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The Kinetics and Mechanism of the Ferrate(VI) Oxidation of Hydroxylamines

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Aqueous solutions of potassium ferrate(VI) cleanly and rapidly oxidize hydroxylamine to nitrous oxide, *N*-methylhydroxylamine to nitrosomethane, *N*-phenylhydroxylamine to nitrosobenzene, and *O*-methylhydroxylamine to methanol and nitrogen. The kinetics show first-order behavior with respect to each reactant and a two term component representing acid dependent and independent pathways. A general mechanism involving intermediate formation coupled with a two-electron oxidation is proposed.

Introduction

Hydroxylamines play a significant role in modern industrial chemistry due to their wide range of chemical properties. These include changes in reactivity with pH, formation of N and O bonded compounds, and solubility in both aqueous and nonaqueous solvents.[1] This diversity of properties and uses makes the study of hydroxylamine reactions an important area of investigation.

The oxidation of hydroxylamine, NH_2OH, is complex since it can function as a one or two-electron donor and form a variety of products. A one-electron pathway has been suggested for the reductions of Pt(IV),[2] Ce(IV),[3] and V(V)[4], and the mechanism is thought to involve initial complex formation followed by rate determining dissociation to product $NH_2O\bullet$.

$$NH_2OH + M^{n+} \rightarrow M{-}NH_2OH^{n+}$$

$$M{-}NH_2OH^{n+} \rightarrow NH_2O\bullet + M^{(n-1)+} + H^+$$

This radical is subject to different chemical fates depending on the oxidant and reaction conditions.

Rapid coupling of these radicals to produce molecular nitrogen was observed in reactions of hydroxylamine with the aforementioned oxidants.

$$2NH_2O\bullet \rightarrow N_2 + 2H_2O$$

When the coupling rate is slower than the oxidation rate of the radical, alternate products are observed. For example, the radical is quantitatively oxidized by an excess of Fe(III) in acid to NOH which then rapidly dimerizes to form N_2O.[5]

$$NH_2O\bullet + Fe^{3+} \rightarrow NOH + Fe^{2+} + H^+$$

$$2NOH \rightarrow N_2O + H_2O$$

Mononitrogen species may also be produced from initial one-electron oxidations of hydroxylamine. For example, the oxidation of hydroxylamine by Mn(III)[6] or Ag(II)[7] in acidic solution produces only nitrate. In this case, the rapid oxidation of $H_2NO\bullet$ surpasses NOH coupling thereby suppressing the dinitrogen pathway as shown here.

$$M^{n+} + NH_3OH^+ \rightarrow M^{(n-1)+} + NH_2O\bullet + 2H^+ \quad k$$

$$5M^{n+} + 2H_2O + NH_2O\bullet \rightarrow 5M^{(n-1)+} + NO_3^- + 6H^+ \text{ rapid}$$

Alternatively, the oxidation of hydroxylamine can take place via a two-electron pathway. Margerum and co-workers have shown hydroxylamine oxidation by halogens to occur

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through two-electron, halogen transfer steps (X = Br, Cl, I).[8]

$$X_2 + NH_2OH \rightleftarrows X_2NH_2OH$$

$$X_2NH_2OH \rightarrow X^- + XNHOH + H^+$$

$$XNHOH \rightarrow X^- + NOH + H^+$$

$$2NOH \rightarrow N_2O + H_2O$$

The proposed mechanism involves rate determining formation of a nitrogen−halogen complex followed by electron transfer and halogen loss. In excess hydroxylamine, NOH is produced and undergoes rapid dimerization to form N_2O and H_2O, $k = (4.5 \pm 2.7) \times 10^9\ M^{-1}s^{-1}$.[9] With excess bromine, HONO was observed which led Margerum to propose a mechanism that includes two two-electron oxidations of N(−I) to eventually form N(III).[8]

$$Br_2 + NH_2OH \rightleftharpoons BrNHOH + HBr$$

$$BrNHOH + Br_2 \rightarrow Br_2NOH + Br^- + H^+$$

$$Br_2NOH \rightarrow BrNO + H^+ + Br^-$$

$$BrNO + H_2O \rightarrow Br^- + HONO + H^+$$

Haight proposed that the Cr(VI) oxidation of hydroxylamine also proceeds by two-electron steps.[10] Initial formation of a H_2NOCrO_3H ester is followed by an intramolecular two-electron redox reaction to produce Cr(IV) and NOH. This mechanism dominates when the reaction is carried out with excess reductant. In contrast, excess Cr(VI) rapidly oxidizes NOH to HNO_2 before dimerization can take place.

High oxidation state complexes, in particular those that involve Fe(IV) and Fe(V), are proposed to play a significant role in biological systems.[11] To further our understanding of high oxidation state iron chemistry, the oxidation of hydroxylamine and substituted hydroxylamines with potassium ferrate, K_2FeO_4, was examined.

Although the ferrate ion, FeO_4^{2-}, has been known for over a century, its chemistry remains relatively unexplored. With recent developments in the synthesis of potassium ferrate,[12] its applications in the areas of environmental and organic chemistry are likely to increase.

Ferrate is a tetrahedral ion, isostructural with chromate or manganate.[13] Its reduction potentials are 0.9 and 1.9 V (versus NHE) in base and acid, respectively.[14] Although one might expect its reactivity to resemble that of chromate or manganate, significant differences are emerging. Potassium ferrate oxidizes alcohols to aldehydes or ketones,[15] thiols to disulfides or sulfonic acids, and arylamines to azo or nitro compounds[16−18] and deaminates primary alkylamines to form aldehydes.[18] Surprisingly, under no conditions does ferrate add to double or triple carbon−carbon bonds. An advantage ferrate has over many other oxidants is that the final iron product is rust, which is easily separated from the desired products and disposed of safely. With such advantages over other transition metal oxidants, ferrate has the potential to become an important “green” reagent in organic oxidation studies.

To date, relatively few kinetic studies of ferrate oxidations have appeared in the literature. In 1974, Goff and Murmann published the first kinetic study for the ferrate oxidation of hydrogen peroxide and sulfite along with an oxygen exchange study.[19] The oxidation was reinvestigated by Johnson and found to be different from the original report. Read and Sharma have examined the oxidation of several sulfur centers by ferrate.[20] Bielski has reported the oxidation of amino acids by ferrate[21] occurs via one-electron radical pathways. He also proposed that the oxidation of phenol by ferrate occurs by a one-electron pathway to produce Fe(V) and phenoxyl radical.[22] In this system, Fe(V) rapidly undergoes a two-electron transfer to form an inner-sphere Fe(III) complex. The exact mechanism by which this occurs is not known; however, it is thought to involve either inner-sphere substitution or an electrophilic addition.

In contrast to the one-electron mechanisms suggested by Bielski, Johnson and Lee have proposed two-electron reductions of ferrate. Johnson favored a quasistable ferrate/substrate bridged intermediate for the reaction with selenite and sulfite[24] as well as for thiosulfate.[19] The proposed bridged species contains an ester linked, Fe−O−S moiety (S = substrate) accompanied by consecutive two-electron reduc-

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tions of Fe(VI) that results in Fe(II). Direct oxygen transfer was observed by oxygen tracer studies thereby supporting this mechanism. The reduction of ferrate in two-electron steps is also postulated by Lee in the oxidation of secondary alcohols.[29] As opposed to an ester bridge between ferrate and substrate, Lee suggests a direct inner-sphere attack of the alcohol on the iron center prior to electron transfer to form a five-coordinate intermediate.

In recent investigations, Johnson and Hornstein studied the oxidation of aniline with ferrate. New kinetic and spectral evidence suggests a key step in the reaction mechanism is the formation of an iron–imido complex that either yields nitrosobenzene or reacts with another aniline to produce *cis*-azobenzene.[23] To shed light on these complex mechanisms, we have studied the reaction of the ferrate ion with hydroxylamines.

Experimental Section

Materials. Hydroxylamine, *N*-methylhydroxylamine, and *O*-methylhydroxylamine were purchased from Aldrich Chemicals as their hydrochloride salts and dried on a vacuum line before use. *N*-Phenylhydroxylamine was prepared by reduction of nitrobenzene with zinc powder as described in the literature[24] and recrystallized from warm benzene. Water enriched in ^{18}O or ^{17}O was a gift from Dr. R. Kent Murmann. All other chemicals were of reagent grade.

Potassium ferrate was prepared by the method reported by Thompson, Ockermann, and Schreyer.[25] The crude product was recrystallized from saturated potassium hydroxide and the purity checked by spectrophotometric analysis at 505 nm ($\epsilon = 1170\ M^{-1}\ cm^{-1}$). Purities up to 95% were obtained, and the measured rates were found to be independent of the sample purity. $H_2{}^{17}O$ (27% atom) or $H_2{}^{18}O$ (99.9% atom) was used to label ferrate oxygens. Samples of ferrate were dissolved in a minimum of water, allowed to stand for about 10 min, and dried under reduced pressure.[19]

Kinetic Measurements. Stock solutions of the reductants were prepared using Nanopure water, and ionic strength was maintained with sodium perchlorate. Sodium phosphate was used to control pH, and it also prevents precipitation of iron hydroxides formed during the reaction. Argon bubbling was used to remove dissolved oxygen and maintain anaerobic conditions.

The reaction rates were measured spectrophotometrically using a D110 Durrum stopped-flow spectrophotometer with an OLIS computer interface.[26] All reactions were carried out under pseudo-first-order conditions with the reductant in at least 10-fold excess. Reductant concentrations ranged from 0.005 to 0.050 M. Changes in absorbance versus time were fit to appropriate kinetic equations with OLIS data fitting software. Each rate constant determined from stopped-flow experiments was an average of 3–5 trials. Rapid scanning experiments were carried out using an OLIS RSM 1000 rapid scanning spectrophotometer.

Product Analysis. Spent reaction mixtures were extracted with methylene chloride, dried over anhydrous sodium sulfate, and analyzed with a Hewlett-Packard 5880 gas chromatograph equipped with a Superox II capillary column. Spectral characterization used an HP 8452A diode array spectrophotometer. Isotopic tracer studies were carried out using a Nuclide RMS-16 isotope ratio mass spectrometer at the University of Missouri–Columbia with the aid of Professor R. Kent Murmann.

Results and Discussion

Stoichiometry. Hydroxylamine, *N*-methylhydroxylamine, *O*-methylhydroxylamine, and *N*-phenylhydroxylamine all rapidly (<20 s) bleach aqueous solutions of ferrate over the pH range 8–11. When the reaction is carried out in the presence of oxygen and no buffer, the precipitation of iron(III) hydroxide is observed. In contrast, when oxygen is excluded, iron(II) is formed as shown by the formation of an intense red color upon acidification immediately after the reaction is over and addition of 1,10-phenanthroline. Further evidence for the sole production of iron(II) in the absence of oxygen was obtained by adding potassium thiocyanate to the spent reaction mixture. Under these conditions, the blood red $[Fe(SCN)_4]^-$ ion is not formed. However, upon exposure to oxygen, the addition of SCN^- turned the solutions red, indicating the formation of iron(III).[28] These observations are consistent with the initial production of iron(II) followed by its rapid oxidation to iron(III) by molecular oxygen under alkaline conditions.

Gas was rapidly evolved in the ferrate/hydroxylamine reaction. To identify this gas, solutions of each reactant were first flushed with argon to remove dissolved oxygen or carbon dioxide and then mixed anaerobically in a sealed vial. After the reaction was complete, a headspace sample was removed with a gastight syringe and analyzed using mass spectroscopy. A single peak at m/e 44 indicated the sole production of N_2O. The gas phase IR shows absorptions at 2230 and 1280 cm^{-1} which are also consistent with N_2O.[27] The presence of nitrate or nitrite was excluded by the absence of any adsorption in the UV after iron(III) was removed by ion exchange chromatography.

The *N*-methylhydroxylamine and *O*-methylhydroxylamine oxidation products were determined with a combination of GC and GC/MS. Characterization of the gaseous product was the same as for NH_2OH. The oxidation of *O*-methylhydroxylamine produced N_2O whereas analysis of the *N*-methylhydroxylamine reaction headspace showed only a peak for argon, the gas used for flushing, indicating the absence of gaseous products.

The nongaseous reaction products were identified by gas chromatography. The spent aqueous reaction mixture was extracted into methylene chloride and analyzed by GC. For the oxidation of *O*-methylhydroxylamine, a single peak was obtained with a retention time identical to that of a methanol standard. The oxidation of *N*-methylhydroxylamine with an excess of ferrate was allowed to proceed for 1 h, and only traces of nitromethane were detected. Similar results were observed using phenylhydroxylamine where only nitrosobenzene was observed as the final product.

A precise direct titration of a ferrate solution with excess hydroxylamine to determine the reaction stoichiometry was not possible due to the production of reduced iron species that catalyze the decomposition of ferrate before the end point was reached. Crude determinations, made by rapidly mixing

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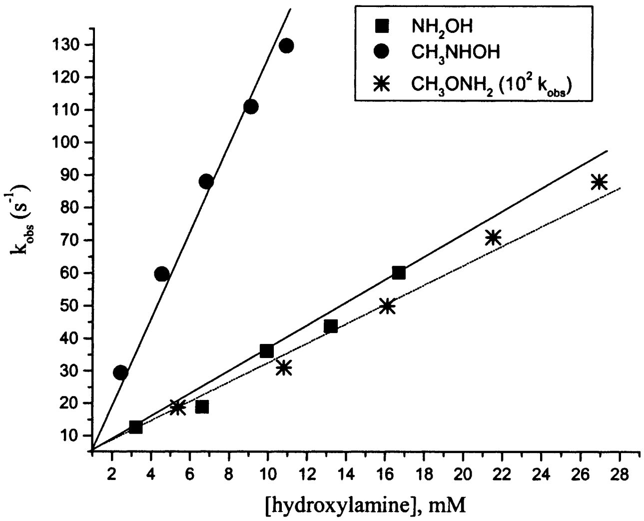

Figure 1. Typical plot of k_{obs} versus [hydroxylamine]. Conditions: T = 25 °C, I = 1.0 M ($NaClO_4$), [Na phosphate] = 50 mM; NH_2OH, pH = 9.0; CH_3NHOH, pH 8.8; CH_3ONH_2, pH 8.8.

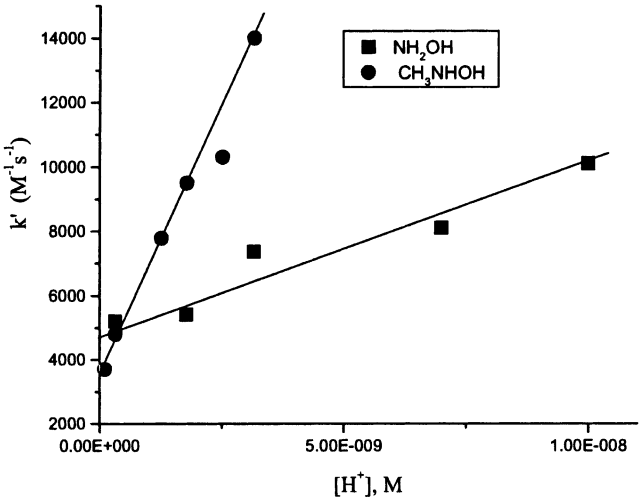

Figure 2. Representative hydrogen ion dependence for the hydroxylamine and *N*-methylhydroxylamine oxidation by ferrate. Conditions: T = 25 °C, I = 1.0 M ($NaClO_4$), [Na phosphate] = 50 mM.

Table 1. Proton Independent and Proton Dependent Rate Constants for Hydroxylamine/Ferrate Reactions at 25 °C, 0.05 M Phosphate Buffer, 1.0 M Ionic Strength

	$k_1 = k_o$ (M^{-1} s^{-1})	k_2 (M^{-2} s^{-1})	k_h (M^{-1} s^{-1})[a]
NH_2OH	$(4.8 \pm 0.3) \times 10^3$	$(6.5 \pm 0.8) \times 10^{10}$	$(3.3 \pm 0.4) \times 10^4$
CH_3NHOH	$(3.5 \pm 5) \times 10^3$	$(3.2 \pm 0.4) \times 10^{11}$	$(1.60 \pm 0.2) \times 10^5$
CH_3ONH_2	1.9 ± 0.9	$(2.2 \pm 0.4) \times 10^9$	110 ± 20

[a] $k_h = K_a k_2$.

Table 2. Phosphate Buffer Concentration on the Hydroxylamine/Ferrate Reaction at 25 °C, 1.0 M Ionic Strength ($NaClO_4$) and pH 10.3

$[\text{phosphate}]_T$, M	k' (M^{-1} s^{-1})
0.010	850
0.050	770
0.10	930
0.15	960
0.25	1100

ferrate and the hydroxylamine in known ratios until the purple ferrate color persists, indicate 2:1 reductant to ferrate stoichiometries for hydroxylamine and *N*-methylhydroxylamine and *N*-phenylhydroxylamine. In an attempt to better define the stoichiometry of these reactions, the addition of excess hydroxylamine to a known quantity of aqueous ferrate followed by back-titration of the remaining hydroxylamine with dichromate gave 2.01 ± 0.35:1 and 2.1 ± 0.8:1 reductant/ferrate ratios for hydroxylamine and *N*-methylhydroxylamine, respectively, over the entire pH range of the studies (pH 8.0−11.0). Similar experiments were attempted with the O-methyl derivative; however, inconsistent results were obtained presumably due to its relatively slow reaction with ferrate or reaction of Cr(VI) with the methanol produced from the Fe(VI) reaction. On the basis of product analysis and the available stoichiometric data, the following reactions can be written.

$$2NH_2OH + FeO_4^{2-} + 4H^+ \rightarrow N_2O + Fe^{2+} + 5H_2O$$

$$2CH_3NHOH + FeO_4^{2-} + 4H^+ \rightarrow 2CH_3NO + Fe^{2+} + 4H_2O$$

$$2CH_3ONH_2 + FeO_4^{2-} + 4H^+ \rightarrow 2CH_3OH + Fe^{2+} + N_2O + 3H_2O$$

$$2PhNHOH + FeO_4^{2-} + 4H^+ \rightarrow 2PhNO + Fe^{2+} + 4H_2O$$

Kinetics. The reaction rates were measured anaerobically under pseudo-first-order conditions with at least a 10-fold excess of reductant. Absorbance decreases were monitored at 505 nm, λ_{max} for ferrate, and observed rate constants, k_{obs}'s, were calculated using single-exponential fit routines, indicating a first-order dependence on ferrate(VI). Linear plots of k_{obs} versus the concentration of hydroxylamine show first-order behavior for all the hydroxylamines, see Figure 1, where the slope of these plots equals the second-order rate constant, k'. The ferrate oxidation of phenylhydroxylamine was too fast to study under these conditions. On the basis of these observations, a general rate law for the disappearance of ferrate may be written as follows.

$$-d[Fe(VI)]/dt = k'[Fe(VI)][reductant]$$

Figure 2 shows a representative plot of k' versus the hydrogen ion concentration for hydroxylamine and *N*-methylhydroxylamine. A similar linear proton dependence was observed for *O*-methylhydroxylamine, and each is best described by the following equation.

$$k' = k_1 + k_2[H^+]$$

Values of k_1 and k_2 for each of the hydroxylamines were determined, see Table 1. Since the pH was maintained with phosphate buffer, a buffer concentration dependence study was carried out. Table 2 shows that an increase in buffer concentration, keeping the ionic strength constant with sodium perchlorate, resulted in only a slight increase in rate, 30% increase over a 25-fold increase in phosphate concentration. This effect was considered minimal, probably due to medium effects and not to general acid catalysis. The lack of sensitivity to phosphate also probably indicates that no significant amounts of phosphatoferrate(VI) complexes were formed.

Mechanism. The simplest mechanism for the oxidation of hydroxylamine by ferrate consistent with this above information is given in Scheme 1. Since the pH range over which the study was carried out was higher than the pK_a of the hydroxylamines,[30] protonation was assumed to occur at the ferrate ion, pK_a 7.3.[30] In addition, as will be discussed later, if the protonation occurs on hydroxylamine, a one-electron or outer-sphere process is expected and is inconsistent with the experimental data.

Scheme 1

$$(\mathrm{R} = \mathrm{H\ or\ CH_3})$$

$$\mathrm{HFeO_4^{2-}} \rightleftarrows \mathrm{H^+} + \mathrm{FeO_4^{2-}} \quad K_a$$

$$\mathrm{NH_2OR} + \mathrm{FeO_4^{2-}} \rightarrow \mathrm{NOR} + \mathrm{Fe^{IV}} \quad k_o$$

$$\mathrm{NH_2OR} + \mathrm{HFeO_4^{-}} \rightarrow \mathrm{NOR} + \mathrm{Fe^{IV}} \quad k_h$$

$$\mathrm{NH_2OR} + \mathrm{Fe^{IV}} \rightarrow \mathrm{NOR} + \mathrm{Fe^{2+}} \quad \text{fast}$$

$$\mathrm{H_2O} + 2\mathrm{NOR} \rightarrow \mathrm{N_2O} + 2\mathrm{ROH} \quad \text{rapid}$$

Similar oxidation mechanisms may be written for the N-substituted hydroxylamines:

$$\mathrm{RNHOH} + \mathrm{FeO_4^{2-}} \rightarrow \mathrm{RNO} + \mathrm{Fe^{IV}} \quad k_o$$

$$\mathrm{RNHOH} + \mathrm{HFeO_4^{-}} \rightarrow \mathrm{Fe^{IV}} + \mathrm{RNO} \quad k_h$$

$$\mathrm{Fe^{IV}} + \mathrm{RNHOH} \rightarrow \mathrm{RNO} + \mathrm{Fe^{2+}} \quad \text{rapid}$$

Because the precise nature of the $\mathrm{Fe^{IV}}$ species is unknown, we have not balanced these reactions with respect to oxygens or protons. On the basis of this mechanism, $k_1 = k_0$ and $k_2 = K_a^{-1}k_h$. Values for k_0 and k_h are shown in Table 1.

Since nitrate was not observed in the oxidation of hydroxylamine, the coupling reaction of NOH with itself must be significantly faster than further oxidation by either ferrate(VI) or ferrate(IV). Under our conditions, the coupling constant may be calculated; it is 5×10^8 M^{-1} s^{-1} at pH 9.[9] At this pH, the ferrate/hydroxylamine rate constant is 5.38×10^3 M^{-1} s^{-1}, see Figure 2, well below the coupling rate. Assuming even a 10^3 faster rate for Fe(IV),[33] the coupling remains much faster than further oxidation to nitrate.

Ferrate intermediates previously proposed involve a substrate bound to the iron through a ferrate oxygen. For example, Murmann first suggested such an intermediate to explain the transfer of a ferrate oxygen to the final products in the oxidation of sulfite.[19]

$$\mathrm{Fe^{18}O_4^{2-}} + \mathrm{SO_3^{2-}} \rightarrow \mathrm{^{18}O_3Fe{-}^{18}O{-}SO_3^{4-}}$$

$$\mathrm{^{18}O_3Fe{-}^{18}O{-}SO_3^{4-}} \rightarrow \mathrm{^{18}OSO_3^{2-}} + \mathrm{Fe^{IV}}$$

The formation of an Fe−O−S species is followed by oxygen transfer to the sulfate products. Subsequent studies by Johnson and Bernard on the oxidation of selenite[22] suggested a similar oxidation mechanism, which is supported by recent ^{17}O NMR studies that show oxygen transfer from ferrate to form selenate.[31]

In contrast, the oxidation of hydroxylamine by $\mathrm{Fe^{18}O_4^{2-}}$ shows no incorporation of labeled oxygen into the final product. The same result is found when the reaction is carried out in $\mathrm{H_2{}^{18}O}$ with unlabeled ferrate. These studies demonstrate that the oxygen in the $\mathrm{N_2O}$ final product comes from the hydroxylamine itself; i.e., no oxygen transfer occurs during oxidation. Similar studies were carried out with the methylated hydroxylamines and ^{17}O labeled ferrate. In these experiments, the absence of ^{17}O signals in the final products again suggests a lack of oxygen transfer from the ferrate ion. On the basis of these observations, the formation of bridged intermediates via the ferrate oxygen seems unlikely.

Stanbury et al. reported large reorganizational energies in the oxidation of hydroxylamine by hexachloroiridate(IV).[32] After tying up any trace metals with oxalate, they were able to calculate an unprecedently small self-exchange rate constant for the $\mathrm{NH_2OH/NH_2OH^+}$ couple of 5×10^{-13} M^{-1} s^{-1} at 25 °C. On the basis of their observation, they concluded that outer-sphere redox reactions with hydroxylamine would be rare. Ferrate does not oxidize oxalate under these experimental conditions, and studies carried out in 1 mM sodium oxalate showed no diminution of reaction rates of ferrate with hydroxylamine. This suggests that catalysis by trace metals is negligible, and the rapid oxidation rate implies that an outer-sphere redox reaction is unlikely between ferrate and hydroxylamine. A one-electron oxidation is unlikely on the basis of negative results for radical formation using acrylonitrile as a radical trap. These trapping experiments have been shown to be successful for the detection of radicals for the oxidation of some substituted anilines and are expected to be reliable in the present studies with hydroxylamines.

Two-electron transfers are implied in Scheme 1 for each of the rate determining steps. Since an outer-sphere process is energetically unfavorable for two-electron transfers, we are forced to propose an inner-sphere mechanism. As discussed in the Introduction, rapid dimerization of NOH and production of $\mathrm{N_2O}$ in the case of hydroxylamine oxidation is indicative, although not proof, of a two-electron mechanism, whereas one-electron oxidations of hydroxylamine typically produce $\mathrm{N_2}$.[2−4] Two-electron reductions of ferrate have been proposed in other studies,[24,29,31] and while the Fe(IV) species has yet to be characterized, its existence in aqueous media has been established by Bielski and co-workers.[33] Their studies show Fe(IV) reacts at least an order of magnitude

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(30) $K_a = 7.24 \times 10^{-7}$, 1.1×10^{-6}, 2.51×10^{-5} for $\mathrm{NH_2OH}$, $\mathrm{CH_3NHOH}$, and $\mathrm{CH_3ONH_2}$, respectively. Marque, H. M. *J. Chem. Soc., Dalton Trans.* **1991**, 339. pK_a for $\mathrm{HFeO_4^-}$ is 7.3. Sharma, V. K.; Burnett, C. R.; Millero, F. *Chem. Phys.* **2001**, *3*, 2059.

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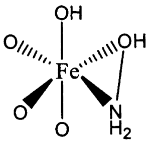
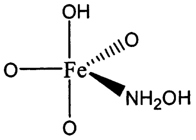
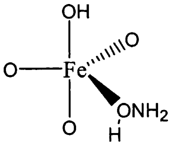
faster than ferrate with reductant. This is consistent with the assumption that mechanistic steps involving Fe(IV) are not rate determining. In light of the experimental evidence, an intermediate in which the substrate is bound directly to the iron in the ferrate ion is likely. Since the ferrate/hydroxylamine reaction occurs much faster than oxygen exchange on ferrate, an expanded first coordination sphere intermediate seems likely. Three proposed structures are shown here.







Unfortunately, it is impossible to distinguish between these possibilities on the basis of the present kinetic studies, and all attempts to trap or spectrally observe an intermediate were unsuccessful. Although there are no examples of similar iron−hydroxylamine complexes, Weighardt and others have established analogous structures for the hydroxylamine adducts of tungstate, molybdate and vanadate.[34,35] On the basis of these analogues, the side-on binding of hydroxylamine to ferrate would seem most likely.

A general mechanism that incorporates both the proposed intermediate and tracer studies is shown in Scheme 2.

From this mechanism, k_o and k_h reported in Table 1 are actually composites of $k_o'K_f$ and $k_h'K_{hf}$. Unfortunately, the formation constants are unknown so values for the intramolecular steps cannot be determined. Rapid scanning spectrophotometry does not show any change in the shape or position of the absorption spectrum of ferrate during the redox reaction. This implies that the majority of the iron(VI) species present exists as “free” ferrate and that the values of K_{hf} and K_f are small.

Scheme 2

$$HFeO_4^{-} \rightleftarrows H^+ + FeO_4^{2-} \quad K_a$$

$$FeO_4^{2-} + HNROR' \rightleftarrows [O_4Fe{-}(NHROR')]^{2-} \quad K_{hf}$$

$$HFeO_4^{-} + HNROR' \rightleftarrows [HO_4Fe{-}(NHROR')]^{-} \quad K_f$$

when $R = H$ and $R' = H$ or CH_3

$$[HO_4Fe{-}(NH_2OR)]^{-} \rightarrow NOR + Fe^{IV} \quad k_h'$$

$$[O_4Fe{-}(NH_2OR)]^{2-} \rightarrow NOR + Fe^{IV} \quad k_o'$$

$$NH_2OH + Fe^{IV} \rightarrow NOR + Fe^{2+} \quad \text{rapid}$$

$$H_2O + 2NOR \rightarrow N_2O + 2ROH \quad \text{rapid}$$

when $R = CH_3$ and $R' = H$

$$[HO_4Fe{-}NHCH_3(OH)]^{-} \rightarrow CH_3NO + Fe^{IV} \quad k_h'$$

$$[O_4Fe{-}NHCH_3(OH)]^{2-} \rightarrow CH_3NO + Fe^{IV} \quad k_o'$$

$$CH_3NHOH + Fe^{IV} \rightarrow CH_3NO + Fe^{2+} \quad \text{rapid}$$

Conclusions

A thorough study of the oxidation of hydroxylamine, *N*-methylhydroxylamine, and *O*-methylhydroxylamine is reported. When the reductant is present in excess, NH_2OH is oxidized to N_2O, CH_3NHOH is oxidized to CH_3NO, and CH_3ONH_2 is converted to CH_3OH and N_2O. Each oxidation is presumed to occur via a two-electron mechanism. This is consistent with recent observations of ferrate oxidations[17,19,23,29] and supports an emerging theme for ferrate in that it preferentially acts as a two-electron oxidant.

Although no intermediates are observed spectrally for the oxidation of hydroxylamines by ferrate, their presence is suggested by the oxidation products. An intermediate formed between the hydroxylamine oxygen and the iron(VI) center is similar to the one proposed by Lee in the oxidation of alcohols by ferrate.[29] Oxygen bridged (through the iron oxygen) structures are disfavored on the basis of the lack of oxygen transfer from ferrate to the hydroxylamine final product. Further kinetic studies involving the oxidation of nitrogen based compounds are needed to elucidate these suggested intermediates and the propensity of ferrate to oxidize by two electrons.

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