Published in final edited form as:

Inorg Chem. 2006 October 2; 45(20): 8009–8011. doi:10.1021/ic061263i.

Electrochemical Generation of a Nonheme Oxoiron(IV) Complex

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Abstract

The complex $[\text{Fe}^{\text{IV}}\text{O}(\text{N4Py})]^{2+}$ ($\text{N4Py} = \text{N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine}$) has been prepared by bulk electrolysis in aqueous CH_3CN and CH_2Cl_2 and its redox properties characterized. Bulk chronocoulometry and spectropotentiometry experiments in CH_3CN show that $[\text{Fe}^{\text{II}}(\text{N4Py})(\text{NCCH}_3)]^{2+}$ can be oxidized quantitatively to its iron(III) derivative at an applied potential of +0.71 V vs. ferrocene and then to the oxoiron(IV) complex (in the presence of added water) at potentials above +1.3 V. The $E_{1/2}$ value for the $\text{Fe}^{\text{IV/III}}$ couple has been estimated to be +0.90 V from spectropotentiometric titrations in CH_3CN and cyclic voltammetric measurements in CH_2Cl_2 .

In the past few years, a number of mononuclear complexes with oxoiron(IV) units supported by polydentate nonheme ligands have been characterized.¹ These complexes serve as models for high-valent intermediates in the catalytic cycles of nonheme iron enzymes that carry out a range of oxidative transformations.² One such intermediate has been identified as the oxidant in taurine:α-ketoglutarate dioxygenase.³ Several of the biomimetic nonheme iron-oxo complexes have been isolated and structurally characterized by X-ray crystallography,^{4a,4b} and by Fe K-edge X-ray absorption spectroscopy,^{4c} thereby providing a structural basis for the interpretation of their spectroscopic properties. These oxoiron(IV) complexes have been shown to carry out a number of substrate oxidations,^{4a,5} including the hydroxylation of cyclohexane by $[\text{Fe}^{\text{IV}}\text{O}(\text{N4Py})]^{2+}$ (**3**)^{5a} [$\text{N4Py} = \text{N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine}$], suggesting that these complexes can be powerful oxidants.⁶ To date, no detailed electrochemical study has been reported on any of the above nonheme oxoiron(IV) complexes that provides a rationale for their oxidative reactivity.⁷ Our initial investigations have focused on the electrochemistry of $[\text{Fe}^{\text{II}}(\text{N4Py})(\text{NCMe})](\text{OTf})_2$ (**1a**(OTf)₂)^{4c} and its oxoiron(IV) derivative **3** because of the latter's significant thermal stability. In this paper, we report the electrochemical generation of **3** from **1a** and the determination of its $\text{Fe}^{\text{IV/III}}$ potential.

The redox chemistry of $\text{Fe}(\text{N4Py})$ can be thought of as a series of one-electron reactions traversing from the iron(II) starting point **1a** via iron(III) species **2a** and **2b** to **3** (Scheme 1). As reported previously⁸ and shown in Figure 1a, cyclic voltammetry (CV) experiments with a glassy carbon microelectrode show that **1a** undergoes a quasi-reversible one-electron oxidation in CH_3CN solvent at +0.61 V associated with the **2a/1a** couple (all potentials reported relative to the ferrocinium/ferrocene couple, $\text{Fc}^{+/0}$). Scanning anodically up to +1.6 V does not elicit another feature corresponding to a further oxidation to form **3**. Since

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Supporting Information Available: Experimental procedures, the CV of **1a** in dry and wet CH_3CN (Fig. S1), the solvent windows for the CV experiments in 'dry' and 'wet' solvents (Fig. S2), and the spectroelectrochemistry of **1a** in CH_2Cl_2 (Fig. S3). This material is available free of charge via the internet at <http://pubs.acs.org>.

formation of **3** may be prevented by the lack of an oxygen-atom source, additional CV experiments were carried out in the presence of added water (Figs. S1 and S2). Indeed addition of water elicits the appearance of a new reduction wave at $E_{p,c} = +0.15$ V that intensifies with increased water concentration at the expense of the wave at +0.61 V. This feature is assigned to the $\text{Fe}^{\text{III/II}}$ couple of $[\text{Fe}^{\text{II}}(\text{N4Py})(\text{OH}_2)]^{2+}$ (**1b**) and becomes more evident in the return scan after **1a** undergoes oxidation, suggesting the more facile displacement of CH_3CN from **1a** by water upon oxidation to **2a**. Even under these ‘wet’ conditions, CV experiments at higher potential did not elicit a feature that can be assigned to the formation of **3**, suggesting that either the incorrect potential range was being monitored or that there is a kinetic barrier to the oxidation.

As an alternative strategy, controlled potential bulk electrolysis experiments using a large-surface-area reticulated vitreous carbon electrode (see SI for details) were carried out on **1a** in CH_3CN . Application of a potential of +0.71 V, sufficient to oxidize >99% of **1a** by one electron, based on the $E_{1/2}$ value of +0.61 V, elicited within 20 min the conversion of the amber color characteristic of **1a** to a lemon yellow solution. The initial amber color could be restored upon switching the potential to 0.0 V. The lemon yellow species exhibits a UV shoulder at about 300–320 nm that is assigned to $[\text{Fe}^{\text{III}}(\text{N4Py})(\text{OH})]^{2+}$ (**2b**), which could be independently prepared by the addition of 0.5 eq H_2O_2 to **1a**.^{8a} These observations support a reaction sequence in which **1a** is first oxidized to **2a**, which is in turn converted to **2b** in a ligand exchange step promoted by the added water.

Electrolysis at +1.3 V resulted in the much slower conversion of the lemon yellow solution to a pale blue-green solution (see supporting information for details). The UV-vis spectrum of the blue-green solution gave an absorbance maximum and a molar absorbance identical to those reported earlier^{5a} for **3** (*vide infra*). Switching from a high poisoning potential to 0.0 V resulted in the rapid reduction of **3** back to **1a**.

As a further substantiation of the redox chemistry, spectroelectrochemistry experiments were carried out to monitor the spectral changes associated with **1a**, **2b**, and **3** as a function of the applied potential. Controlled potential spectro-chronocoulometry from an initial poise of –0.20 V jumped to +0.71 V showed a complete loss, over a 15–20 min period, of the 455- and 380-nm bands associated with **1a**. Currents peaked at about 1 mA and declined to less than 10 μA over this time period. Subsequent reduction back to **1a** was rapid and quantitative. Chronocoulometry gave within 5% of the expected number of coulombs for a one-electron redox reaction (Figure 2a). Subsequent jumps to +1.4 V gave complete conversion to **3** within 30 min, based on the appearance of its characteristic 695-nm absorption band.^{5a} Initial currents again were in the 1 mA range, but the residual oxidizing current was much higher at +1.4 V, about 50 μA , due to competing oxidation of the added water (Fig. S2). As a result, chronocoulometry gave about 30% more mC than would be expected for a one-electron oxidation. In all cases, the return jump from +1.4 V to +0.71 V elicited no reducing current nor spectral changes over 20 minutes or more. However, a jump from +0.71 V to –0.20 V initiated immediate spectral changes and large reducing currents (Figure 2b), eventually restoring the initial spectrum of **1a**. These results show that **1a** in CH_3CN can be oxidized to **3** in two one-electron steps, but reduction of **3** is a two-electron process.

The rate of formation of **3** at +1.3 V increased with increasing concentration of added water. Electrolysis at higher potentials, up to +2 V, also increased the rate of formation of **3**. Thus the rate of electrolytic formation of **3** is a function of the applied potential, the working electrode surface area relative to cell volume, and the concentration of added H_2O . The absence of a **2b/3** oxidation wave in the CV experiment can thus be attributed to the small surface area of the microelectrode and the low concentration of **2b** formed at the electrode

surface. As will be presented below, a switch from CH₃CN to CH₂Cl₂ allows the **2b/3** oxidation wave to be observed by CV (Fig. 1b).

A spectropotentiometric titration was carried out in 1M H₂O to estimate the midpoint potential of the irreversible formation of **3** from **2**. The conversion of **1** to **2** was essentially complete under these conditions with the application of a +0.71 V potential, and **3** began to form only above this potential. Difference spectra vs. the spectrum obtained at +0.71 V were computed and representative spectra are shown in Figure 3. The changes in absorbance at 305 and 695 nm for all difference spectra are shown in the inset. The solid line in each case is the line computed from a fit to the Nernst equation⁹ (see supporting information for further details). The best fit at 695 nm gave $\Delta\epsilon = 0.38 \text{ mM}^{-1}\text{cm}^{-1}$ and a midpoint oxidation potential of $E_{1/2} = +0.90 \text{ V}$, while the fit at 305 nm gave $E_{1/2} = +0.88 \text{ V}$, with $\Delta\epsilon = -3.25 \text{ mM}^{-1}\text{cm}^{-1}$.

Analogous experiments carried out in CH₂Cl₂ corroborate the results obtained in CH₃CN and enhance our understanding of the redox chemistry of **3**. Figure 1b (green line) shows the cyclic voltammogram of **1a** in CH₂Cl₂ with a quasi-reversible wave for the **1a/2a** couple at +0.58 V, provided that the CV scan does not go beyond +0.8 V. The Fe^{III}/Fe^{II} reduction wave assigned to **1b** is also present in CH₂Cl₂ at +0.15 V and becomes more evident in the return scan after **1a** undergoes oxidation when residual water is present in the solvent. This wave is more intense in CH₂Cl₂ than in CH₃CN, indicating a higher concentration of **2b** in CH₂Cl₂ upon oxidation of **1a**, as expected for a mass action effect on the **2a/2b** equilibrium.

An irreversible oxidative wave appears at +1.4 V ($i_a = 11 \mu\text{A}$) upon scanning above +0.8 V in CH₂Cl₂, which is notably absent in CH₃CN (Fig. 1); this feature is observed only when trace water is present in the solvent. On the reverse scan there is a dramatic change in the appearance of the reducing wave near +0.4 V, with a near doubling of the reducing current (Figure 1b, black line; $i_c = 20 \mu\text{A}$). Spectroelectrochemistry in CH₂Cl₂ at 5 °C shows quantitative conversion of **2b** to **3** between 1.1 and 1.4 V (Fig. S3), with a visible spectrum virtually identical to that obtained in CH₃CN. Moreover, **3** can be quantitatively reduced back to **2b**, which is not possible in CH₃CN. It is thus reasonable to assign the oxidative wave at +1.4 V ($E_{p,a}$) to the oxidation of **2b** to **3** in CH₂Cl₂ and its reduction to the wave at +0.4 V ($E_{p,c}$). The absence of a similar feature in CH₃CN suggests that the rate of electrochemical formation of **3** is much slower in CH₃CN than in CH₂Cl₂ and further corroborates the notion that the substitution of CH₃CN in **2a** by hydroxide to form **2b** must occur for **3** to be formed (Scheme 1). The slower ligand exchange in CH₃CN makes the formation of **3** kinetically too hindered to be directly observed by CV in CH₃CN, in contrast to the results obtained in CH₂Cl₂.

The large potential difference ($\Delta E = 1 \text{ V}$) between the oxidizing and reducing peaks associated with **3** in CH₂Cl₂ is similar to those observed for [(L)₂Fe^{III}(O)(OAc)₂]ⁿ⁺ (L = tridentate N3 ligand) complexes,¹⁰ reflecting very slow electron transfer at the working electrode. We speculate that the kinetic barrier to the reduction of the Fe^{IV} species may be due to converting an $S = 1 \text{ Fe}^{\text{IV}}$ center to an $S = 5/2 \text{ Fe}^{\text{III}}$ center. From the CV data in CH₂Cl₂, the $E_{1/2}$ value for the **2b/3** couple can be estimated to be +0.90 V by using the relation $E_{1/2} = (E_{p,a} + E_{p,c})/2$,¹⁰ in good agreement with the spectropotentiometric results in CH₃CN.

Within the context of the limited database of Fe^{IV}/Fe^{III} couples ranging from 1.2 to -0.3 V vs. Fc^{+/0}, the redox potential of **3** falls at the high end of these values, comparable to those measured for [(L)₂Fe^{III}(O)(OAc)₂]ⁿ⁺ complexes¹⁰ but 0.3–1.1 V higher than for the values found for complexes of dianionic porphyrin,^{11a} trianionic ureaylate,^{11b} and tetraanionic amidate ligands.^{11c} Our value for **3** differs significantly from the $E_{p,c}$ value of -0.44 V

observed by Sastri *et al.*⁷ in the cyclic voltammetry of chemically produced **3** in CH₃CN. In our view, the latter negative value reflects not the true reduction potential of **3**, but instead the large kinetic barrier associated with its reduction,¹⁰ particularly in the absence of protons needed to form **2b**. The redox potential for **3**, determined in our experiments from spectropotentiometric titrations in wet CH₃CN and cyclic voltammetric experiments in wet CH₂Cl₂, is much more positive ($E_{1/2} = +0.9$ V vs Fc^{+/0}). In light of Mayer's work,¹² the high potential of **3** provides a strong rationale for its observed ability to oxidize hydrocarbons, including cyclohexane.^{5a}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the National Science Foundation (CHE0113894, MJC) and the National Institutes of Health (GM-33162, LQ). We are grateful to Mr. Sang-Mok Lee for the synthesis of **1a**.

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Figure 1.

Cyclic voltammetry of **1a** in a) CH_3CN and b) CH_2Cl_2 at 25 °C (0.1 M NBu_4BF_4 supporting electrolyte, glassy carbon working and platinum auxiliary electrodes; scan rate of 0.2 V s^{-1}). Potentials are vs. the $Fc^{+/0}$ couple and the arrow indicates the direction of scans.

Figure 2.

Spectrochronocoulometry of **1a** (2.30 mL of a 0.27 mM solution in CH₃CN containing 0.1 M H₂O and 0.1 M NBu₄BF₄ as supporting electrolyte at 20 °C). (a) Oxidizing jump from -0.20 to +0.71 V, followed by a reducing jump to -0.20 V; charges passed were -52 and +54 mC, respectively. (b) Reducing jump from +1.3 to +0.71 V, followed by a jump to -0.20 V; charges passed were -7 and +118 mC, respectively.

Figure 3. Representative difference spectra relative to the spectrum at 0.71 V in the spectropotentiometric titration of 0.2 mM **2b** to form **3** in CH₃CN at 20 °C. Inset shows the plot of ΔA vs. potential for the respective bands at 695 nm and 305 nm. AU = absorbance units.

Scheme 1.

Redox chemistry of Fe(N4Py) species.