron-transfer mechanism,\textsuperscript{50,51} is easily ruled out because this mechanism implies the formation of an iron(III) oxo complex and alcohol radical cations (ROH\textsuperscript{+}), both unlikely intermediates. Mayer and co-workers have shown that the Marcus cross-relation, which uses bond dissociation free energies (BDFEs) instead of BDEs, provides a better description of HAT reactivity in such cases.\textsuperscript{52-54} Unfortunately, the BDFEs for most of the substrates used in this study are not known. To probe the size of the entropic activation barrier, we measured the rates for the i-PrOH oxidation by [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} at different temperatures. As shown in Figure 3D, this yielded a negative activation entropy of ΔS\textsuperscript{⧧} = −23 ± 4 cal mol\textsuperscript{−1} K\textsuperscript{−1} (1 T\&S\textsuperscript{⧧} = 7 kcal mol\textsuperscript{−1} at 25 °C vs ΔH\textsuperscript{⧧} = 13 ± 1 kcal mol\textsuperscript{−1}), suggesting a significant entropic component to these HAT reactions. The combination of an aqueous medium, a dangling pyridine/pyridinium, and the carboxylate group furnishes hydrogen-bonding opportunities. These have the potential of lowering the entropic penalty associated with desolvation of a substrate in the transition state.\textsuperscript{54} It is worth noting that, although slower by up to 10\textsuperscript{7} times, the relative order for the rate constants for the oxidation of the various substrates by [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} is the same as those reported for the hydroxyl radical (HO\textsuperscript{•}, Figure 4). Our interpretation is that a HAT mechanism is at play for both oxidants. The transition state for HAT reactions by HO\textsuperscript{•} involves the transfer of a negative charge to the oxygen atom of HO\textsuperscript{•} and positive charge generation on the hydrogen atom of the substrate. This is stabilized by interaction with a polar solvent, and particularly by hydrogen bonding with water, leading to significant rate acceleration in water.\textsuperscript{55} It is conceivable that the tpena-derived iron(IV) oxo moiety shows radical character analogous to that of HO\textsuperscript{•} and also participates in HAT chemistry\textsuperscript{54} (e.g., an “iron(III) oxyl”-type species). Involvement of the lone pair of the uncoordinated pyridine in stabilizing the positive charge on the substrate H in the transition state may be contributing to the increased rates observed at higher pH (Scheme 2). After hydrogen-atom abstraction, the immediate Fe\textsuperscript{III}-OH product can itself be intramolecularly stabilized through hydrogen bonding to the second coordination sphere base. Formic acid is a notable exception to the correlation observed in Figure 4, exhibiting a rate constant for the reaction with [Fe\textsuperscript{IV}(O)-(tpenaH)]\textsuperscript{2+} of 0.2 M\textsuperscript{−1} s\textsuperscript{−1}, which is many orders of magnitude greater than that predicted from the correlation (10\textsuperscript{−1} M\textsuperscript{−1} s\textsuperscript{−1}). The reaction of HO\textsuperscript{•} with formic acid is proposed to involve the acidic hydrogen atom in a cyclic hydrogen-bonded [HO\textsuperscript{•}:HOOCH] adduct transition state.\textsuperscript{56} An analogous interaction is, however, not feasible for the [Fe\textsuperscript{IV}(O)-(tpenaH)]\textsuperscript{2+} oxidant, which is instead more likely to react with the weaker C–H bond (BDE of 96.6 kcal mol\textsuperscript{−1}; cf. 112.3 kcal mol\textsuperscript{−1}). Thus, we can provide a rationalization for why this particular substrate does not fit into the parallel of reactivity for [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} and HO\textsuperscript{•}. It should be noted that the formate ion, which has only the C–H hydrogen available for
abstraction, cannot proceed through such a pathway and does
fit with the correlation in Figure 4.

Comparison of the Iron(IV) Oxo Potencies in Aqueous Oxidations of Organic Substrates. The rates we measure
for the oxidation of benzyl alcohol by electrochemically
generated [FeIV(O)(tpenaH)]2+ are higher than those that
have been reported for chemically generated [FeIV(O-)
(bztpen)]2+ and [FeIV(O)(N4Py)]2+ (Scheme 1) in
acetonitrile. Unfortunately, apart from the aforementioned

<table>
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<th>substrate</th>
<th>k2/M-1 s-1</th>
<th>BDE/kcal mol-1</th>
<th>k2(HO*)/M-1 s-1</th>
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“Gas-phase BDE for the weakest bond, taken from Luo36 unless indicated otherwise. Value given in Blanksby and Ellison,37 from the work of Ruscic et al.38 Value from Buxton.39 Values from the review by Buxton et al.40 The BDE is for the O–H bond.41 Values from Land and Ebert.42 Average of the five listed in Luo.43 Value from Stafford et al.44 Sodium salt. Value for camphor used was an estimate. Average of the values reported by Brutz and Sommermeyer45 and Kucherenko.46

Figure 4. Correlation between the second-order rate constants for oxidation reactions of [FeIV(O)(tpenaH)]2+ and the hydroxyl radical. See Table 1 for HO* rate constants and their sources. HCOOH is not included; see the text.

Inorganic Chemistry

Table 1. Second-Order Rate Constants for Substrate Oxidations by [FeIV(O)(tpenaH)]2+ at pH 4 and Those Compiled from the Literature for HO* Oxidation of the Same Substrate along with Gas-Phase BDEs for the Weakest C–H or O–H Bond, as Indicated by the Bold Hydrogen Atom

Scheme 2. Catalytic HAT from Substrate to Iron(IV) Oxidant and the Proposed Resultant Product FeIII-OH Complex

Fe-TAML system, there is a paucity of oxidative reactivity studies of iron(IV) oxo systems in aqueous solution, and the known iron(IV) oxo complexes have not been synthesized in this medium. To address this, Wang et al.27 used isolated powders of [FeIV(O)(N4Py)](ClO4)2 recovered from its synthesis in acetonitrile and, subsequently, redissolved the powder in water at pH ~7. When MeOH and THF were added, the decay of [FeIV(O)(N4Py)]2+ occurred with rate constants of k2 = 5 × 10-5 M-1 s-1 and k2 = 1.7 × 10-3 M-1 s-1, respectively. A comparison with our data in water indicates that
[FeIV(O)(tpenaH)]2+ oxidizes MeOH and THF at least >12 and ∼17 times faster, respectively, than [FeIV(O)(N4Py)]2+.

To further evaluate the potency of [FeIV(O)(tpenaH)]2+, we carried out bulk electrolysis on the closely related system [FeII(Cl)(bztpen)](ClO4) (in which the carboxylate arm is replaced by a benzyl arm; Scheme 1) at +1.42 V in water, with 10% acetonitrile added for solubility reasons. We found that, even though a two-electron oxidation of the iron is required in this case, [FeIV(O)(bztpen)]2+ could be generated. The CV is shown in Figure 5A. Replacement of the carboxylato donor by a pyridine donor results in a slight blue shift of the d-d absorption to λmax = 720 nm (ε ~ 220 M⁻¹ cm⁻¹) compared to that of [FeIV(O)(tpenaH)]2+. The Faradaic charge transferred indicates ∼91% conversion and a three-electron-transfer process, with the last electron equivalent assumed to be due to Cl⁻ oxidation (eq 1).

\[
\begin{align*}
[\text{Fe}^{II}(\text{Cl})(\text{bztpen})]^{+} + \text{H}_2\text{O} \\
\rightarrow [\text{Fe}^{IV}(\text{O})(\text{bztpen})]^{2+} + 2\text{H}^+ + \frac{1}{2} \text{Cl}_2 + 3\text{e}^- \quad (1)
\end{align*}
\]

The simplicity of the CVs recorded for [FeII(Cl)(bztpen)]+ is striking compared to those for Fe-tpena. This is not surprising given the more complicated speciation and pH profiles for Fe-tpena. The electrochemically generated [FeIV(O)(bztpen)]2+ is able to oxidize i-PrOH (Figures 5B and S16); however, the rate constant of 8.6 × 10⁻³ M⁻¹ s⁻¹ (at pH 4) is only half the rate constant obtained for the reaction with [FeIV(O)(tpenaH)]2+.

**Figure 5.** (A) CVs of solutions containing [FeII(Cl)(bztpen)](ClO4) (unbuffered, pH 4.7). (B) Time-resolved UV/visible spectra of the reaction of [FeIV(O)(bztpen)]2+ (0.8 mM) with i-PrOH (120 equiv) in a pH 4 acetate-buffered electrolyte.

**Electrocatalytic Degradation of Cyclohexanol.** [Fe-(tpena)]2+ catalyzes the degradation of cyclohexanol under electroanodic conditions with turnover. Using a bulk graphite felt electrode as the charge carrier, the oxidation of cyclohexanol (∼80 mM, emulsion) proceeds under both galvanostatic and potentiostatic conditions. When electrolyzed at 1.51 V in the presence of 0.8 mol % Fe-tpena, GC analysis showed that 44% of cyclohexanol was oxidized after 5 h (Figures S17 and S18). By comparison, only 18% was oxidized in the same time period in the absence of a catalyst. After 16 h, ∼81% of the original cyclohexanol content had disappeared from the catalyzed sample. In these solutions, cyclohexanone amounting to 3–5% of the mass balance was detected by GC. The cyclohexanone concentration reaches a steady state despite ongoing cyclohexanol loss, suggesting that cyclohexanone is further oxidized with the possibility of eventual total mineralization, as depicted in eq 2.

\[
\text{C}_6\text{H}_{11}\text{OH} + 11\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 34\text{H}^+ + 24\text{e}^- \quad (2)
\]

This observation is consistent with other studies of chemical and electrochemical cyclohexanol oxidations where the ring-opened carboxylic acids (6-hydroxyhexanoic acid, 6-oxohexanoic acid, and adipic acid) have been identified as major products of the oxidation of cyclohexanol.58–60 We assume therefore that the missing mass balance in the gas chromatograms is due to the formation of these GC-incompatible carboxylic acids or total mineralization (producing undetected CO2). NMR analysis supports the notion of total mineralization occurring because the spectra of 24 h electrocatalysis experiments show no other signals apart from those due to water (Figure S17). The charging curves show a significant 23% enhancement (after 5 h; Figure S18) in the charge transferred in the catalyzed experiments, compared to the control. The catalytic charge transferred after 16 h gives a turnover number of 12 for Fe-tpena.

The CV of cyclohexanol in water reveals an oxidation wave with onset at E ≥ 1.32 V. Upon titration with increasing concentrations of [FeIV(O)(tpenaH)]4+, a clear enhancement in this current is observed (Figure 6A). A plot of the catalytic current (i_cat) at 1.50 V against the iron concentration gives a linear correlation (Figure 6A, inset). Likewise, the CVs of [Fe(tpena)]2+ with increasing concentrations of cyclohexanol reveal that i_cat increases linearly with the square root of the cyclohexanol concentration until the point of maximal solubility is reached (Figure 6B). The concentration dependence indicates that the reaction rate has the form given in eq 3 and that it can be modeled as a kinetically controlled two-step catalytic process (EC’ mechanism).61–64 Essentially, the active iron-based oxidant is generated in a diffusion-controlled (heterogeneous) electron transfer between the resting catalyst and the electrode surface. The catalytically competent product species then diffuses into the solution and reacts with the substrate in a kinetically controlled homogeneous reaction. In turn, the iron(III) resting catalyst is regenerated. The scan rate (ν) dependence for an EC’ mechanism is given by eq 4.

\[
\text{rate} = k_{\text{cat}}[\text{Fe}^{IV}(\text{O})][\text{ROH}] \quad (3)
\]

\[
i_{\text{cat}} = \frac{n_F}{0.4463n_p} \sqrt{\frac{k_{\text{cat}}[\text{ROH}]RT}{n_Fv}} \quad (4)
\]

The anodic peak potential (i_p) for the reversible [FeIII(tpenaH)(OH)]2+/[FeII(tpenaH)(OH)]1 redox couple is...
Article

Figure 6. (A) CVs of cyclohexanol (0.04 M) titrated with increasing concentrations of [Fe\textsuperscript{III}(μ-O)(tpenaH)\textsubscript{2}]\textsuperscript{4+} (0–1 mM per Fe, 50 mV s\textsuperscript{−1}, and 0.1 M NaClO\textsubscript{4}). Inset: Plot of the catalytic current for increasing concentrations of Fe-tpena, extracted from the CVs. (B) CVs of [Fe\textsuperscript{III}((O)(tpenaH))\textsubscript{2}(ClO\textsubscript{4})\textsubscript{4}] (0.8 mM per Fe, 0.1 M NaClO\textsubscript{4}) titrated with increasing concentrations of cyclohexanol (0–0.18 M). Inset: Plot of the catalytic current for increasing concentrations of cyclohexanol, extracted from the CVs. (C) CVs of mixtures of [Fe\textsuperscript{III}(μ-O)(tpenaH)]\textsuperscript{4+} and cyclohexanol (0.8 mM Fe, 40 mM cyclohexanol, and 0.1 M NaClO\textsubscript{4}) recorded at different scan rates (2.5–200 mV s\textsuperscript{−1}). Inset: Plot of \(i_{\text{cat}}/i_{\text{peak}}\) taken at 0.6 and 1.50 V, respectively, against the inverse square root of the scan rate.

diffusion controlled (Figure S19) and therefore a good choice for normalizing \(i_{\text{cat}}\) according to eq 4. A fit of the values of \(i_{\text{cat}}/i_{\text{p}}\) extracted from the CVs of cyclohexanol in the presence of hydrated [Fe(tpena)]\textsuperscript{2+} and recorded over a range of scan rates (Figure 6C), gives a turnover frequency of \(k_{\text{cat}} = 3.1\) s\textsuperscript{−1} for the initial oxidation of cyclohexanol by [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+}

**Stability of [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+}**. The clear evidence of turnover provided here indicates that the Fe-tpena system must be reasonably robust; however, to investigate this further, we subjected a solution containing [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} to six cycles of repeated electrochemical oxidation and decay (Figure S20). The UV/visi\(ble\) spectra of the generated [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} did not change throughout the cycles, with all spectra consistent with [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} reverting back to an iron(III) resting state (with an isosbestic point at 502 nm); however, the concentration diminished by an average of 5% with each cycle. Importantly, however, crystalline [Fe\textsubscript{2}(O)(tpenaH\textsubscript{2}))(ClO\textsubscript{4})\textsubscript{4} can be reisolated from multiply electrolyzed solutions (purity checked by X-ray diffraction and ESI-MS spectra; Figure S21). The ESI-MS spectra of the supernatant solutions show no indication of demetalation or ligand breakdown, and GC did not reveal peaks due to light organics. The absence of identifiable breakdown products or spectral changes does not, however, exclude the possibility that slow catalyst decomposition occurs because any organic fragments are likely to be mineralized.

**CONCLUSIONS**

We have demonstrated that the nonheme iron(IV) oxo complex acid–base congeners [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} and [Fe\textsuperscript{IV}(O)(tpena)]\textsuperscript{+} can be generated electrochemically in aqueous solution over a relatively large pH window (2–8). These complexes can oxidize a broad range of substrates containing C=H and O–H bonds under both acidic and neutral conditions in water. The oxidation of aqueous solutions of formate to CO\textsubscript{2} and bleaching of rhodamine B suggests that the iron(IV) oxo species can oxidatively degrade otherwise recalcitrant organic pollutants and, as such, the results are highly pertinent for the development of electrocatalytic water purification. Under the conditions and potentials applied, [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} appears to be relatively robust, with [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} electrochemically regenerated repeatedly. Catalytic activity in the electrooxidation of cyclohexanol was observed with at least 12 turnovers.

The weak field carboxylate donor, positioned cis to the oxo group, likely plays an important role in the enhanced reactivity observed for [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+}/[Fe\textsuperscript{IV}(O)(tpena)]\textsuperscript{+} compared to the aminopolypyridyl [Fe\textsuperscript{IV}(O)(btpen)]\textsuperscript{2+} and [Fe\textsuperscript{IV}(O)(N\textsubscript{4}Py)]\textsuperscript{2+} analogues. Interestingly, cis-carboxylate donors are commonly found in the active sites of nonheme iron enzymes involved in biological oxidation reactions. Despite this fact, monocarboxylate ligands have rarely been employed in biomimetic iron chemistry. In addition, the positively charged Fe-tpena complexes show remarkable flexibility with respect to metal geometry and ligand protonation and denticity. In water, a second coordination sphere base is enabled and catalytic activity is observed over a wide pH range.

We have noted a parallel in the oxidative activity trend of [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} with that of the HO\textsuperscript{•} radical. Not surprisingly given their relative sizes, the rates of substrate oxidation by the iron-based system are orders of magnitude slower. This might not be of practical disadvantage with respect to implementation in the electrocatalytic water purification because [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} can be generated in concentrations many orders of magnitude higher than HO\textsuperscript{•}. A drawback, however, is that the time required to generate [Fe\textsuperscript{IV}(O)(tpenaH)]\textsuperscript{2+} electrochemically is much longer than its chemical generation by cerium(IV) in water. The latter is instantaneous, whereas it approaches 30 min for a steady-state concentration using electrochemical means (Figure 2A). Clearly, this will result in much slower catalysis, with reoxidation of Fe\textsuperscript{III} to Fe\textsuperscript{IV} being rate-determining. Ultimately, for practical purposes, immobilization onto electrode materials is likely to be necessary, and it can be expected to improve the reoxidation efficiency. Immobilization also offers the practical advantage of preventing discharge of the complex and/or ligand, which is undesirable from both an efficiency standpoint and the potential of trace amounts to act as a contaminant in its own right, which would need to be established in future work, e.g., assessing for any endocrine-disrupting potential.
Although immobilization is a large and unpredictable hurdle, the discovery of a candidate molecular iron-based oxidant that can be electrochemically activated and that can operate under both neutral and acidic conditions, with insignificant background oxidation of water, represents a significant step toward fundamentally new and potentially sustainable methods for water remediation.

**EXPERIMENTAL SECTION**

**Materials and Preparations.** Commercially available reagents were purchased from Sigma-Aldrich and used without further purification (unless otherwise noted). $^{14}$C-labeled sodium formate was purchased from American Radiolabeled Chemicals. Rhodamine B (laser grade, 99%) was purchased from Acros. $[^{57}Fe_{IV}(tpenaH)]_{2}^{+}$- (ClO$_4$)$_2$$(H_2O)$ and $[^{57}Fe(bztpen)(Cl)]$(ClO$_4$)$_2$$(H_2O)$ were prepared as described previously.$^{36}$ Standard commercial electrodes and electrochemical cells were purchased from ALS Japan or BASi, either directly or through retailer J&J Cambria UK. Graphite felt (99%, G100 PAN-based battery felt, AVCarb) and Nafion-117 sheets (Dupont) were purchased from FuelCellStore.com. Sealed nafion bags were prepared by folding sheets together and heat-fusing the edges using an impulse sealer, with one side left open to allow insertion of the electrode mesh and electrolyte. Graphite rods (1 mm, 99.95%), reticulated vitreous carbon (100 ppi glassy carbon), and platinum mesh (1 x 1 cm, 99.9%) were purchased from GoodFellow. Platinum and titanium coil electrodes were made by manually coiling metal wire with a glassy carbon disk working electrode (0.28 cm$^2$), a platinum or titanium coil electrode (0.3 cm$^2$), and a Zebron ZB-WAX column. Products formed in the stoichiometric oxidation of phenols, benzyl alcohol, and isopropyl alcohol, GC traces from stoichiometric ethanol, isopropyl alcohol, 1-butanol, 2-butanol, and benzyl alcohol oxidations by $[^{57}Fe^{IV}(O)(tpenaH)]^{2+}$, GC and $^{1}$H NMR spectra from anodic oxidation of cyclohexanol catalyzed by Fe-tpena, used as the charge carrier, with a platinum mesh (1 x 1 cm$^2$) counter electrode housed in a sealed nafion bag. The reference electrode for all electrolysis experiments was a micro Ag/AgCl electrode (3 M KCl). All potentials have been given versus the normal hydrogen electrode (NHE). Experimental potentials measured versus the micro Ag/AgCl electrode (3 M KCl) were referenced to the NHE by adding +0.2 V. Potentials measured versus the micro Ag/AgCl electrode (3 M KCl) were referenced to the NHE by adding +0.25 V. These calibration values were determined using the redox potential of the $[^{57}Fe^{III}(CN)]^{3-}/[^{57}Fe^{II}(CN)]^{4-}$ couple (10 mM, 0.5 M KCl, $E_{1/2} = 0.456$ V vs NHE$^{37}$) as the standard.

**Kinetic Measurements.** $[^{57}Fe_{IV}(tpenaH)]_{2}^{+}$ClO$_4$ (0.8 mM per Fe) in a pH 4 buffered electrolyte (0.05 M acetate and 0.1 M NaClO$_4$) was electrolyzed at a constant potential (1.42 V vs NHE) using the setup described above until the measured current had dropped from $\sim$10 to $\sim$0.5 mA. The degradation of rhodamine B was quickly filtered, and 3000 μL was transferred to a cuvette. The kinetics of the reaction was determined by monitoring the loss of the iron(IV) oxo complex at its near-IR absorbance peak at 730 nm. The UV/visible spectrum was first monitored for 120–200 s to determine the background decay rate, after which an aliquot of substrate (3–400 equiv) from a concentrated aqueous stock solution was added and the reaction rate measured. The background decay rate ($k_{bkgd}$) and the substrate reaction rate ($k_{act}$) were determined by least-squares fitting the absorbance at 730 nm to an expression appropriate for (pseudo)-first-order exponential decay, i.e.,

$$Abs(t) = Abs_0 + (Abs_b - Abs_0) \cdot e^{-k_{act}t}$$

Second-order rate constants ($k_2$) were extracted from linear regressions of plots of $k_{act} = k_{bkgd} - k_{bkgd}$ against the substrate concentrations. For the pH-dependent formate/formic acid reactivity studies, unbuffered media were used, and the pH was adjusted manually with dilute NaOH prior to starting the UV/visible measurements. The second-order rate constant for the oxidation of iPrOH by $[^{57}Fe^{IV}(O)(tpenaH)]^{2+}$ was determined in pH 4 acetate-buffered electrolytes containing 10 vol % acetonitrile added for solubility reasons. The degradation of rhodamine B by $[^{57}Fe^{IV}(O)(tpenaH)]^{2+}$ was semiquantitatively followed by UV/visible spectroscopy using the approach described by Miller et al.$^{68}$ with molar absorption coefficients taken from Watanabe et al.$^{69}$

**Radiolabeling Experiments.** $^{14}$C-labeled sodium formate was spiked at 40 nM in experimental solutions, with the remaining desired formate concentration made up with unlabeled sodium formate. Experiments were performed in an enclosed apparatus with the exhaust gas passing through a 1 M NaOH trap to recover $^{14}$CO$_3$. The concentrations of $^{14}$C-formate and Na$_2$CO$_3$ were determined by scintillation counting using an Ultima Gold scintillation cocktail (PerkinElmer) and a PerkinElmer Tri-Carb 2910TR liquid scintillation analyzer.

**Caution!** Perchlorate salts of metal complexes are potentially explosive and should be handled with caution in small quantities. $^{14}$C is a β-emitting isotope that should be handled in a way minimizing this potential radiation risk and in accordance with any applicable legal regulations.
Randles–Sevcik plot of the $[\text{Fe}^{III}/\text{II}(\text{tpenaH})(\text{OH})]^{2+/3+}$ peak currents, ESI-MS spectrum of recovered catalyst, and data for repeat electrolysis and decay cycles of the catalyst (PDF)

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**Notes**
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