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Reaction of an Oxoiron(IV) Complex with Nitrogen Monoxide: Oxygen Atom or Oxide(•1−) Ion Transfer?

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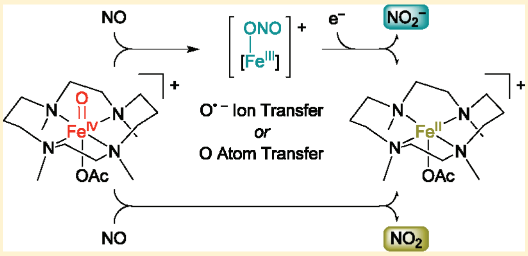
Supporting Information



ABSTRACT: Reaction of $[FeO(tmc)(OAc)]^+$ with the free radical nitrogen monoxide afforded a mixture of two Fe^{II} complexes, $[Fe(tmc)(OAc)]^+$ and $[Fe(tmc)(ONO)]^+$ (where tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane and AcO^- = acetate anion). The amount of nitrite produced in this reaction (ca. 1 equiv with respect to Fe) was determined by ESI mass spectrometry after addition of ^{15}N-enriched $NaNO_2$. In contrast to oxygen atom transfer to PPh_3, the NO reaction of $[FeO(tmc)(OAc)]^+$ proceeds through an Fe^{III} intermediate that was identified by UV−vis−NIR spectroscopy and ESI mass spectrometry and whose decay is dependent on the concentration of methanol. The observations are consistent with a mechanism involving oxide(•1−) ion transfer from $[FeO(tmc)(OAc)]^+$ to NO to form an Fe^{III} complex and NO_2^-, followed by reduction of the Fe^{III} complex. Competitive binding of AcO^- and NO_2^- to Fe^{II} then leads to an equilibrium mixture of two Fe^{II}(tmc) complexes. Evidence for the incorporation of oxygen from the oxoiron(IV) complex into NO_2^- was obtained from an ^{18}O-labeling experiment. The reported reaction serves as a synthetic example of the NO reactivity of biological oxoiron(IV) species, which has been proposed to have physiological functions such as inhibition of oxidative damage, enhancement of peroxidase activity, and NO scavenging.

INTRODUCTION

Reactions of the free radical nitrogen monoxide with metal−oxygen species of metalloproteins have been recognized as mechanisms relevant to NO metabolism and detoxification in vivo. For example, oxygenated metalloproteins such as oxyhemoglobin and oxymyoglobin react rapidly with NO, causing dioxygenation to nitrate.[1] The reaction of NO with the ferryl state of these and related proteins is of interest, as well. Studies with several globins have shown that NO can efficiently and rapidly reduce the high-valent state to the Fe^{III} state under concomitant formation of innocuous nitrite.[2,3] It has been suggested that the role of NO could be that of an antioxidant of oxoiron(IV) and oxoiron(IV) protein radical species to inhibit oxidative damage.[2−4] Conversely, the transformation of NO into nitrite mediated by ferryl globins may be important as a mechanism for NO scavenging and detoxification.[2,3] Nitrogen monoxide may then be viewed as a substrate for globins displaying peroxidase activity.[3]

In reactions of NO with the compounds **I** of peroxidase enzymes, reduction occurs in two one-electron steps via compound **II** to the Fe^{III} state.[5,6] At low NO levels, NO increases the activity of some peroxidases, and this effect has been linked to the ability of NO to accelerate the reduction of compound **II** to the Fe^{III} state, which is the rate-limiting step in the catalytic cycles of these enzymes.[6] Similar to the interaction between NO and ferryl globins, the idea of a bidirectional relationship between NO and peroxidases has been put forward where NO affects peroxidase catalysis and compound **I** functions as a sink for NO.[6] Also catalase has been reported to consume NO in the presence of H_2O_2, presumably by reaction of NO with catalase compound **I**.[7] Lastly, the possibility of a direct reaction between the ferryl group of cytochrome *bd* and NO has been discussed in the context of inhibition of this oxidase by NO.[8]

While synthetic precedent exists for the chemistry of superoxometal complexes and NO showing conversion of NO into peroxynitrite and subsequently into nitrate, nitrite, and/or nitrogen dioxide,[9−12] knowledge of the fundamental reactivity between oxometal complexes and NO is limited. Studies with Cr and Mn complexes suggested that the reactions of oxometal species with NO are very fast.[10,13,14] For example, the first step in the NO reaction of aqueous $Cr^{IV}O^{2+}(aq)$ is too fast to be observed spectrophotometrically, but $Cr^{III}(ONO)^{2+}(aq)$ is believed to be the primary product based on its decay kinetics.[10] In another case, photolysis of the macrocyclic ligand complex *trans*-$[Cr^{III}([14]aneN_4)(ONO)_2]^+$ generated a transient species, proposed to be the corresponding Cr^{IV}O complex, which underwent rapid recombination with NO.[13,15] The reactions of oxoiron(IV) porphyrin π-cation radicals, $[Fe^{IV}O(tpfpp)^{+\bullet}]^+$ and $[Fe^{IV}O(ppIX)^{+\bullet}]^+$,[15] with NO were studied in the gas phase.[16] These reactions were proposed to proceed through oxygen atom transfer, because the corresponding iron(III) porphyrins, which are two oxidizing equivalents below the oxoiron(IV) porphyrin π-cation radicals, were detected as primary products.[16] Consequently, NO_2 was inferred as the product of oxidation of NO. In contrast, the reaction of electrochemically

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generated oxoiron(IV) and oxomanganese(IV) porphyrins with NO in aqueous solution yielded nitrite.[17]

In the reverse direction, some oxo complexes and NO were produced irreversibly by thermal or photoinduced dissociation of nitrito complexes[18] of Mn^{III} and Cr^{III} and by oxygen atom transfer[19] from NO_2 to a Cr^{III} complex. Other examples of reactions related to NO reactivity of oxo complexes are nitrogen atom transfer reactions from nitrido complexes to NO, which have been reported to liberate N_2O.[20]

We report here the reaction of an oxoiron(IV) complex, $[Fe^{IV}O(tmc)(OAc)]^+$,[15] with NO. While the equatorial coordination of the Fe center by the macrocyclic ligand offers a stabilizing environment for the $Fe^{IV}{=}O$ group, the acetate anion was chosen as the sixth ligand to discourage direct interaction between NO and the Fe center. The reaction described here complements the established reactivity modes of oxoiron(IV) complexes, which include oxygen atom transfer to organic substrates and other iron complexes, hydrogen-atom abstraction, electron transfer, and hydride transfer.[21]

■ EXPERIMENTAL SECTION

Materials. All reagents and solvents were purchased from commercial sources and were used as received, unless noted otherwise. Acetonitrile, dichloromethane, and diethyl ether were deoxygenated by sparging with N_2 and purified by passage through two packed columns of molecular sieves under an N_2 pressure (MBraun solvent purification system). Nitromethane was refluxed over CaH_2 under an Ar atmosphere, distilled, and passed through a column of basic Al_2O_3.[22] Preparation and handling of air- and moisture-sensitive materials were carried out under an inert gas atmosphere by using standard Schlenk and vacuum line techniques or a glovebox. Nitrogen monoxide was prepared by reaction of concentrated hydrochloric acid with sodium nitrite.[23] The gas mixture produced was passed through a 50-cm column of KOH pellets, a 2-m stainless steel coil cooled to −94 °C (acetone−liquid N_2), and a bubbler charged with a concentrated aqueous NaOH solution for removal of unwanted nitrogen oxides; the gas was dried by passing it through a short column (ca. 20 cm) of KOH pellets.[22] (*Caution*: Nitrogen monoxide is a toxic gas.) $Fe(OTf)_2\cdot 2MeCN$[15] was synthesized by a modified literature method[24] from anhydrous $FeCl_2$ and trimethylsilyl trifluoromethanesulfonate in acetonitrile and recrystallized from acetonitrile−diethyl ether.[25] The ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane,[15,26] $[Fe^{II}(tmc)(OTf)]OTf$[27] [**1**−OTf(OTf), stored under an N_2 atmosphere], and iodosylbenzene[28] were prepared following published procedures. (*Caution*: Iodosylbenzene is potentially explosive, if dried extensively, and should be handled with care.[29]) Isotope-enriched $H_2{}^{18}O$ (98% ^{18}O) and $Na^{15}NO_2$ (98% ^{15}N) were purchased from Cambridge Isotope Laboratories, Andover, MA.

Physical Methods. UV−visible spectra were recorded on an HP 8453A diode array spectrophotometer (Agilent Technologies) with samples maintained at the desired temperature using a cryostat/heater from Unisoku Scientific Instruments. For solutions containing both nitromethane and methanol, the same solvent mixture was used for the background sample. NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer at ambient temperature. ^{19}F and ^{31}P chemical shifts are reported in parts per million (ppm) and were referenced to an external standard [$CFCl_3$ (δ = 0 ppm) for ^{19}F NMR and H_3PO_4 (85%, 0 ppm) for ^{31}P NMR spectra]. Mass spectral data were acquired on a quadrupole ion trap ThermoFinnigan LCQ Deca mass spectrometer using an electrospray ionization source. Analysis by GC−MS was performed on a TRACE GC 2000 gas chromatograph (column, TRACE TR-1) coupled with a single quadrupole ThermoFinnigan Voyager mass spectrometer.

Generation of $[Fe^{IV}O(tmc)(OTf)]OTf$, 2−OTf(OTf), and $[Fe^{IV}O(tmc)(OAc)]OTf$, 2−OAc(OTf). *Method A.* For the purpose of investigating the reaction of **2**−OAc with NO, the preparation of **2**−OTf and **2**−OAc was carried out in an N_2 atmosphere. A 1 mM solution of **1**−OTf(OTf) (0.002 mmol) in 2.0 mL of nitromethane was placed in a 1-cm UV−vis cuvette and precooled to −20 °C. Upon addition of 0.050 mL of a solution of iodosylbenzene (0.002 mmol) in methanol (anhydrous, 99%), **2**−OTf formed within 5 min. ESI(+) MS ($MeNO_2$) m/z: M^+ calcd for $C_{15}H_{32}F_3FeN_4O_4S$ ({**2**−OTf}$^+$), 477.14; found, 477.1 (M^+), 461.2 ($\{M - O\}^+$), 257.3 ($\{tmc + H\}^+$). UV−vis ($MeNO_2$) λ_{max}, nm (ε): 825 (230).

Subsequently, a solution of 0.002 mmol of tetraethylammonium acetate in 0.050 mL of nitromethane was added to the solution of **2**−OTf in nitromethane at −20 °C. The formation of **2**−OAc from **2**−OTf was indicated by a decrease of intensity at λ = 825 nm and the appearance of a new peak at λ = 995 nm over a period of ca. 1 h. ESI(+) MS ($MeNO_2$) m/z: M^+ calcd for $C_{16}H_{35}FeN_4O_3$ ({**2**−OAc}$^+$), 387.21; found, 387.0 (M^+), 371.3 ($\{M - O\}^+$), 257.3 ($\{tmc + H\}^+$). UV−vis ($MeNO_2$) λ_{max}, nm (ε): 825 (120), 995 (100).

For the conversion of **2**−OTf into **2**−OAc by incremental addition of NEt_4AcO, a 1 mM solution of **2**−OTf (0.002 mmol) in 2.0 mL of nitromethane was prepared in a 1-cm UV−vis cuvette at −20 °C as described above. Volume increments of 0.015 mL of a 33 mM solution of NEt_4AcO ($5 \cdot 10^{-4}$ mmol) in nitromethane were added in 2-min intervals to the solution of the Fe complex up to a total of 1.5 molar equiv of NEt_4AcO (with respect to Fe).

Method B. Upon addition of 0.150 mL of a solution of (diacetoxyiodo)benzene (0.006 mmol) in nitromethane to a 1 mM solution of **1**−OTf(OTf) (0.002 mmol) in 2.0 mL of nitromethane at 20 °C, **2**−OTf formed within 30 s. UV−vis ($MeNO_2$) λ_{max}, nm (ε): 825 (230). Samples for ^{19}F NMR spectroscopy were prepared at a concentration of 10 mM in CD_3NO_2. ^{19}F NMR (282.4 MHz, CD_3NO_2, δ): −77.5 ($[FeO(tmc)\{OS(O)_2CF_3\}]^+$), −79.2 ($CF_3SO_3^-$). For comparison, ^{19}F NMR of **1**−OTf(OTf) (282.4 MHz, CD_3NO_2, δ): −0.6 ($[Fe(tmc)\{OS(O)_2CF_3\}]^+$), −79.3 ($CF_3SO_3^-$).

Addition of a solution of 0.002 mmol of NEt_4AcO in 0.050 mL of nitromethane to this solution caused conversion of **2**−OTf into **2**−OAc (ca. 30 s). UV−vis ($MeNO_2$) λ_{max}, nm (ε): 832 (120), 1005 (110). ^{19}F NMR (282.4 MHz, CD_3NO_2, δ): −79.4 ($CF_3SO_3^-$).

Reaction of 2−OAc with Triphenylphosphine. A 1 mM solution of **2**−OAc (0.002 mmol) in 2.0 mL of nitromethane was prepared in a UV−vis cuvette at −20 °C as described above (method A), cooled to −25 °C, and treated with a solution of 0.020 mmol of triphenylphosphine in 0.35 mL of nitromethane. The half-life of the reaction was ca. 10 min. The product solution was subjected to ESI mass spectrometry. ESI(+) MS ($MeNO_2$) m/z calcd for $C_{16}H_{35}FeN_4O_2$ ($[Fe^{II}(tmc)(OAc)]^+$, {**1**−OAc}$^+$), 371.21; found, 371.4 ({**1**−OAc}$^+$). The product solution was evaporated to dryness, and the residue was dissolved in $CDCl_3$ for ^{31}P NMR spectroscopy. ^{31}P NMR (121.5 MHz, $CDCl_3$, δ): 29.0 ($OPPh_3$), −5.4 (PPh_3).

Reaction of 2−OAc with NO. A 1 mM solution of **2**−OAc (0.002 mmol) in 2.0 mL of nitromethane was prepared as described above (method A) in a UV−vis cuvette at −20 °C and then cooled to −25 °C. A total of 5 mL of NO(g) was purged via gastight syringe through this solution (<5 s), and the reaction was monitored by UV−visible spectroscopy. (The solubility of NO in nitromethane is not known but may be similar to that in other organic solvents, which is in the range of ca. 10−20 mM at −25 °C.[30] Here, the actual concentration of dissolved NO will likely be below the solubility limit.) After complete disappearance of the characteristic bands of **2**−OAc, the solution was purged for 10 min with Ar to remove excess NO. ESI(+) MS ($MeNO_2$) m/z calcd for $C_{16}H_{35}FeN_4O_2$ ({**1**−OAc}$^+$), 371.21; $C_{14}H_{32}FeN_5O_2$ ($[Fe^{II}(tmc)(ONO)]^+$, {**1**−ONO}$^+$), 358.19; found, 371.3 ({**1**−OAc}$^+$), 358.1 ({**1**−ONO}$^+$), 328.1 ($\{$**1**$-ONO - NO\}^+$), 257.3 ($\{tmc + H\}^+$).

Mass spectra of samples withdrawn from the reaction solution within 1.5 min of the initiation of the reaction showed additional peaks: ESI(+) MS (MeNO$_2$) m/z: 492.1 ([Fe^{III}(tmc)(OMe)(OTf)]$^+$), 402.2 ([Fe^{III}(tmc)(OMe)(OAc)]$^+$), 343.3 ([Fe^{II}(tmc)(OMe)]$^+$), 171.7 ([Fe^{III}(tmc)(OMe)]$^{2+}$). Relative abundance of Fe^{III} ions, 10−25% (t = 1.5 min), <5% (1 h), not observed (4 h). For samples prepared using deuterated methanol (CD$_3$OD, 99.8% D), ESI(+) MS (MeNO$_2$) m/z: 495.2, 405.2, 346.4, 173.2.

Comparison of Self-Decay and NO Reaction of 2−OAc. A 1 mM solution of **2**−OAc in nitromethane was prepared at −20 °C, as described above (method A), and then warmed to 20 °C. The half-life of the decay, as determined by UV−visible spectroscopy, was ca. 25 min. ESI(+) MS (MeNO$_2$) m/z calcd for $C_{16}H_{35}FeN_4O_2$ ({**1**−OAc}$^+$), 371.21; found, 371.3 ({**1**−OAc}$^+$), 257.3 ({tmc + H}$^+$).

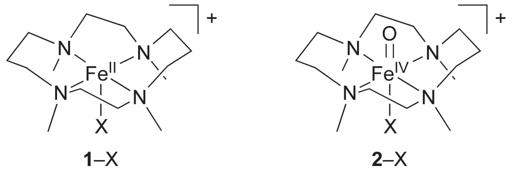
In a separate experiment, a solution of **2**−OAc was prepared at −20 °C, warmed to 20 °C, and immediately purged with 5 mL of NO(g) (<5 s). After complete disappearance of the characteristic bands of **2**−OAc (<10 s), the solution was purged for 10 min with Ar to remove excess NO and subjected to ESI mass spectrometry. The mass spectrum displayed peaks identical to those observed for the reaction of **2**−OAc with NO at −25 °C.

Quantification of NO$_2^-$ Formed in the Reaction of 2−OAc with NO. The reaction of **2**−OAc with NO at −25 °C was carried out as described above. After removal of excess NO, a solution of Na^{15}NO$_2$ (0.002 mmol, 98% ^{15}N) in 0.015 mL of methanol was added as a standard to the product solution at 20 °C (1 equiv of Na^{15}NO$_2$ with respect to Fe). Following an equilibration time of 1 h, the solution was subjected to ESI mass spectrometry. The isotope distribution pattern of {**1**−ONO}$^+$ was simulated using the patterns calculated for {**1**−O^{na}NO}$^+$ and a mixture of {**1**−O^{14}NO}$^+$ (2%) and {**1**−O^{15}NO}$^+$ (98%) (na, natural abundance). In six trials, the ratio of ^{na}NO$_2^-$ produced to ^{15}N-enriched NO$_2^-$ added (and thus to Fe) ranged from 1.03:1 to 1.49:1 [average, 1.32(18)]. [Because 0.27(6) equiv of NO$_2^-$ (with respect to Fe) was found in solutions of **1**−OAc treated with an excess of NO (vide infra), the average amount of NO$_2^-$ produced from the NO reaction of **2**−OAc was estimated as 1.05(19) equiv of NO$_2^-$ (with respect to Fe).] The validity of this method was tested on two series of authentic samples consisting of (a) equimolar amounts of **1**−OTf(OTf) and Na^{15}NO$_2$ and varying amounts of Na^{na}NO$_2$ (0.25−1.5 equiv) and (b) equimolar amounts of **1**−OTf(OTf), NEt$_4$AcO and Na^{15}NO$_2$ and varying amounts of Na^{na}NO$_2$ (0.25−1.5 equiv). The ratio of ^{na}NO$_2^-$ to ^{15}N-enriched NO$_2^-$ [i.e., ratio of {**1**−O^{na}NO}$^+$ to a mixture of {**1**−O^{14}NO}$^+$ (2%) and {**1**−O^{15}NO}$^+$ (98%)] determined from the observed intensity ratio was typically slightly overestimated (<20%).

The amount of NO$_2^-$ present in solutions of NO in MeNO$_2$−MeOH was estimated as follows. A mixture of 2.0 mL of nitromethane and 0.050 mL of methanol was purged with 5 mL of NO(g) and, after standing for 30 min, purged for 10 min with Ar to remove excess NO. To this solution were added a solution of 0.002 mmol of **1**−OTf(OTf) in 2.0 mL of nitromethane and a solution of Na^{15}NO$_2$ (0.002 mmol, 98% ^{15}N) in 0.015 mL of methanol. Analysis of the isotope distribution pattern of {**1**−ONO}$^+$ by ESI mass spectrometry indicated that typically less than 0.1 mM ^{na}NO$_2^-$ was present (<0.2 equiv of ^{na}NO$_2^-$ with respect to ^{15}N-enriched NO$_2^-$ and Fe added).

Similarly, the possible formation of NO$_2^-$ from the reaction of **1**−OAc with NO was tested. A solution of 0.002 mmol of **1**−OTf(OTf) and 0.002 mmol of NEt$_4$AcO in 2.0 mL of nitromethane and 0.050 mL of methanol was purged with 5 mL of NO(g) and, after standing for 30 min, purged for 10 min with Ar to remove excess NO. To this solution was added a solution of Na^{15}NO$_2$ (0.002 mmol, 98% ^{15}N) in 0.015 mL of methanol. Analysis of the isotope distribution pattern of {**1**−ONO}$^+$ by ESI mass spectrometry showed that 0.27(6) equiv of ^{na}NO$_2^-$ was present (with respect to ^{15}N-enriched NO$_2^-$ and Fe).

Chart 1. Structures of 1−X and 2−X^a



^{a}X = TfO$^-$, AcO$^-$, NO$_2^-$.

Isotope Labeling Experiments. For the generation of ^{18}O-enriched [Fe^{IV}(^{18}O)(tmc)(OAc)]$^+$, [^{18}O]-**2**−OAc, a solution of iodosylbenzene in methanol was treated with 10 equiv of H$_2$^{18}O (98% ^{18}O) for 30 min at 20 °C. The generation of [^{18}O]-**2**−OAc at −20 °C and subsequent reaction with NO at −25 °C were carried out as described above for **2**−OAc. To determine the extent of ^{18}O incorporation, the isotope distribution patterns observed by ESI mass spectrometry for {**2**−OAc}$^+$ and {**1**−ONO}$^+$, respectively, were simulated using the patterns calculated for the ^{16}O and ^{18}O isotopologues. For **2**−OAc, ^{18}O incorporation was in the range of 52−72% (based on the peaks at m/z = 387.0 and 389.0 for {[^{16}O]-**2**−OAc}$^+$ and {[^{18}O]-**2**−OAc}$^+$, respectively). For **1**−ONO, ^{18}O incorporation was in the range of 6−18% (based on the peaks at m/z = 358.1 and 360.1 for {**1**−^{16}ON^{16}O}$^+$ and {**1**−^{18}ON^{16}O}$^+$, respectively). The retention of ^{18}O in **1**−ONO from **2**−OAc was 12−25% (average of six trials, 18%). When the reaction of unlabeled **2**−OAc with NO was carried out in the presence of 10 equiv of H$_2$^{18}O, no incorporation of ^{18}O into **2**−OAc or **1**−ONO was observed.

■ RESULTS AND DISCUSSION

Generation and Characterization of Oxoiron(IV) Complexes. The complex [Fe^{IV}O(tmc)(OAc)]$^+$, **2**−OAc (Chart 1), was generated by oxidation of [Fe^{II}(tmc)(OTf)]$^+$, **1**−OTf, and subsequent ligand substitution in a manner similar to that reported for the corresponding trifluoroacetato complex, [Fe^{IV}O(tmc){OC(O)CF$_3$}]$^+$.[31] Reaction of **1**−OTf with iodosylbenzene in the weakly coordinating solvent nitromethane at −20 °C produced [Fe^{IV}O(tmc)(OTf)]$^+$, **2**−OTf, which was converted into **2**−OAc by exchange of the triflato ligand with acetate. Both **2**−OTf and **2**−OAc exhibit absorption bands in the near-IR region characteristic of [Fe^{IV}O(tmc)(L/X)]$^{2+/+}$ complexes[31] [**2**−OTf, λ_{max} = 825 nm (ε = 230 M^{-1}·cm^{-1}); **2**−OAc, λ_{max} = 825 (ε = 120 M^{-1}·cm^{-1}) and 995 nm (100)]. As shown by incremental addition of NEt$_4$AcO, 1 equiv of acetate is required for the conversion of **2**−OTf into **2**−OAc in nitromethane (Figure 1). The complexes also were identified by peaks at m/z = 477 (**2**−OTf) and 387 (**2**−OAc) in their ESI mass spectra.

The coordination of the triflate anion to the Fe centers in **1**−OTf and **2**−OTf in solution and its dissociation upon addition of NEt$_4$AcO were investigated by ^{19}F NMR spectroscopy. For this purpose, **2**−OTf was generated by oxidation of **1**−OTf with PhI(OAc)$_2$, because **2**−OTf exhibits greater stability under these conditions. The ^{19}F NMR spectrum of **1**−OTf(OTf) in CD$_3$NO$_2$ displays two resonance signals at δ = −0.6 and −79.3 ppm, where the latter is attributed to the free CF$_3$SO$_3^-$ anion and the former to CF$_3$SO$_3^-$ bound to the high-spin Fe^{II} center. On the basis of the relative intensities of these two peaks, the resonance signal at δ = −0.6 ppm accounts for ca. 40% of the CF$_3$SO$_3^-$ present (i.e., ca. 0.8 equiv with respect to Fe). This indicates that ca. 80% of the Fe^{II}(tmc) is present in the form of **1**−OTf, whereas the remainder corresponds to a complex

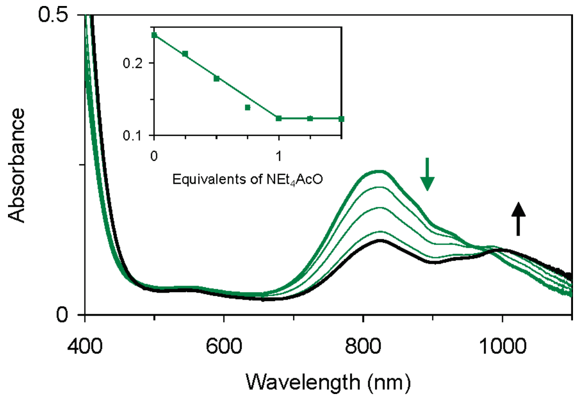


Figure 1. Conversion of 1 mM **2**−OTf (bold green line) into **2**−OAc (bold black line) in nitromethane by addition of NEt$_4$AcO in increments of 0.25 equiv at −20 °C as monitored by electronic absorption spectroscopy (path length, 1 cm). Inset: Corresponding changes of absorbance at 825 nm (green squares).

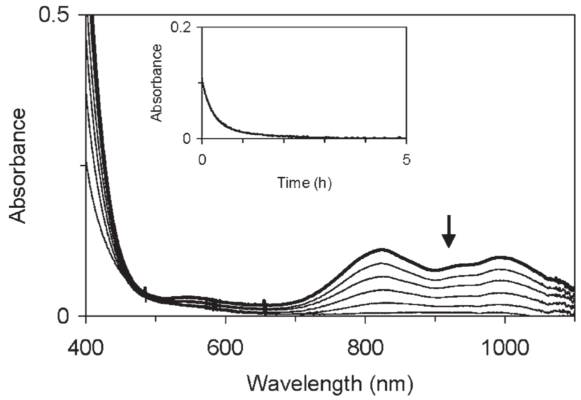


Figure 2. Reaction of 1 mM **2**−OAc (bold black line) with 10 equiv of PPh$_3$ in nitromethane at −25 °C as monitored by electronic absorption spectroscopy (path length, 1 cm). Inset: Time course of the reaction (λ = 825 nm).

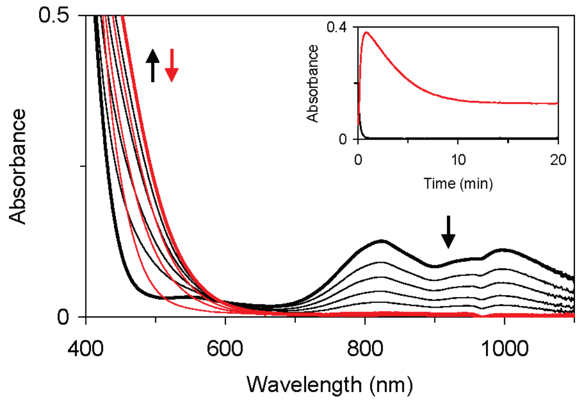


Figure 3. Reaction of 1 mM **2**−OAc (bold black line) in nitromethane with NO at −25 °C (reaction solution after ca. 1 min, bold red line), as monitored by electronic absorption spectroscopy (path length, 1 cm). Inset: Time course of the reaction [λ = 825 (black line) and 470 nm (red line)].

without coordinated $CF_3SO_3^-$, presumably the solvento complex $[Fe^{II}(tmc)\{ON(O)CD_3\}]^{2+}$. Similarly, two ^{19}F resonance signals were observed for **2**−OTf(OTf), δ = −77.5 and −79.2 ppm. Here, the peak at δ = −77.5 ppm is attributed to $CF_3SO_3^-$ bound to the Fe^{IV} center and accounts for ca. 30% of the $CF_3SO_3^-$ present. Thus, ca. 60% of the Fe in CD_3NO_2 solution corresponds to **2**−OTf and 40% to $[Fe^{IV}O(tmc)\{ON(O)CD_3\}]^{2+}$ or perhaps $[Fe^{IV}O(tmc)]^{2+}$. Upon addition of NEt$_4$AcO to the solution of **2**−OTf(OTf), the resonance signal of coordinated $CF_3SO_3^-$ disappeared, while that of free $CF_3SO_3^-$ became more intense and sharper (δ = −79.4 ppm). These observations confirm the displacement of the $CF_3SO_3^-$ ligand in **2**−OTf by AcO$^-$ to afford **2**−OAc.

To explain the different ^{19}F chemical shifts for the triflato ligands in **1**−OTf and **2**−OTf, several factors must be considered. First, coordination of the triflate ion to a Lewis-acidic metal center can be expected to cause a downfield shift of the ^{19}F resonance relative to that of free triflate. Second, the ^{19}F resonances in **1**−OTf and **2**−OTf may be subject to a hyperfine shift due to the presence of a paramagnetic metal center. By comparison with related S = 2 $[Fe(tmc)X]^+$ complexes,[32] the Fe d_{z^2} orbital in **1**−OTf is singly occupied (orientation of z axis defined by Fe−O bond), so a direct σ contact likely is the predominant mechanism for delocalization of unpaired spin density into triflato ligand molecular orbitals. (A π-contact contribution arising from the singly occupied d_{xz} and d_{yz} orbitals should be negligible due to insignificant, if any, Fe−OTf π bonding.) Complex **2**−OTf, on the other hand, should lack a σ-contact contribution to the ^{19}F chemical shift, because its Fe d_{z^2} orbital is vacant (S = 1). Furthermore, the oxo ligand being a strong ($\sigma + \pi$) donor ligand may be expected to attenuate the Lewis acidity of the Fe^{IV} center and weaken the Fe−OTf interaction. This is indeed observed as the equilibrium of triflate-bound and dissociated forms is further shifted toward the dissociated form for **2**−OTf than for **1**−OTf. The differences in hyperfine shift contributions and Fe−OTf binding between **1**−OTf and **2**−OTf may account for the large shift difference of ca. 77 ppm.

Reactivity of $[Fe^{IV}O(tmc)(OAc)]^+$, 2−OAc. The principal oxygen atom transfer reactivity of **2**−OAc was established by reaction with PPh$_3$ affording $[Fe^{II}(tmc)(OAc)]^+$ (**1**−OAc) and OPPh$_3$ (eq 1). When a solution of 1 mM **2**−OAc was reacted with 10 equiv of PPh$_3$ at −25 °C, the half-life was ca. 10 min, as indicated by the disappearance of the near-IR features associated with **2**−OAc (Figure 2). No intermediate was detected in this reaction.

$$[Fe^{IV}O(tmc)(OAc)]^+ + PPh_3 \rightarrow [Fe^{II}(tmc)(OAc)]^+ + OPPh_3 \qquad (1)$$

Under the same conditions, **2**−OAc reacted rapidly with an excess of NO. Experiments with different amounts of NO revealed that a large excess is required for complete decomposition of **2**−OAc. As shown in Figure 3, spectral changes were also observed between 400 and 600 nm. These changes suggest the formation of an intermediate, which reached maximum accumulation within 1 min. An isosbestic point close to 600 nm persisted for about the same time frame (Figure 3 and Figure S1 in the Supporting Information). When a smaller excess of NO was used, **2**−OAc decayed only partially, followed by tailing of the time trace at 825 nm (Figure S2 in the Supporting Information). The dependence of the total absorbance change at 825 nm on the concentration of NO is consistent with an equilibrium process in the first reaction step, while the continuing slow decay in experiments with a smaller excess of NO can be explained by removal of the unstable intermediate from the equilibrium mixture.

Analysis of the product solution by ESI mass spectrometry revealed peaks at m/z = 358 and 371, whose masses and isotope distribution patterns are consistent with $[Fe^{II}(tmc)(ONO)]^+$ (**1**−ONO) and **1**−OAc, respectively. Both features also were observed in the mass spectrum of an authentic sample prepared from equimolar amounts of **1**−OTf(OTf), NEt_4AcO, and $NaNO_2$, demonstrating competitive binding of AcO^- and NO_2^- to the Fe^{II} center. Consistent with the ^{19}F NMR spectroscopic data for **1**−OTf (vide supra) and $[Fe^{II}(tmc)\{OC(O)CF_3\}]^+$,[31] the Fe^{II} center is expected to be coordinated by only one apical ligand. To quantify the yield of NO_2^-, we added $Na^{15}NO_2$ to the product solution prior to mass spectrometric analysis and utilized the peak arising from **1**−$O^{15}NO$ as reference. Because the ratio of $Fe^{II}(tmc)$:$^{15}NO_2^-$ was known, the yield of NO_2^- from the reaction of **2**−OAc with NO could be calculated from the intensity ratio of the peaks associated with **1**−$O^{14}NO$ (m/z = 358) and **1**−$O^{15}NO$ (m/z = 359). The results from six trials indicate that approximately 1 equiv of NO_2^- (with respect to Fe) was produced (Figure 4).[33] Taken together, the observations reveal that the reaction of **2**−OAc with NO caused reduction of the Fe^{IV} center to Fe^{II} and produced NO_2^-.

A plausible mechanism entails attack of NO on the oxo ligand of **2**−OAc to give $[Fe^{III}(tmc)(OAc)(ONO)]^+$ or its dissociated form, $[Fe^{III}(tmc)(OAc)]^{2+} + NO_2^-$ (net $O^{\bullet-}$ ion transfer), followed by reduction of the Fe^{III} center to Fe^{II} (Scheme 1). The absorbance increase and decrease in the 400−600 nm region may then be related to the accumulation and decay of the Fe^{III} intermediate. Indeed, analysis of the reaction mixture by ESI mass spectrometry at earlier reaction times indicated the presence of $Fe^{III}(tmc)$ complexes that are derived from $[Fe^{III}(tmc)(OAc)(ONO)]^+$ by solvent exchange, i.e., $[Fe^{III}(tmc)(OAc)(OMe)]^+$ and $[Fe^{III}(tmc)(OTf)(OMe)]^+$. These species dissipated over time. When deuterated methanol was used, the peaks associated with these ions shifted accordingly (cf. the Experimental Section). The fact that the putative $[Fe^{III}(tmc)(OAc)(ONO)]^+$ complex was not directly detected is not surprising as it likely is a consequence of steric constraints imposed by the tetradentate tmc ligand. Fe(tmc) complexes with two axial ligands are only known where at least one of the two axial ligands is either a monatomic (e.g., O^{2-}) or a linearly coordinated diatomic ligand (e.g., NO, OH^-).[27,31,32,38] Since the nitrite ion is bent and expected to form at the sterically more hindered coordination site, dissociation may be favored. Whether the $[Fe^{III}(tmc)X(OMe)]^+$ ions are the predominant intermediate species in solution or are only formed from $[Fe^{III}(tmc)(OAc)(ONO)]^+$ and methanol during the mass spectrometry experiment cannot be answered at this time.

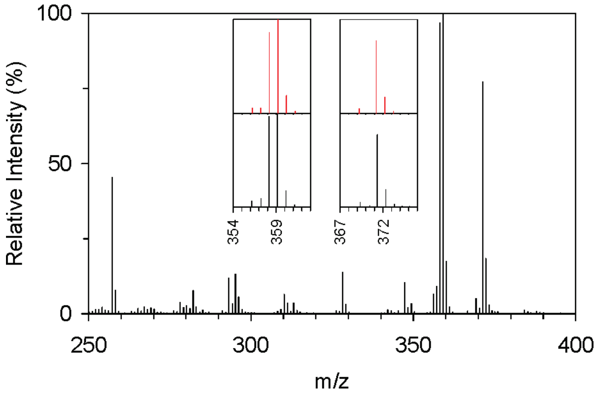
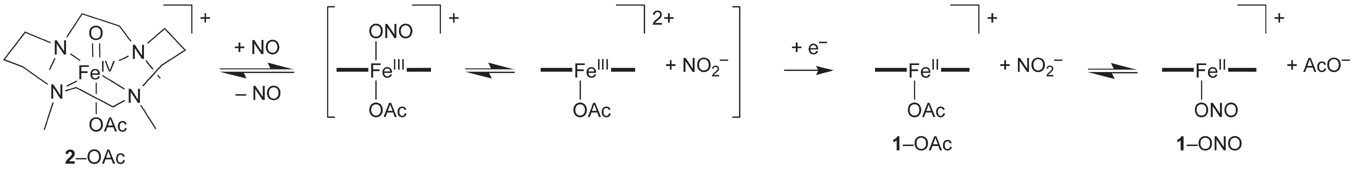


Figure 4. Electrospray ionization mass spectrum of the products of the reaction of **2**−OAc with NO in nitromethane followed by addition of 1 equiv of $Na^{15}NO_2$ (98% ^{15}N). Inset: Expanded views of the features attributed to $\{$**1**−ONO$\}^+$ and $\{$**1**−OAc$\}^+$ (bottom, black lines) and their calculated isotope distribution patterns (top, red lines). For $\{$**1**−ONO$\}^+$, the simulated data represent the isotope distribution pattern calculated for a mixture of $\{$**1**−$O^{na}NO\}^+$ (50%), $\{$**1**−$O^{14}NO\}^+$ (1%), and $\{$**1**−$O^{15}NO\}^+$ (49%).

The apparent instability of the Fe^{III} state is peculiar but must be viewed in the light of the almost complete absence of $Fe^{III}(tmc)$ complexes from the literature. There is only one report of an isolated Fe(tmc) complex with a formal Fe^{III} center.[38] We also note that the self-decay of **2**−OAc yields the Fe^{II} complex **1**−OAc rather than an Fe^{III} complex (cf. the Experimental Section). In the reaction of **2**−OAc with NO, methanol must be involved in the decay of the Fe^{III} intermediate, because its decay was decelerated with decreasing concentration of methanol. The decay of **2**−OAc was not affected (Figure S3 in the Supporting Information).

Because of the presence of NO and methanol, we have considered the possibility that reductive nitrosylation (and solvolysis) of the Fe^{III} intermediate takes place, which would result in the formation of an Fe^{II} complex and methyl nitrite (eq 2).[39−41] In addition, NO_2^- is known to catalyze the reductive nitrosylation of some Fe complexes (eqs 3 and 4).[35,41] To assess the relevance of reductive nitrosylation here, we have attempted to determine whether MeONO was produced. GC−MS analysis of the product mixture for MeONO is complicated by solvent interference, so we have opted to analyze the headspace of samples prepared with deuterated methanol. No significant increase in CD_3ONO concentration was observed compared to samples of NO in the same solvent system but without **2**−OAc. In contrast, the CD_3ONO concentration increased upon addition of O_2 to samples of NO in $MeNO_2$−CD_3OD. This increase correlated with the increase in nitrite yield, consistent with chemistry ensuing from

Scheme 1. Reaction of 2−OAc with NO[a]



[a] —Fe— = Fe(tmc).

oxidation of NO to NO_2.[36]

$$[\mathrm{Fe^{III}(tmc)(OAc)}]^{2+} + \mathrm{NO} + \mathrm{MeOH} \rightarrow [\mathrm{Fe^{II}(tmc)(OAc)}]^{+} + \mathrm{MeONO} + \mathrm{H^{+}} \tag{2}$$

$$[\mathrm{Fe^{III}(tmc)(OAc)}]^{2+} + \mathrm{NO} + \mathrm{NO_2^{-}} \rightarrow [\mathrm{Fe^{II}(tmc)(OAc)}]^{+} + \mathrm{N_2O_3} \tag{3}$$

$$\mathrm{N_2O_3} + \mathrm{MeOH} \rightarrow \mathrm{NO_2^{-}} + \mathrm{MeONO} + \mathrm{H^{+}} \tag{4}$$

Alternatively, a two-electron pathway with oxygen atom transfer from **2**−OAc to NO would produce **1**−OAc and NO_2 (eq 5). Nitrite along with MeONO could be formed from equilibration of NO_2 and NO with N_2O_3 and methanolysis (eqs 6 and 4). This mechanism cannot be ruled out on the basis of the Fe products, **1**−OAc and **1**−ONO. It is incompatible, however, with the lack of MeONO formation and the dependence of the decay rate of the Fe^{III} intermediate on the concentration of methanol.

$$[\mathrm{Fe^{IV}O(tmc)(OAc)}]^{+} + \mathrm{NO} \rightarrow [\mathrm{Fe^{II}(tmc)(OAc)}]^{+} + \mathrm{NO_2} \tag{5}$$

$$\mathrm{NO_2} + \mathrm{NO} \rightleftharpoons \mathrm{N_2O_3} \tag{6}$$

As a third alternative, a mechanism initiated by outer-sphere electron transfer from NO to **2**−OAc would likely be unfavorable due to the slow electron-transfer properties of related oxoiron(IV) complexes[21b] and the high NO/NO^+ redox potential.[40,41] This mechanism would yield MeONO upon trapping of NO^+ by MeOH and no NO_2^- (in the absence of H_2O).

Isotope Labeling Study. Further insights into the mechanism by which NO_2^- is formed were sought from an ^{18}O-labeling study. When the reaction was carried out with ^{18}O-enriched **2**−OAc, ca. 20% of the ^{18}O was incorporated into **1**−ONO, demonstrating that the oxoiron(IV) unit is capable of transferring its oxygen to NO to afford NO_2^-. In contrast, the reaction of unlabeled **2**−OAc with NO in the presence of $H_2{}^{18}O$ did not lead to incorporation of ^{18}O into **2**−OAc or the nitrite product. The low ^{18}O incorporation into **1**−ONO from ^{18}O-enriched **2**−OAc indicates that isotope scrambling had occurred. A possible mechanism accounting for loss of labeled O atoms involves linkage isomerization of the nitrito ligand in $[\mathrm{Fe^{III}(tmc)(OAc)(^{18}ONO)}]^{+}$ and reversible N−O bond cleavage. This process generates unlabeled **2**−OAc (and $N^{18}O$), which in turn reacts with unlabeled NO to produce unlabeled NO_2^- (eqs 7 and 8).

$$\mathrm{L}_n\mathrm{Fe^{III}{-}^{18}ONO} \rightleftharpoons \mathrm{L}_n\mathrm{Fe^{III}{-}ON^{18}O} \rightleftharpoons \mathrm{L}_n\mathrm{Fe^{IV}{=}O} + \mathrm{N^{18}O} \tag{7}$$

$$\mathrm{L}_n\mathrm{Fe^{IV}{=}O} + \mathrm{NO} \rightleftharpoons \mathrm{L}_n\mathrm{Fe^{III}{-}ONO} \rightleftharpoons \mathrm{L}_n\mathrm{Fe^{III}} + \mathrm{NO_2^{-}} \tag{8}$$

A similar mechanism has previously been described for a nitratooxoruthenium(IV) complex that was formed by oxygen atom transfer from a dioxoruthenium(VI) complex to NO_2^-. On the basis of isotope scrambling, the $\mathrm{L}_n\mathrm{Ru^{IV}(^{18}O)(^{18}ONO_2)}^{+}$ complex was proposed to undergo linkage isomerization of the nitrato ligand followed by reversible N−O bond cleavage.[42] Another scrambling mechanism would be possible in the event that NO_2 (or N_2O_3) is formed (eqs 3 and 5). Oxygen exchange would then take place between NO_2 and NO via N_2O_3 (eq 6). In the presence of methanol, however, the chemistry in eqs 3 and 5 inadvertently leads to formation of MeONO (eq 4), but this was not observed.

CONCLUSION

The reaction of an oxoiron(IV) complex, **2**−OAc, with the free radical NO is rapid and produces NO_2^-, which has been identified in the form of a nitritoiron(II) complex, **1**−ONO. This reaction is considerably faster than oxygen atom transfer from **2**−OAc to PPh_3 and differs from the latter reaction in the formation of an intermediate, presumably an Fe^{III} complex. Two possible mechanistic scenarios for the reaction between the $Fe^{IV}O$ complex and NO involve (i) $O^{\bullet-}$ ion transfer to afford an Fe^{III} complex and NO_2^-, followed by reduction of the Fe^{III} complex (Scheme 1), or (ii) oxygen atom transfer to afford an Fe^{II} complex and NO_2, which is converted into NO_2^- and MeONO via formation of N_2O_3 and methanolysis (eqs 5, 6, and 4). While an ^{18}O-labeling study provides evidence for the incorporation of oxygen from the $Fe^{IV}O$ group into the NO_2^- product, the observation of an intermediate Fe^{III} complex, the dependence of its decay on the concentration of methanol, and the lack of MeONO formation support an $O^{\bullet-}$ ion transfer mechanism. An outer-sphere electron transfer from NO to **2**−OAc may also be considered, but this seems unlikely due to unfavorable electron-transfer properties and redox potentials and must be ruled out because it would produce MeONO and not NO_2^-. In addition to expanding the fundamental chemistry of oxoiron(IV) complexes, the reaction described here serves as a synthetic example of the NO reactivity of biological ferryl species, such as those in myoglobin, hemoglobin, and peroxidase enzymes.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Spectral changes and time courses for the reaction of **2**−OAc with NO (Figures S1−S3, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Abbreviations: [14]aneN_4, 1,4,8,11-tetraazacyclotetradecane or cyclam; H_2ppIX, 7,12-diethenyl-3,8,13,17-tetramethyl-21*H*,23*H*-porphine-2,18-dipropanoic acid or protoporphyrin IX; H_2tpfpp, 5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)-21*H*,23*H*-porphine; TfOH (=CF_3SO_3H), trifluoromethanesulfonic or triflic acid; tmc, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

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(33) We have also probed other sources of NO_2^-. First, NO_2^- has been reported to be commonly present in aqueous NO solutions[10,11,34,35] due to oxidation of NO by trace amounts of O_2.[36] Here, solutions of NO in $MeNO_2$−MeOH were found to contain less than 0.1 mM NO_2^-. Second, a number of transition metal complexes are known to produce NO_2^- by disproportionation of NO.[37] When solutions of **1**−OAc, which was identified as a product of the reaction of **2**−OAc with NO, were treated with an excess of NO, we found ca. 0.3 equiv of NO_2^- (with respect to Fe). Thus, these two sources of NO_2^- play a minor role in the formation of NO_2^- here but likely are responsible for the observation of NO_2^- in excess of 1 equiv (cf. the Experimental Section for details).

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