Enzyme Models

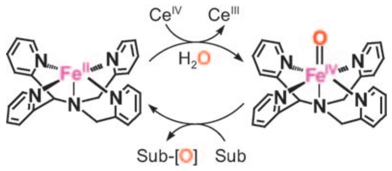
DOI: 10.1002/ange.200805670

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

Yong-Min Lee, Sunder N. Dhuri, Sarvesh C. Sawant, Jaeheung Cho, Minoru Kubo, Takashi Ogura, Shunichi Fukuzumi, and Wonwoo Nam**

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.[1] Such nonheme iron(IV) oxo species were observed and characterized recently in enzymatic and biomimetic reactions.[2,3] For example, intermediate high-spin iron(IV) oxo species were identified and proposed as active oxidants in the catalytic cycles of *E. coli* taurine:α-ketoglutarate dioxygenase (TauD), prolyl-4-hydroxylase, and halogenase CytC3.[2] 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.[3] A notable example is the first crystal structure of a nonheme iron(IV) oxo complex, $[Fe^{IV}(O)(tmc)(NCCH_3)]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).[4] 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,[4,5] and more recently using molecular oxygen.[6] The synthetic iron(IV) oxo intermediates have shown reactivities in a variety of oxidation reactions, including alkane hydroxylation,[7a] olefin epoxidation,[5d] alcohol oxidation,[7b] aromatic hydroxylation,[7c] nitrogen dealkylation,[7d] and the oxidation of sulfides[7e] and PPh_3.[4,7f]

High-valent metal oxo species have also been invoked as key intermediates in the oxygen-evolving complex (OEC) in photosystem II.[8] 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.[8] Thus, the oxygen atom in the Mn^V 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 $[Ru(bpy)_3]^{3+}$.[9–11] 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.[12] 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 $[Ce^{IV}(NO_3)_6](NH_4)_2$ (cerium(IV) ammonium nitrate, CAN; 4 mM) to a reaction solution containing nonheme iron(II) complexes (1 mM) $[Fe^{II}(N4Py)](ClO_4)_2$ or $[Fe^{II}(Bn\text{-}tpen)](OTf)_2$ (N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine, Bn-tpen = *N*-benzyl-*N*,*N′*,*N′*-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 $[Fe^{IV}(O)(Bn\text{-}tpen)]^{2+}$ (**2**)[7a] in H_2O, H_2O/CH_3CN, or buffered H_2O/CH_3CN at 25 °C (Figure 1 a and Figure S2 a in the Supporting Information).[13] 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 1 b and Figure S2 b in the Supporting Information), the mass and isotope distribution patterns of which correspond to $[Fe^{IV}(O)(N4Py)]^{2+}$ (calcd *m*/*z* 219.6) and $[Fe^{IV}(O)(Bn\text{-}tpen)]^{2+}$ (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-

---

[*] Prof. Dr. S. Fukuzumi
Department of Material and Life Science
Graduate School of Engineering, Osaka University
SORST (Japan) Science and Technology Agency (JST)
Suita, Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-7370
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp
Dr. Y.-M. Lee, Dr. S. N. Dhuri, Dr. S. C. Sawant, Dr. J. Cho, Prof. Dr. W. Nam
Department of Chemistry and Nano Science and
Department of Bioinspired Science, Ewha Womans University
Seoul 120–750 (Korea)
Fax: (+82) 2-3277-4441
E-mail: wwnam@ewha.ac.kr
Dr. M. Kubo, Prof. Dr. T. Ogura
Picobiology Institute, Graduate School of Life Science
University of Hyogo
Koto 3-2-1, Kamigori-cho, Ako-gun, Hyogo 678-1297 (Japan)

[**] The research at EWU was supported by KOSEF/MOST through CRI Program and the WCU Project (to W.N.), a Grant-in-Aid (No. 19205019 to S.F.), and a Global COE program, “the Global Education and Research Centre for Bio-Environmental Chemistry” from the Ministry of Education, Culture, Sports, Science and Technology (Japan) (to S.F.).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200805670.

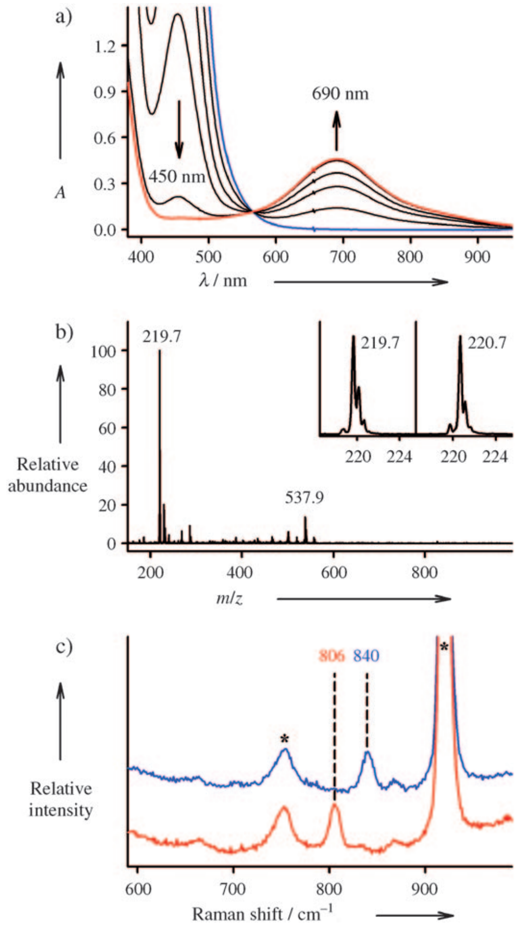


Figure 1. a) UV/vis spectral changes showing the formation of $[(N4Py)Fe^{IV}(O)]^{2+}$ (red line) in the reaction of $[(N4Py)Fe^{II}](ClO_4)_2$ (1 mM, blue line) and $[Ce^{IV}(NO_3)_6](NH_4)_2$ (4 mM) in H_2O/CH_3CN (1:3) at 25 °C. b) ESI MS of $[(N4Py)Fe^{IV}(O)]^{2+}$ formed in the reaction of $[(N4Py)Fe^{II}](ClO_4)_2$ and CAN (4 equiv) in H_2O/CH_3CN (1:3) at 25 °C. A peak at m/z 537.9 corresponds to $[Fe^{IV}(O)(N4Py)(ClO_4)]^+$. Insets show the observed isotope distribution patterns for $[(N4Py)Fe^{IV}(^{16}O)]^{2+}$ (left panel, prepared with $H_2{}^{16}O$) and $[(N4Py)Fe^{IV}(^{18}O)]^{2+}$ (right panel, prepared with $H_2{}^{18}O$). c) Resonance Raman spectra (0 °C, 407 nm excitation) of $[(N4Py)Fe^{IV}(^{16}O)]^{2+}$ (blue line) formed by the reaction of $[(N4Py)Fe^{II}](ClO_4)_2$ (16 mM) and four equivalents CAN in $H_2{}^{16}O/CH_3CN$ (1:3) and of $[(N4Py)Fe^{IV}(^{18}O)]^{2+}$ (red line) formed in $H_2{}^{18}O/CH_3CN$ (1:3). The peaks marked with * are from solvent.

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

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

comparison with the reported rR data of $[Fe^{IV}(O)(tmc)(X)]^{n+}$,[17] the observed Fe–O stretching frequency and the isotope shift of −34 cm⁻¹ with ^{18}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_3CN ($t_{1/2} \approx 60$ and 6 h at 25 °C for **1** and **2**, respectively).[7a] 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 $[Fe^{IV}(O)(tpa)]^{2+}$ (**3**, tpa = tris-(2-pyridylmethyl)amine),[5d] $[Fe^{IV}(O)(bpmen)]^{2+}$ (**4**, bpmen = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine),[18a] and $[Fe^{IV}(O)(bqen)]^{2+}$ (**5**, bqen = *N,N'*-dimethyl-*N,N'*-bis(8-quinolyl)ethane-1,2-diamine;[18b] 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 H_2O and the slow decay of the intermediates at 25 °C (Figure S3 in the Supporting Information), thus indicating that the intermediates generated by H_2O and CAN are stabilized under the present reaction conditions.[19] As the enhanced stability of the iron oxo intermediates might be due to the high acidity of CAN,[10a] we compared the stability of **3** in the presence and absence of $HClO_4$ in H_2O/CH_3CN at 25 °C (Figure S4 in the Supporting Information).[5b,20] The stability of **3** increased by a factor of approximately four when it was prepared with CH_3CO_3H in the presence of $HClO_4$, thus indicating that the high stability of nonheme iron(IV) oxo intermediates prepared with H_2O and cerium(IV) can be ascribed to the low pH value of the reaction solution.[5b] Furthermore, and in contrast to the reactions of H_2O and CAN (see above), the formation of **4** and **5** was not observed when $[Fe^{II}(bpmen)]^{2+}$ and $[Fe^{II}(bqen)]^{2+}$ were treated with CH_3CO_3H in the presence and absence of $HClO_4$ at 25 °C. It is also worth noting that other nonheme iron(IV) oxo complexes reported in the literature, including $[Fe^{IV}(O)(tmc)]^{2+}$,[3,4] 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 $[Fe^{II}(Bn\text{-}tpen)](OTf)_2$ and CAN in H_2O/CH_3CN (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.[10a] 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**.[7a] 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_2O and CAN under the reaction conditions.

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

Entry	Substrate	Products	TON[b]
1	thioanisole	methyl phenyl sulfoxide	10 ± 1
2[c]	thioanisole	methyl phenyl sulfoxide	95 ± 5
3	benzyl alcohol	benzaldehyde	10 ± 1
4	cyclohexene	hexanedioic acid	5.6 ± 0.5
5	ethylbenzene	*sec*-phenethyl alcohol	1 ± 0.2
		acetophenone	9 ± 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_2O/CH_3CN (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 ^{1}H NMR spectroscopy for the reaction of cyclohexene.[10a] [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 % ^{18}O derived from 95 % ^{18}O-enriched $H_2{}^{18}O$.[21] The ^{18}O percentage in the sulfoxide product was sensitive neither to the ratio of $H_2{}^{18}O$ to CH_3CN in the solvent mixture[14] nor to the presence of O_2. 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.[10a]

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,[9,22] design of ligands for dinuclear iron complexes (e.g., [{Fe(O)}$_2$L] 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_2.

Received: November 20, 2008

Keywords: bioinorganic chemistry · enzyme models · iron · oxygenation · reaction mechanisms

---

[1] a) M. M. Abu-Omar, A. Loaiza, N. Hontzeas, *Chem. Rev.* **2005**, *105*, 2227–2252; b) M. L. Neidig, E. I. Solomon, *Chem. Commun.* **2005**, 5843–5863; c) M. Costas, M. P. Mehn, M. P. Jensen, L. Que, Jr., *Chem. Rev.* **2004**, *104*, 939–986.
[2] C. Krebs, D. G. Fujimori, C. T. Walsh, J. M. Bollinger, Jr., *Acc. Chem. Res.* **2007**, *40*, 484–492.
[3] a) W. Nam, *Acc. Chem. Res.* **2007**, *40*, 522–531; b) L. Que, Jr., *Acc. Chem. Res.* **2007**, *40*, 493–500.
[4] J.-U. Rohde, J.-H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E. Münck, W. Nam, L. Que, Jr., *Science* **2003**, *299*, 1037–1039.
[5] a) W. H. Harman, C. J. Chang, *J. Am. Chem. Soc.* **2007**, *129*, 15128–15129; b) C. V. Sastri, M. S. Seo, M. J. Park, K. M. Kim, W. Nam, *Chem. Commun.* **2005**, 1405–1407; c) V. Balland, M.-F. Charlot, F. Banse, J.-J. Girerd, T. A. Mattioli, E. Bill, J.-F. Bartoli, P. Battioni, D. Mansuy, *Eur. J. Inorg. Chem.* **2004**, 301–308; d) M. H. Lim, J.-U. Rohde, A. Stubna, M. R. Bukowski, M. Costas, R. Y. N. Ho, E. Münck, W. Nam, L. Que, Jr., *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3665–3670; e) C. A. Grapperhaus, B. Mienert, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 5306–5317.
[6] a) S. O. Kim, C. V. Sastri, M. S. Seo, J. Kim, W. Nam, *J. Am. Chem. Soc.* **2005**, *127*, 4178–4179; b) A. Thibon, J. England, M. Martinho, V. G. Young, Jr., J. R. Frisch, R. Guillot, J.-J. Girerd, E. Münck, L. Que, Jr., F. Banse, *Angew. Chem.* **2008**, *120*, 7172–7175; *Angew. Chem. Int. Ed.* **2008**, *47*, 7064–7067.
[7] a) J. Kaizer, E. J. Klinker, N. Y. Oh, J.-U. Rohde, W. J. Song, A. Stubna, J. Kim, E. Münck, W. Nam, L. Que, Jr., *J. Am. Chem. Soc.* **2004**, *126*, 472–473; b) N. Y. Oh, Y. Suh, M. J. Park, M. S. Seo, J. Kim, W. Nam, *Angew. Chem.* **2005**, *117*, 4307–4311; *Angew. Chem. Int. Ed.* **2005**, *44*, 4235–4239; c) S. P. de Visser, K. Oh, A.-R. Han, W. Nam, *Inorg. Chem.* **2007**, *46*, 4632–4641; d) K. Nehru, M. S. Seo, J. Kim, W. Nam, *Inorg. Chem.* **2007**, *46*, 293–298; e) M. J. Park, J. Lee, Y. Suh, J. Kim, W. Nam, *J. Am. Chem. Soc.* **2006**, *128*, 2630–2634; f) C. V. Sastri, J. Lee, K. Oh, Y. J. Lee, J. Lee, T. A. Jackson, K. Ray, H. Hirao, W. Shin, J. A. Halfen, J. Kim, L. Que, Jr., S. Shaik, W. Nam, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 19181–19186.
[8] a) T. J. Meyer, M. H. V. Huynh, H. H. Thorp, *Angew. Chem.* **2007**, *119*, 5378–5399; *Angew. Chem. Int. Ed.* **2007**, *46*, 5284–5304; b) J. P. McEvoy, G. W. Brudvig, *Chem. Rev.* **2006**, *106*, 4455–4483; c) M. H. V. Huynh, T. J. Meyer, *Chem. Rev.* **2007**, *107*, 5004–5064.
[9] a) G. Süss-Fink, *Angew. Chem.* **2008**, *120*, 5972–5974; *Angew. Chem. Int. Ed.* **2008**, *47*, 5888–5890; b) Z. Deng, H.-W. Tseng, R. Zong, D. Wang, R. Thummel, *Inorg. Chem.* **2008**, *47*, 1835–1848; c) T. J. Meyer, M. H. V. Huynh, *Inorg. Chem.* **2003**, *42*, 8140–8160.
[10] a) Y. Hirai, T. Kojima, Y. Mizutani, Y. Shiota, K. Yoshizawa, S. Fukuzumi, *Angew. Chem.* **2008**, *120*, 5856–5860; *Angew. Chem. Int. Ed.* **2008**, *47*, 5772–5776; b) A. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N. D. McDaniel, S. Bernhard, M. Bonchio, *J. Am. Chem. Soc.* **2008**, *130*, 5006–5007; c) Y. V. Geletii, B. Botar, P. Kögerler, D. A. Hillesheim, D. G. Musaev, C. L. Hill, *Angew. Chem.* **2008**, *120*, 3960–3963; *Angew. Chem. Int. Ed.* **2008**, *47*, 3896–3899; d) W. W. Y. Lam, W.-L. Man, C.-F. Leung, C.-Y. Wong, T.-C. Lau, *J. Am. Chem. Soc.* **2007**, *129*, 13646–13652.
[11] a) C.-M. Che, V. W.-W. Yam, T. C. W. Mak, *J. Am. Chem. Soc.* **1990**, *112*, 2284–2291; b) J. A. Gilbert, D. S. Eggleston, W. R. Murphy, Jr., D. A. Geselowitz, S. W. Gersten, D. J. Hodgson, T. J. Meyer, *J. Am. Chem. Soc.* **1985**, *107*, 3855–3864; c) S. W. Gersten, G. J. Samuels, T. J. Meyer, *J. Am. Chem. Soc.* **1982**, *104*, 4029–4030.
[12] Electrochemical generation of a nonheme iron(IV) oxo complex in aqueous CH_3CN and CH_2Cl_2 has been reported: M. J. Collins, K. Ray, L. Que, Jr., *Inorg. Chem.* **2006**, *45*, 8009–8011.
[13] The generation and stability of iron(IV) oxo intermediates do not depend on solvent systems (e.g. organic vs. aqueous solutions).
[14] The rate of oxygen exchange between nonheme iron(IV) oxo systems and labeled water is slow: M. S. Seo, J.-H. In, S. O. Kim, N. Y. Oh, J. Hong, J. Kim, L. Que, Jr., W. Nam, *Angew. Chem.*

2004, *116*, 2471 – 2474; *Angew. Chem. Int. Ed.* **2004**, *43*, 2417 – 2420. Thus, the full ^{18}O incorporation from $H_2{}^{18}O$ into the iron oxo complex is strong evidence that water is the oxygen source.

[15] Very recently, Solomon and co-workers reported the Fe−O stretching vibration of **1** to be 820 cm^{-1} (788 cm^{-1} with ^{18}O) by nuclear resonance vibrational spectroscopy (NRVS; see Ref. [16]). We find that **1** prepared with PhIO in CH_3CN exhibits a vibration at 840 cm^{-1} that shifts to 807 cm^{-1} upon introduction of ^{18}O. The latter result indicates that the Fe−O stretching vibration of **1** does not change depending on solution conditions (e.g. aqueous vs. CH_3CN).

[16] C. B. Bell III, S. D. Wong, Y. Xiao, E. J. Klinker, A. L. Tenderholt, M. C. Smith, J.-U. Rohde, L. Que, Jr., S. P. Cramer, E. I. Solomon, *Angew. Chem.* **2008**, *120*, 9211 – 9214; *Angew. Chem. Int. Ed.* **2008**, *47*, 9071 – 9074.

[17] a) C. V. Sastri, M. J. Park, T. Ohta, T. A. Jackson, A. Stubna, M. S. Seo, J. Lee, J. Kim, T. Kitagawa, E. Münck, L. Que, Jr., W. Nam, *J. Am. Chem. Soc.* **2005**, *127*, 12494 – 12495; b) T. A. Jackson, J.-U. Rohde, M. S. Seo, C. V. Sastri, R. DeHont, A. Stubna, T. Ohta, T. Kitagawa, E. Münck, W. Nam, L. Que, Jr., *J. Am. Chem. Soc.* **2008**, *130*, 12394 – 12407.

[18] a) M. P. Jensen, M. Costas, R. Y. N. Ho, J. Kaizer, A. M. i Payeras, E. Münck, L. Que, Jr., J.-U. Rohde, A. Stubna, *J. Am. Chem. Soc.* **2005**, *127*, 10512 – 10525; b) J. Yoon, S. A. Wilson, Y. K. Jang, M. S. Seo, K. Nehru, B. Hedman, K. O. Hodgson, E. Bill, E. I. Solomon, W. Nam, *Angew. Chem.* **2008**, DOI: 10.1002/ange.200802672; *Angew. Chem. Int. Ed.* **2008**, DOI: 10.1002/anie.200802672.

[19] The relative stability of iron(IV) oxo complexes under the present conditions is in the order **1** > **2** > **3** > **5** ≥ **4**.

[20] J. Bautz, M. R. Bukowski, M. Kerscher, A. Stubna, P. Comba, A. Lienke, E. Münck, L. Que, Jr., *Angew. Chem.* **2006**, *118*, 5810 – 5813; *Angew. Chem. Int. Ed.* **2006**, *45*, 5681 – 5684.

[21] The ^{16}O and ^{18}O compositions in methyl phenyl sulfoxide were determined by the relative abundances of $m/z = 141$ for ^{16}O and $m/z = 143$ for ^{18}O in LC-ESI MS analysis of the reaction solution. See the Experimental Section in the Supporting Information for detailed reaction procedures.

[22] a) X. Yang, M.-H. Baik, *J. Am. Chem. Soc.* **2008**, *130*, 16231 – 16240, and references therein; b) J. J. Concepcion, J. W. Jurss, J. L. Templeton, T. J. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 16462 – 16463.