## Water as an Oxygen Source in the Generation of Mononuclear Nonheme Iron(IV) Oxo Complexes\*\*

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High-valent iron(IV) oxo species have been implicated as the active oxidizing species in metabolically important oxidative transformations performed by mononuclear nonheme iron enzymes.<sup>[1]</sup> Such nonheme iron(IV) oxo species were observed and characterized recently in enzymatic and biomimetic reactions.<sup>[2,3]</sup> For example, intermediate high-spin iron(IV) oxo species were identified and proposed as active oxidants in the catalytic cycles of E. coli taurine: a-ketoglutarate dioxygenase (TauD), prolyl-4-hydroxylase, and halogenase CytC3.<sup>[2]</sup> In biomimetic studies, a number of mononuclear nonheme iron(IV) oxo complexes bearing tetradentate N4 and pentadentate N5 and N4S ligands were synthesized and characterized with various spectroscopic techniques.<sup>[3]</sup> A notable example is the first crystal structure of a nonheme iron(IV) oxo complex, [Fe<sup>IV</sup>(O)(tmc)(NCCH<sub>3</sub>)]<sup>2+</sup> (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).<sup>[4]</sup> The mononuclear iron(IV) oxo species were synthesized using artificial oxidants, such as iodosylbenzene, peracids, oxone,  $N_2O$ ,  $XO^-$  (X = Cl, Br), ozone,  $H_2O_2$ , and alkyl

hydroperoxides, <sup>[4,5]</sup> and more recently using molecular oxygen.<sup>[6]</sup> The synthetic iron(IV) oxo intermediates have shown reactivities in a variety of oxidation reactions, including alkane hydroxylation,<sup>[7a]</sup> olefin epoxidation,<sup>[5d]</sup> alcohol

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oxidation,<sup>[7b]</sup> aromatic hydroxylation,<sup>[7c]</sup> nitrogen dealkylation,<sup>[7d]</sup> and the oxidation of sulfides<sup>[7e]</sup> and PPh<sub>3</sub>.<sup>[4,7f]</sup>

High-valent metal oxo species have also been invoked as key intermediates in the oxygen-evolving complex (OEC) in photosystem II.<sup>[8]</sup> At the OEC, manganese(V) oxo species have been proposed to be formed by the oxidation of water in a proton-coupled electron transfer (PCET) mechanism.<sup>[8]</sup> Thus, the oxygen atom in the Mn<sup>V</sup> oxo species derives from water. In biomimetic studies, the formation of high-valent ruthenium oxo complexes has been well established for water oxidation in the presence of a strong oxidant, such as cerium(IV) or  $[Ru(bpy)_3]^{3+}$ .<sup>[9-11]</sup> Since water is the most abundant, readily available oxygen source on earth, we attempted to generate mononuclear nonheme iron(IV) oxo complexes with water as an oxygen source.<sup>[12]</sup> We now report for the first time the generation of mononuclear nonheme iron(IV) oxo complexes and the catalytic oxygenation of organic substrates using water as an oxygen source and cerium(IV) as a one-electron oxidant (Scheme 1).



Scheme 1.

Addition of [Ce<sup>IV</sup>(NO<sub>3</sub>)<sub>6</sub>](NH<sub>4</sub>)<sub>2</sub> (cerium(IV) ammonium nitrate, CAN; 4 mm) to a reaction solution containing nonheme iron(II) complexes (1 mM) [Fe<sup>II</sup>(N4Py)](ClO<sub>4</sub>)<sub>2</sub> or  $[Fe^{II}(Bn-tpen)](OTf)_2$  (N4Py = N,N-bis(2-pyridylmethyl)-N-Bn-tpen = N-benzyl-N, N', N'bis(2-pyridyl)methylamine, tris(2-pyridylmethyl)ethane-1,2-diamine,  $OTf = CF_3SO_3^-;$ see Figure S1 in the Supporting Information) afforded the corresponding iron(IV) oxo complexes  $[Fe^{IV}(O)(N4Py)]^{2+}(1)$ or  $[Fe^{IV}(O)(Bn-tpen)]^{2+}$  (2)<sup>[7a]</sup> in H<sub>2</sub>O, H<sub>2</sub>O/CH<sub>3</sub>CN, or buffered H<sub>2</sub>O/CH<sub>3</sub>CN at 25 °C (Figure 1 a and Figure S2 a in the Supporting Information).<sup>[13]</sup> The electrospray ionization mass spectra (ESI MS) of 1 and 2 exhibit prominent ion peaks at m/z 219.7 and 247.6, respectively (Figure 1b and Figure S2 b in the Supporting Information), the mass and isotope distribution patterns of which correspond to [Fe<sup>IV</sup>(O)-(N4Py)]<sup>2+</sup> (calcd *m*/*z* 219.6) and [Fe<sup>IV</sup>(O)(Bn-tpen)]<sup>2+</sup> (calcd m/z 247.6). When the reactions were carried out in isotopically labeled water ( $H_2^{18}O$ ), mass peaks corresponding to 1 and 2 appeared at m/z 220.7 and 248.6, respectively, thus indicating that the oxygen atom in the iron(IV) oxo com-

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**Figure 1.** a) UV/vis spectral changes showing the formation of  $[(N4Py)Fe^{IV}(O)]^{2+}$  (red line) in the reaction of  $[(N4Py)Fe^{II}](CIO_4)_2$  (1 mm, blue line) and  $[Ce^{IV}(NO_3)_6](NH_4)_2$  (4 mm) in H<sub>2</sub>O/CH<sub>3</sub>CN (1:3) at 25 °C. b) ESI MS of  $[(N4Py)Fe^{IV}(O)]^{2+}$  formed in the reaction of  $[(N4Py)Fe^{II}](CIO_4)_2$  and CAN (4 equiv) in H<sub>2</sub>O/CH<sub>3</sub>CN (1:3) at 25 °C. A peak at *m/z* 537.9 corresponds to  $[Fe^{IV}(O)(N4Py)Fe^{IV}(I^{16}O)]^{2+}$  (left panel, prepared with H<sub>2</sub><sup>16</sup>O) and  $[(N4Py)Fe^{IV}(I^{18}O)]^{2+}$  (right panel, prepared with H<sub>2</sub><sup>16</sup>O). c) Resonance Raman spectra (0 °C, 407 nm excitation) of  $[(N4Py)Fe^{IV}(I^{16}O)]^{2+}$  (blue line) formed by the reaction of  $[(N4Py)Fe^{II}](CIO_4)_2$  (16 mm) and four equivalents CAN in H<sub>2</sub><sup>16</sup>O/CH<sub>3</sub>CN (1:3) and of  $[(N4Py)Fe^{IV}(I^{18}O)]^{2+}$  (red line) formed in H<sub>2</sub><sup>18</sup>O/CH<sub>3</sub>CN (1:3). The peaks marked with \* are from solvent.

plexes derives from water [Eq. (1)].<sup>[14]</sup> The resonance Raman (rR) spectrum of **1** exhibits a vibration at 840 cm<sup>-1</sup> that shifts to 806 cm<sup>-1</sup> upon introduction of <sup>18</sup>O (Figure 1 c).<sup>[15,16]</sup> By

$$[(L)Fe^{II} - OH_2]^{2+} \xrightarrow{-2e^-, -2H^+} [(L)Fe^{IV} = O]^{2+}$$
(1)

comparison with the reported rR data of  $[Fe^{IV}(O)-(tmc)(X)]^{n+}$ ,<sup>[17]</sup> the observed Fe–O stretching frequency and the isotope shift of  $-34 \text{ cm}^{-1}$  with <sup>18</sup>O substitution demonstrate unambiguously that  $[(N4Py)Fe^{IV}=O]^{2+}$  was formed in the oxidation of  $[Fe^{II}(N4Py)]^{2+}$  by water and CAN and that the oxygen atom in the iron oxo group derives from water [Eq. (1)].

The stability of 1 and 2 generated in the present study  $(t_{1/2})$  $\approx$  5 and 1 day at 25 °C for 1 and 2, respectively) was found to be greater than that of the compounds generated in the reaction with PhIO in CH<sub>3</sub>CN ( $t_{1/2} \approx 60$  and 6 h at 25 °C for **1** and 2, respectively).<sup>[7a]</sup> We therefore attempted to generate other nonheme iron(IV) oxo complexes with water as an oxygen source and CAN as an oxidant at 25°C; these were synthesized only at low temperature (e.g. at -40 °C) owing to their thermal unstability. Such complexes include [Fe<sup>IV</sup>(O)-(tpa)]<sup>2+</sup> (3, tpa = tris-(2-pyridylmethyl)amine),<sup>[5d]</sup> [Fe<sup>IV</sup>(O)-(bpmen)<sup>2+</sup> (4, bpmen = N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)ethane-1,2-diamine),<sup>[18a]</sup> and  $[Fe^{IV}(O)(bqen)]^{2+}$  (5, bqen = N,N'-dimethyl-N,N'-bis(8-quinolyl)ethane-1,2-diamine;<sup>[18b]</sup> see Figure S1 in the Supporting Information). Interestingly, we observed the formation of the iron(IV) oxo species in the reactions of the corresponding iron(II) complexes and CAN in the presence of H2O and the slow decay of the intermediates at 25°C (Figure S3 in the Supporting Information), thus indicating that the intermediates generated by H<sub>2</sub>O and CAN are stabilized under the present reaction conditions.<sup>[19]</sup> As the enhanced stability of the iron oxo intermediates might be due to the high acidity of CAN,<sup>[10a]</sup> we compared the stability of 3 in the presence and absence of HClO<sub>4</sub> in H<sub>2</sub>O/CH<sub>3</sub>CN at 25 °C (Figure S4 in the Supporting Information).<sup>[5b,20]</sup> The stability of **3** increased by a factor of approximately four when it was prepared with CH<sub>3</sub>CO<sub>3</sub>H in the presence of HClO<sub>4</sub>, thus indicating that the high stability of nonheme iron(IV) oxo intermediates prepared with H<sub>2</sub>O and cerium(IV) can be ascribed to the low pH value of the reaction solution.<sup>[5b]</sup> Furthermore, and in contrast to the reactions of H<sub>2</sub>O and CAN (see above), the formation of 4 and 5 was not observed when  $[Fe^{II}(bpmen)]^{2+}$  and  $[Fe^{II}-$ (bqen)]<sup>2+</sup> were treated with CH<sub>3</sub>CO<sub>3</sub>H in the presence and absence of HClO<sub>4</sub> at 25 °C. It is also worth noting that other nonheme iron(IV) oxo complexes reported in the literature, including [Fe<sup>IV</sup>(O)(tmc)]<sup>2+,[3,4]</sup> were easily prepared using water as an oxygen source and CAN as an oxidant.

In light of the observation that nonheme iron(IV) oxo complexes are formed using water as an oxygen source, we investigated the catalytic oxygenation of organic substrates by the nonheme iron(II) catalyst [Fe<sup>II</sup>(Bn-tpen)](OTf)<sub>2</sub> and CAN in H<sub>2</sub>O/CH<sub>3</sub>CN (1:3) at 25°C. As the results in Table 1 show, high product yields were obtained in all of the reactions. In the oxidation of thioanisole (Table 1, entry 1), methyl phenyl sulfoxide was the major product, and no formation of sulfone was observed. Benzyl alcohol was oxidized to benzaldehyde with the formation of a small amount of benzoic acid (Table 1, entry 3). In the oxidation of cyclohexene (Table 1, entry 4), hexanedioic acid, which is the product of eight-electron oxidation, was formed, as reported in the ruthenium-catalyzed oxidation of cyclohexene by CAN.<sup>[10a]</sup> The hydroxylation of ethylbenzene (Table 1, entry 5) yielded acetophenone as the major product with the formation of a small amount of sec-phenethyl alcohol, as observed in the hydroxylation of ethylbenzene by 2.<sup>[7a]</sup> The turnover number increased by reducing the catalyst amount (Table 1, entry 2). In the absence of the iron catalyst, only negligible amounts of products were formed by H<sub>2</sub>O and CAN under the reaction conditions.

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**Table 1:** Catalytic oxidation reactions using  $[Fe^{II}(Bn-tpen)]^{2+}$  as a catalyst, water as an oxygen source, and CAN as an oxidant.<sup>[a]</sup>

Entry	Substrate	Products	TON <sup>[b]</sup>
1 2 <sup>[c]</sup>	thioanisole thioanisole	methyl phenyl sulfoxide methyl phenyl sulfoxide	$\begin{array}{c}10\pm1\\95\pm5\end{array}$
3 4 5	benzyl alcohol cyclohexene ethylbenzene	benzaldehyde hexanedioic acid <i>sec</i> -phenethyl alcohol acetophenone	$10 \pm 1$ 5.6 $\pm 0.5$ 1 $\pm 0.2$ 9 $\pm 1$

[a] Reaction conditions: CAN (10 mm, 50 equiv relative to iron catalyst) was added to a reaction solution containing  $[Fe^{II}(Bn-tpen)](OTf)_2$  (0.2 mm) and substrate (40 mm) in H<sub>2</sub>O/CH<sub>3</sub>CN (1:3) at 25 °C. After 30 min stirring, the reaction solution was analyzed by HPLC for the reactions of thioanisole, benzyl alcohol, and ethylbenzene and by <sup>1</sup>H NMR spectroscopy for the reaction of cyclohexene.<sup>[10a]</sup> [b] Turnover number was calculated by dividing product yields by the amount of catalyst used. [c]  $[Fe^{II}(Bn-tpen)](OTf)_2$  (0.02 mm) and CAN (10 mm, 500 equiv relative to iron catalyst) were used.

The catalytic oxidation of thioanisole was also carried out in  $H_2^{18}O/CH_3CN$  (1:3) to confirm the source of oxygen in the oxygenated products. The methyl phenyl sulfoxide produced contained 93 % <sup>18</sup>O derived from 95 % <sup>18</sup>O-enriched  $H_2^{18}O$ .<sup>[21]</sup> The <sup>18</sup>O percentage in the sulfoxide product was sensitive neither to the ratio of  $H_2^{18}O$  to  $CH_3CN$  in the solvent mixture<sup>[14]</sup> nor to the presence of O<sub>2</sub>. The labeled-water experiments demonstrate unambiguously that water was the oxygen source and no autooxidation reaction was involved in the oxidation reactions under aerobic conditions, as reported in [Ru(tpa)]-catalyzed oxygenation reactions with CAN.<sup>[10a]</sup>

In conclusion, we have reported the first example of using water as an oxygen source in the generation of mononuclear nonheme iron(IV) oxo complexes and the catalytic oxygenation of organic substrates. The source of oxygen in the iron oxo complexes and in the oxygenated products was assigned unambiguously by carrying out experiments with isotopically labeled water. We also demonstrated that nonheme iron(IV) oxo complexes are facilely synthesized under mild conditions (e.g. at ambient temperature) using water as an oxygen source and cerium(IV) as an oxidant. In light of the precedent established by water oxidation in manganese and ruthenium chemistry,<sup>[9,22]</sup> design of ligands for dinuclear iron complexes (e.g.,  $[{Fe(O)}_2L]$  for  $Fe^{IV}$  or  $Fe^{V}$ ) and control of the redox potential of the iron catalysts might allow the present results to be expanded to a system in which nonheme iron complexes can oxidize water to O<sub>2</sub>.

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