Kinetics and mechanism of hydroxylamine oxidation by $[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$ in aqueous media[1]

Beauty Chaudhuri and Rupendranath Banerjee

Abstract: Equilibrium studies show that in aqueous solutions containing excess 1,10-phenanthroline (phen) in the range pH 3–9, the complex ion $[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$ (**1**) undergoes rapid but partial hydrolysis and coexists with $[Fe_2^{III}(\mu\text{-}O)(phen)_3(H_2O)_4]^{4+}$ (**1d**), $[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+}$ (**2**), and $[Fe_2^{III}(\mu\text{-}O)(phen)_4(OH)_2]^{2+}$ (**3**). The solution oxidizes hydroxylamine quantitatively to N_2O and is itself reduced to $[Fe(phen)_3]^{2+}$. The reactions in the range pH 3–6 are first-order in concentrations of complex and hydroxylamine but exhibits complex $[H^+]$ dependence, suggesting kinetic contributions from **1**, **1d**, and **2** but not from **3**. Rapid formation of inner-sphere adducts between NH_2OH and different $\{Fe_2O\}^{4+}$ species followed by rate-determining one-electron transfer to produce NHOH and $\{Fe_2O\}^{3+}$ is proposed. All subsequent steps are rapid. Ambient light does not affect kinetics and reaction products.

Key words: kinetics, equilibrium, oxo bridge, iron (III), hydroxylamine.

Résumé : Des études d'équilibre ont montré que, dans des solutions aqueuses contenant un excès de 1,10-phénanthroline (phen), à des pH allant de 3 à 9, l'ion complexe $[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$ (**1**) subit une rapide hydrolyse partielle et qu'il coexiste avec les ions $[Fe_2^{III}(\mu\text{-}O)(phen)_3(H_2O)_4]^{4+}$ (**1d**), $[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+}$ (**2**) et $[Fe_2^{III}(\mu\text{-}O)(phen)_4(OH)_2]^{2+}$ (**3**). Cette solution permet d'oxyder quantitativement l'hydroxylamine en N_2O alors qu'elle est réduite en $[Fe(phen)_3]^{2+}$. Les réactions à des pH allant de 3 à 6 sont du premier ordre en concentrations de complexe et de hydroxylamine, mais la dépendance sur la $[H^+]$ est complexe; ces résultats suggèrent la présence de contributions cinétiques des composés **1**, **1d** et **2**, mais pas du composé **3**. On suggère qu'il y a formation rapide d'adduits dans la sphère interne entre le NH_2OH et diverses espèces de $\{Fe_2O\}^{4+}$ suivie d'un transfert cinétiquement limitant d'un électron conduisant à la formation de NHOH et de $\{Fe_2O\}^{3+}$. Toutes les étapes subséquentes sont rapides. La lumière ambiante n'affecte pas la cinétique et les produits réactionnels.

Mots clés : cinétiques, équilibre, pont oxo, fer(III), hydroxylamine.

[Traduit par la rédaction]

Introduction

The μ-oxo diiron(III) unit, $\{Fe_2O\}^{4+}$, appears conspicuously in iron chemistry, both inside and outside the protein systems. Three reviews (1) emphasized the biological role of this chemical unit and amply represented the interest of inorganic chemists in the synthesis, structural characterization, and spectroscopic and magnetic properties of oxo-bridged diiron(III) complexes. However, reactivity studies appear to be occasional (2), and kinetic and mechanistic studies are extremely rare outside a protein environment (3). The situation appears somewhat surprising when one looks at the rich literature (4) on the substitution and redox kinetics of mononuclear iron(III) species. It might be mentioned at this point that proper interpretation of kinetics of mononuclear species demands detailed knowledge of the solution properties of oxo-bridged binuclear species, which are often difficult to avoid under the kinetic conditions used for mononuclear systems. On the whole, it appeared worthwhile to learn the kinetic and mechanistic features of reactions involving the $\{Fe_2O\}^{4+}$ unit.

The complex salt $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2](NO_3)_4{\cdot}5H_2O$ (phen = 1,10-phenanthroline) can be obtained in a highly pure state and was characterized by X-ray crystallography (5). It is a Raman spectroscopic model (5) for the binuclear iron site in ribonucleotide reductase (6*a*) and *met*-hemerythrin, the oxidized form of the oxygen transport protein hemerythrin (6*b*). In solution, the complex oxidizes hydroxylamine at a moderate rate, measurable by conventional spectrophotometry. Oxidation of hydroxylamine in simple inorganic systems has been studied extensively (7–9), but no report is available on the reaction of NH_2OH with any of the different $\{Fe_2O\}^{4+}$ units.

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Experimental

Materials

Crystals of $[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)_2](NO_3)_4{\cdot}5H_2O$ (5) gave satisfactory elemental analyses (calcd. for $C_{48}H_{32}N_{12}O_{13}Fe_2{\cdot}7H_2O$, C 47.15, H 3.8, N 13.75, Fe 9.1; found: C 47.2, H 3.7, N 13.8, Fe 9.1) and electronic spectrum

(5). Hydroxylamine nitrate was prepared in solution by double decomposition of hydroxylamine hydrochloride (A.R., E. Merck) with barium nitrate (A.R., E. Merck) and standardized by oxidation with Fe^{III} in 1 M H_2SO_4 (eq. [1]) (9*a*). The Fe^{II} formed was titrated with standard $(NH_4)_2Ce(NO_3)_6$. We found the solution to be stable (10) for more than a week at room temperature (27°C).

[1] $2NH_2OH + 2\ Fe_2(SO_4)_3 \rightarrow N_2O + 4\ FeSO_4 + 2\ H_2SO_4 + H_2O$

Tris(phenanthroline)iron(III) nitrate (11) and tris(phenanthroline)iron(II) nitrate (12) were prepared according to the literature. The 1,10-phenanthroline was an E. Merck product and was used without further purification. Solution of recrystallized $NaNO_3$ (A.R., B.D.H.) was standardized by ion-exchange technique (13). All other reagents used were of analytical grade. Chromium(II)-scrubbed dinitrogen gas and triply distilled water were used throughout. Reported kinetic and equilibrium data are at 30.0°C and I = 1.0 M.

Physical measurements and kinetics

Equilibrium constants for equilibria [2]–[4] were evaluated spectrophotometrically. Kinetics were monitored mostly at 510 nm, the visible maximum of the reaction product, $[Fe(phen)_3]^{2+}$ (**4**). Large excess of hydroxylamine (c_R = $[NH_3OH^+] + [NH_2OH]$; 5–50 mM) over the total complex (c_{Fe} = 0.05–0.005 mM) was used, and the reactions

[2] $[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+} + 2H_2O \overset{K_d}{\rightleftharpoons} [Fe_2^{III}(\mu\text{-}O)(phen)_3(H_2O)_4]^{4+} + phen$

[3] $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+} \overset{K_{a1}}{\rightleftharpoons} [Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+} + H^+$

[4] $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+} \overset{K_{a2}}{\rightleftharpoons} [Fe_2^{III}(\mu\text{-}O)(phen)_4(OH)_2]^{2+} + H^+$

were followed in situ in the thermoelectrically controlled (±0.1°C) cell housing (CPS-240A) of a Shimadzu spectrophotometer (UV-1601 PC). For some faster reactions, reactants were mixed in the spectrophotometer cell: 3.0 mL of the reductant solution at the required pH, buffer concentration, and ionic strength (1.0 M) was taken in a cell in the thermostated cell housing and allowed to attain temperature equilibrium. A small volume (<1% of the reductant) of the complex at the same pH, buffer concentration, and ionic strength was rapidly and directly injected into the cell so that the desired complex concentration was achieved after mixing. Recording of absorbance started almost simultaneously in the "kinetic mode" of the spectrophotometer, and the maximum initial absorbance (0.152) indicated that <15% of the initial reaction was missed during mixing. The first-order rate constants, k_o, were obtained from the slope of usual $\log(A_\infty - A_t)$ versus time (t) plots, where A_t and A_∞ are the absorbances at time t and after complete reaction.

We added no external buffer but generally used an excess 1,10-phenanthroline (c_{phen} = $[Hphen^+] + [phen]$) over c_{Fe}. The added phen and hydroxylamine successfully controlled solution pH within ± 0.01 during most of the kinetic studies, and the maximum variation observed was ± 0.03. The pH of experimental solutions were measured with an Orion (710A) pH meter, using a calibrated (13) Orion–Ross combination (model 81-02) electrode. All Y versus X data were analysed using the program package GRAPHER.[3] The reported errors are standard deviations. No attempt was made to estimate the small error propagated from k_o.

Stoichiometry

The UV-vis spectra (14) of product solutions indicate quantitative formation of **4** as a product. The reaction stoichiometry was determined by spectrophotometric titration of the oxidant complex (0.05 mM) with hydroxylamine in the presence of c_{phen} (3.0 mM) at pH 3.5. Different amounts of hydroxylamine were allowed to react with the oxidant solutions. The final absorption, corresponding to consumption of a stoichiometrically equivalent amount of the oxidant, was determined as a function of total hydroxylamine concentration, c_R. The absorbance due to unchanged complex, if any, is negligible (<3%) compared to the absorbance due to **4** formed under the reaction conditions. Stoichiometry was also measured by estimating unchanged hydroxylamine spectrophotometrically. For this purpose, the complex solution (0.02 mM) in excess phen (c_{phen} = 3 mM) was mixed with hydroxylamine (c_R = 0.05 mM). The final optical density at 510 nm indicated the formation of two moles of **4** per mole of **1**. Excess $Fe_2(SO_4)_3$ was then added to the mixture. Two parallel sets were taken. One of them was stored in the dark, the other under the conditions of normal laboratory illumination. The Fe^{2+} ion thus formed produced more of **4**, and absorption at 510 nm increased. The rise in absorption measured after 1 h was used to estimate hydroxylamine.

Since the formation and decay of HNO_2 was observed (15, 16) in some oxidation reactions of NH_2OH, we tested for the presence of any HNO_2 or NO_2^- as by-product. A 25 mL mixture having c_{Fe} = 0.10 mM, c_R = 0.10 mM, and c_{phen} = 5 mM at pH 6.1 was allowed to react completely. The product solution was eluted through a Dowex 50W X-8 cation exchanger in the Na^+ form, made up to 100 mL and subjected to the Griess–Ilsovey reaction for nitrous acid by reaction with sulfanilic acid followed by a coupling reaction with 1-napthyl amine to give an azo dye (λ_{max} = 520 nm, ε (molar extinction coefficient) = $3.3 \times 10^4\ M^{-1}cm^{-1}$). A 1% sulfanilic acid solution was prepared by dissolution of the powder in 25% acetic acid. A 0.6% solution of 1-napthylamine was also prepared in 25% acetic acid.

Results and discussion

Spectral and equilibrium studies

The complex solution is indefinitely stable in the range pH 2–10. However, its spectra change reversibly with changing c_{phen} and media pH. The most prominent spectral change occurs at 440 nm and has been displayed in Fig. 1. The change indicates protic and ligand dissociation equilibria, which can be suppressed almost completely in the presence of excess phen in the range pH 3–4. Under these conditions, **1** is the only absorbing species at λ > 400 nm. Its molar extinction coefficient is $\varepsilon_1 = 1460 \pm 5\ M^{-1}\ cm^{-1}$ at 440 nm.

The absorption versus c_{phen} (≥1.0 mM) data at pH 3.00 yield good fit to eq. [5] for $K_d = (4.97 \pm 0.08) \times 10^{-6}$ M

[3] Grapher. Golden Software Inc. 1988.

and $\varepsilon_{\mathbf{1d}} = (562 \pm 7)\ M^{-1}cm^{-1}$. Equation [5] can be derived for equilibrium [2] provided that $c_{phen} = ([Hphen^+] + [phen]) \approx [Hphen^+]$:

$$[5] \quad \frac{c_{Fe}}{(A_o - A_e)} = \frac{K_{Hphen}\, c_{phen}}{K_d[H^+](\varepsilon_{\mathbf{1}} - \varepsilon_{\mathbf{1d}})} + 1/(\varepsilon_{\mathbf{1}} - \varepsilon_{\mathbf{1d}})$$

where A_e and A_o are absorptions of the equilibrium mixture and of pure **1**, respectively; $\varepsilon_{\mathbf{1d}}$ is the molar extinction coefficient of the species **1d** and K_{Hphen} ($10^{-4.92}$) is the proton dissociation constant (17) for $Hphen^+$. This fit justifies equilibrium [2] and shows that only one phen dissociates under the reaction conditions.

One can safely assume that only equilibrium [3] is responsible for the changes in absorbance of complex solutions containing excess phen in the range pH 3.5–6.0 and thus derive eq. [6].

$$[6] \quad c_{Fe}/(A_o - A_e') = [H^+]/(\varepsilon_{\mathbf{1}} - \varepsilon_{\mathbf{2}})K_{a1} + 1/(\varepsilon_{\mathbf{1}} - \varepsilon_{\mathbf{2}})$$

where A_e' is the equilibrium absorbance in the range pH 3.5–6.0, and $\varepsilon_{\mathbf{2}}$ is the molar absorption coefficient for **2**.

Similarly, in the presence of excess phen, in the range pH 7–9, only equilibrium [4] is assumed to be the cause of change in solution absorbance, with pH in the range 7–9, whereby eq. [7] is valid.

$$[7] \quad c_{Fe}/(A_o' - A_e'') = [H^+]/K_{a2}(\varepsilon_{\mathbf{2}} - \varepsilon_{\mathbf{3}}) + 1/(\varepsilon_{\mathbf{2}} - \varepsilon_{\mathbf{3}})$$

In eq. [7], A_e'' is the equilibrium absorption in the range pH 7–9, $A_o' = \varepsilon_{\mathbf{2}} \times c_{Fe}$, and $\varepsilon_{\mathbf{3}}$ is the molar absorption coefficient for **3**. Absorbance versus pH data in the respective pH ranges were fitted to eqs. [6] and [7] to yield $K_{a1} = (3.84 \pm 0.04) \times 10^{-6}$ M, $K_{a2} = (2.52 \pm 0.08) \times 10^{-8}$ M, $\varepsilon_{\mathbf{2}} = (962 \pm 8)\ M^{-1}\ cm^{-1}$, and $\varepsilon_{\mathbf{3}} = (796 \pm 9)\ M^{-1}cm^{-1}$.

A global fit of absorbance versus $[H^+]$ data in the presence of excess phen was attempted using the $\varepsilon_{\mathbf{2}}$, $\varepsilon_{\mathbf{3}}$ values and eq. [8] for which A is the equilibrium absorption in the range pH 3.5–9.0, $A_2 = \varepsilon_{\mathbf{2}} \times c_{Fe}$, and $A_3 = \varepsilon_{\mathbf{2}} \times c_{Fe}$. A good fit is obtained with $K_{a1} = (4.03 \pm 0.05) \times 10^{-6}$ M and $K_{a2} = (2.54 \pm 0.06) \times 10^{-8}$ M.

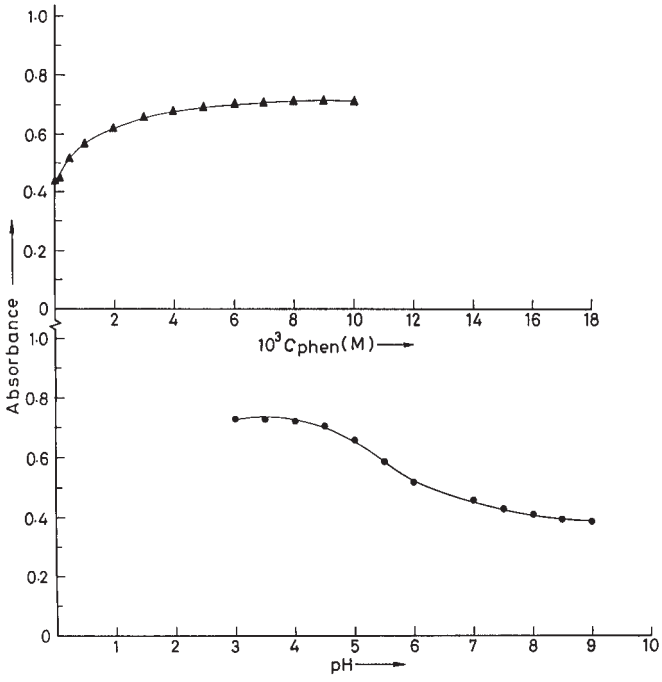
$$[8] \quad (A_o - A)[H^+]/(A - A_2) = K_{a1} + (A - A_3)K_{a1}K_{a2}/(A - A_2)[H^+]$$

The pK_{a1} (5.39 ± 0.01) and pK_{a2} (7.59 ± 0.01) values for **1** are smaller than the respective values ($pK_{a1} = 6.36$; $pK_{a2} = 9.84$) for the ruthenium(III) analogue $[Ru^{III}_2(\mu\text{-}O)(bipy)_4(H_2O)_2]^{4+}$ (**5**) (18). Greater acidity of **1** than **5** is due to smaller size of Fe^{III}. The differences ($pK_{a1} - pK_{a2}$) for the binuclear complexes **1** and **5** are comparable to those for the mononuclear Fe^{III} complexes (19) of the type $[ML_4(H_2O)_2]^{3+}$. Prominent electronic interaction of the two M^{III} centres via the oxo bridge in **1** and **5** is thus indicated and is indeed expected from the *anti* ferromagnetic coupling well known (1) in several μ-oxo-bridged complexes of Fe^{III} and Ru^{III}. Binuclear iron(III) complexes with insulating bridging groups cannot enter into such interactions, and they have small differences between pK_{a1} and pK_{a2} (19).

Stoichiometry

No nitrogen(III) product could be detected by the Griess–Ilsovey reaction at pH 6.1. Under our reaction conditions a 2×10^{-6} M $NaNO_2$ solution gave an absorbance of 0.166 per cm at 520 nm. At pH 6.1 the reaction between hydroxylamine and

Fig. 1. Change in absorbance with c_{phen} at fixed pH (3.00) (▲) and change in absorbance with pH at fixed c_{phen} (0.010 M) (●). λ, 440 nm ; c_R, 0.50 mM; I, 1.0 M; path length, 1.00 cm. The solid lines are drawn using calculated values for eqs. [8] and [5], respectively.



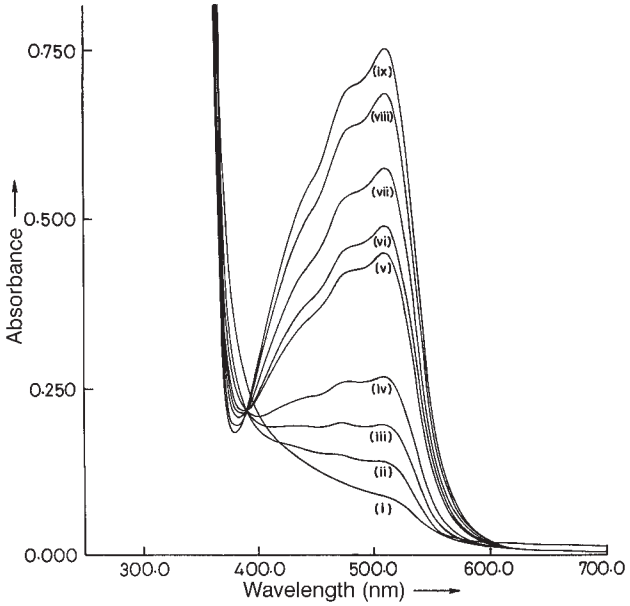
HONO is very slow (20*a*), as is the reaction of HONO with the diiron(III) complexes. Hence, we are confident that HONO did not form at this pH.

Stoichiometric measurements in the presence of excess phenanthroline indicated a 1:1 stoichiometry (eq. [9]) from spectrophotometric titration data and determination of unused hydroxylamine. The measured stoichiometry is independent of whether diffuse light is excluded or not.

$$[9] \quad [Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+} + NH_2OH + 2phen = 0.5N_2O + 2[Fe(phen)_3]^+ + 3.5H_2O$$

Different oxidants oxidize hydroxylamine to nitrous oxide, which seems to be the most common oxidation product. Nevertheless, other products like N_2, NO_2^-, NO_3^-, and NO have been reported (8, 20, 21). Gupta and co-workers (9*b*) studied the oxidation of hydroxylamine by iron(III) in acetate buffer, and proposed $[Fe_3O(O_2CMe)_6]^+$ to be the near exclusive iron(III) species along with a small concentration of iron(III) monomers. Complex kinetics and product inhibition by iron(II) were noted, and the initial rate method was used. They reported N_2 as the oxidation product in diffuse light, but ($N_2O + N_2$) in the dark. Butler and Gordon (9*c*) also noticed the effect of light on oxidation products of hydroxylamine with iron(III) in dilute perchloric acid media. The observations are difficult to explain, but two potent sources of complications may be considered: (*a*) auto-oxidation of iron(II) to iron(III), which further consumes hydroxylamine; effectively this implies an additional pathway in which hydroxylamine is oxidized by oxygen (22) under the aerobic conditions used, and (*b*) catalysed oxidation by trace metal ions, which were apparently not excluded. Trace catalysts strongly affect both rate

Fig. 2. Spectral changes with time for a mixture containing c_{Fe} = 0.05 mM, c_R = 0.02 M, and c_{phen} = 3 mM at pH 4.50. (*i*) Spectrum of 0.05 mM complex at the same c_{phen} and pH. Time: (*ii*) 0, (*iii*) 60, (*iv*) 120, (*v*) 270, (*vi*) 360, (*vii*) 480, (*viii*) 660, and (*ix*) 870 s. Cell path length, 1.00 cm.



and product of oxidation (23) of NH_2OH and may lead to wrong conclusions about the uncatalyzed process. Light may affect stoichiometry and kinetics by its influence on either (*a*) or (*b*). Moreover, both groups worked with complex mixtures of iron(III) species of different nuclearity, which can oxidize hydroxylamine differently.

We observed no such effect of light in our system, but note that trace metal ions should be sequestered in the presence of added phen. Also, all the oxidant species are well defined and the reaction product, $[Fe(phen)_3]^{2+}$, is stable in air.

Kinetics

During the reaction course, an isosbestic point sets up at 389 nm, and absorption at this point increases with increasing c_R. Some typical values of absorbances are 0.225, 0.246, and 0.274 at c_R = 0.02, 0.04, and 0.06 M, respectively. This strongly suggests incomplete formation of precursor complexes between hydroxylamine and the oxidants. Spectrum of the complex solution, however, does not pass through this point (Fig. 2), and we propose that the isosbestic point sets up between the precursor and the final reaction product. Non-reducing substrates (for example, NCS^-) rapidly form inner-sphere adducts with **1** (24) and analogous complexes (25). Similar adducts seem reasonable with hydroxylamine. The absorbance versus time data at 510 nm obeyed first-order kinetics at least up to 95% reaction. Table 1 shows that k_o decreases with increasing c_{phen} until a constant value is reached for c_{phen} > 1 mM. Qualitatively, the data indicate that **1d** is more reactive than 1 and that [**1d**] decreases with increasing [phen] until [**1d**] becomes kinetically negligible. The value of k_o increases linearly with c_R (≤ 0.05 M), decreases with increase in pH, but does not change (± 5%) with a ten-fold (0.05–0.005 mM) change in concentration of complex. Values of k_o also do not change (± 3%) on changing the monitoring wavelength from 510 to 365 nm, or when the reaction media were purged with dinitrogen, or when stray light was excluded. Scheme 1 seems to be a reasonable explanation for the observed kinetics and equilibria.

Table 1 First-order rate constants.[a]

pH	$c_R \times 10^3$ (M)	$c_{phen} \times 10^3$ (M)	$k_o \times 10^2$ (s^{-1})[b]
3.00	20.0	3.0	0.01 (0.006)
3.50			0.02 (0.015)
4.00			0.04 (0.04)
4.50			0.16 (0.15)
5.00			0.85 (0.88)
5.26			2.17 (2.08)
5.50			4.27 (4.19)
5.70			7.50 (6.9)
5.85			9.61 (9.3)
6.00			13 (12)
4.50	5.0		0.04 (0.037)
	10.0		0.08 (0.074)
	15.0		0.12 (0.11)
	20.0		0.16 (0.15)
	25.0		0.17 (0.18)
	30.0		0.23 (0.22)
	35.0		0.25 (0.26)
	40.0		0.28 (0.30)
4.5	45.0	3.0	0.35 (0.33)
	50.0		0.39 (0.37)
	20.0	0.05	0.81 (0.39)
		0.10	0.34 (0.29)
		0.20	0.23 (0.22)
		0.30	0.17 (0.17)
		0.40	0.18 (0.18)
		0.50	0.155 (0.17)
		0.60	0.155 (0.17)
		1.00	0.15 (0.159)
		2.00	0.145 (0.151)
		4.00	0.150 (0.147)
		6.00	0.145 (0.146)

[a] Temperature, 30.0°C; concentration of complex, 0.05 mM; *I*, 1.0 M ($NaNO_3$).

[b] Average of two or three determinations; standard deviation, 2–4%; parenthetical values are calculated using eq. [10].

Scheme 1

$$\mathbf{1} \rightleftharpoons \mathbf{2} + H^+, \qquad K_{a1} = 4.0 \times 10^{-6}\ M$$

$$\mathbf{1} \rightleftharpoons \mathbf{1d} + \text{phen}, \qquad K_d = 5.0 \times 10^{-6}\ M$$

$$Hphen^+ \rightleftharpoons H^+ + \text{phen}, \qquad K_{Hphen} = 1.2 \times 10^{-5}\ M$$

$$NH_3OH^+ \rightleftharpoons H^+ + NH_2OH, \qquad K_a = 1 \times 10^{-6}\ M \text{ (23)}$$

$$\mathbf{1} + NH_2OH \overset{K_1}{\rightleftharpoons} \mathbf{I_1} \overset{k_1}{\rightarrow} \text{products}$$

$$\mathbf{2} + NH_2OH \overset{K_2}{\rightleftharpoons} \mathbf{I_2} \overset{k_2}{\rightarrow} \text{products}$$

$$\mathbf{1d} + NH_2OH \overset{K_3}{\rightleftharpoons} \mathbf{I_3} \overset{k_3}{\rightarrow} \text{products}$$

In this scheme, $\mathbf{I_1}$ is $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)(NH_2OH)]^{4+}$, $\mathbf{I_2}$ is $[Fe_2(\mu\text{-}O)(phen)_4\text{-}(OH)(NH_2OH)]^{3+}$, $\mathbf{I_3}$ is $[Fe_2(\mu\text{-}O)(phen)_3(H_2O)_3(NH_2OH)]^{4+}$; **1**, **2**, and **1d** are as defined previously.

Provided $K_i[NH_2OH] << 1$ ($i = 1$–4) and $c_R >> c_{Fe}$, the scheme leads to eq. [10].

$$[10] \quad k_o\{([H^+] + K_{a1})[phen] + K_d[H^+]\}/ [NH_2OH] = (k_1K_1[H^+] + k_2K_2K_{a1})[phen] + k_3K_3K_d[H^+] = m_1[phen] + c_1 \text{ (say)}$$

The assumption, $K_i[R] << 1$ seems justified because k_o and the absorbance at the isosbestic point increase linearly with c_R. The maximum value of $[NH_2OH]$ used in kinetics is 0.015 M (pH 4.50, $c_R = 0.05$ M) up to which we observed no indication for rate saturation. Hence, an upper limit for K_i is 5 M^{-1}. Stynes and co-workers (26) noted that weakly basic amines form weak adducts with the oxo-bridged diiron complex $[Fe^{III}(dmgBF_2)_2]_2O$, ($dmgBF_2$ is difluoro(dimethylglyoximato)borate). Hydroxylamine is a weak base and hence expected to form weak adducts with **1** and its derivatives. Hydroxylamine can form O-bonded complexes, but stability constants for such complexes also are very small ($K \leq 0.1$) (21*a*). It is not possible for NH_3OH^+ to coordinate to Fe^{III} without loss of a proton first. Hence, the small values for K_i and the weak acidity of NH_3OH^+ excludes the possibility of NH_3OH^+ to act as an active reducing agent.

The k_o data at fixed pH (4.50) and c_R (0.020 M) but variable c_{phen} yielded a good fit ($r = 0.9989$; $m_1 = 8.29 \times 10^{-5}$; $c_1 = 2.92 \times 10^{-9}$) into eq. [10]. However, a better fit results ($r = 0.9997$; $m_1 = 8.43 \times 10^{-5}$; $c_1 = 1.40 \times 10^{-9}$) if k_o data at the three lowest c_{phen} (0.05, 0.10, 0.20 mM) are excluded (Fig. 3). In the presence of excess phen, [**1d**] is negligible compared to ([**1**] + [**2**]), and (K_{a1} + [H^+])[phen] is >> $K_d[H^+]$. Equation [10] may then be transformed to equation [11].

$$[11] \quad k_o([H^+] + K_{a1})([H^+] + K_a) / c_R = a[H^+]^2 + b[H^+] + c$$

where $a = k_3K_3K_dK_a/K_{Hphen}c_{phen}$, $b = (k_1K_1K_a + k_3K_3K_dK_a/c_{phen})$, and $c = k_2K_2K_{a1}K_a$. Values for k_o at different pH (≥3.5) but fixed c_{phen} and c_R were fitted into eq. [11] and yielded $a = (2.66 \pm 0.01) \times 10^{-3}$ M^{-1} s^{-1}, $b = (2.31 \pm 0.003) \times 10^{-6}$ s^{-1}, and $c = (5.46 \pm 0.03) \times 10^{-11}$ M s^{-1}. From these values, one can extract $k_1K_1 = 0.93 \pm 0.005$ M^{-1} s^{-1}, $k_2K_2 = 13.6 \pm 0.06$ M^{-1} s^{-1}, $k_3K_3 = 19.1 \pm 0.04$ M^{-1} s^{-1}. These parameters and eq. [10] generally reproduce k_o values within ± 10% (see parenthetical values in Table 1). The calculated values also follow the expected trend of variation, but they are considerably smaller than the experimental data when [phen] is very low. Trace-metal ion catalysis may become effective at low [phen] and is a probable cause for the observed deviations.

The second-order rate constants are composite constants (K_ik_i) and both K_i and k_i can control the reactivity of the intermediates. A higher value for K_3 than either K_1 or K_2 seems reasonable, since an iron(III) centre in **1d** should be more electron deficient than that in either **1** or **2**. Moreover, **1d** is structurally less rigid due to the absence of a bulky phen ligand, and can easily accommodate structural changes associated with the electron transfer step,

$$\{Fe^{III}_2O\}^{4+} \rightarrow \{Fe^{III}Fe^{II}O\}^{3+}$$

On this ground, k_3 is likely to be larger than both k_1 and k_2. The higher reactivity of $\mathbf{I_3}$ thus seems justified. It is more difficult to assess the order of reactivity of $\mathbf{I_1}$ with respect to $\mathbf{I_2}$. The water molecule in $\mathbf{I_1}$ is ≈4 times a stronger acid than NH_3OH^+. So internal proton transfer in $\mathbf{I_1}$ may weaken the adduct. This is not possible for $\mathbf{I_2}$. Thus, K_1 should be less than K_2. On the other hand, the smaller charge borne by $\mathbf{I_2}$ should render an intramolecular electron transfer less facile, and k_1 is expected to be greater than k_2. The overall effect of such opposing factors is difficult to predict.

Concentration of the dihydroxo species **3** is very small in the pH range used in kinetics. It does not contain any replaceable water molecule, and all the ligands present are held more tightly than H_2O. It should also be a weak oxidant due to the smaller positive charge on its iron(III) centres. Kinetic activity of **3** is therefore inappreciable in the range pH 3–6.

Conversion of intermediates $\mathbf{I_1}$–$\mathbf{I_3}$ to products must be multistep processes. We propose the rate-determining steps to be one-electron reduction of the intermediates to respective Fe^{II}-O-Fe^{III} dimers, which quickly collapse to Fe^{II} and Fe^{III} monomers. The iron(III) monomer $[Fe(phen)_2(H_2O)_2]^{3+}$ is further reduced to the iron(II) monomer $[Fe(phen)_2(H_2O)_2]^{2+}$, which rapidly forms **4** in the presence of phen. We have verified that $[Fe(phen)_3]^{3+}$ is reduced by hydroxylamine within the time of mixing; $[Fe(phen)_2(H_2O)_2]^{3+}$ is expected to react faster. It is also known that formation of **4** from Fe^{2+} and excess phen is a fast reaction (27) (rate constant ~10^5 s^{-1}). Inner-sphere reduction of $[Fe(phen)_3]^{3+}$ by NH_2OH should be slow since substitution on this iron(III) complex is slow. Such is not the case for the diaqua derivative. Even with $[Fe(phen)_3]^{3+}$ the outer-sphere reaction should be fast. We used simple Marcus relation to calculate the rate constant for outer-sphere oxidation of NH_2OH by $[Fe(phen)_3]^{3+}$ to be 490 $M^{-1}s^{-1}$. Consequently, even at the lowest c_R (= 0.005 M,) used in kinetics, half life for this reaction is only 0.28 s. The parameters used in this calculation are $E^0 = 1.05$ V for the couple $[Fe(phen)_3]^{3+/2+}$, its self-exchange rate constant (≈10^7 M^{-1} s^{-1}) (28), $E^0 = 0.42$ V for the couple NH_2OH^+/ NH_2OH, and its self-exchange rate constant, 5×10^{-13} M^{-1} s^{-1} (8).

Further, the oxo bridge in **1** is stable, and the complex suffers no autodecomposition within the time of kinetic studies. Martell and co-workers (29) explained that the $\{Fe_2O\}^{4+}$ core unit gains stability from superexchange of the d^5 high-spin iron(III) centres across the oxo bridge. But the high-spin Fe^{II} and Fe^{III} are probably less strongly bound to O^{2-}, since both oxidation states have two *anti* bonding electrons directed towards the formal bond axes. This would impart weaker Fe^{II}—O—Fe^{III} and Fe^{II}—O—Fe^{II} bonds, both of which should be rapidly broken by aquation. In fact the oxo bridge in the mixed valence system Fe^{II}-O-Fe^{III} is rare and in general putative outside a protein environment (1*c*). It thus appears that reduction of $\{Fe_2O\}^{4+}$ complexes by hydroxylamine involves several steps, but the rate-determining step is

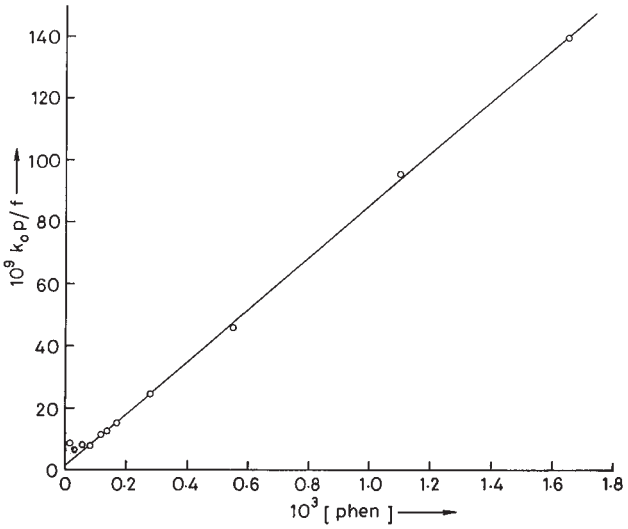
$$\{Fe_2O\}^{4+} \rightarrow \{Fe_2O\}^{3+}$$

All other steps are either too fast or too slow to qualify as the rate-determining step. The immediate oxidation product of hydroxylamine should be NH_2OH^+. This is known to generate N_2O via HNO (20*a*, 23):

$$NH_2OH \rightarrow H^+ + NHOH + e^- \rightarrow H^+ + HNO + e^- \rightarrow 0.5N_2O + 0.5H_2O$$

The values for K_i could refer to outer-sphere precursor complex formation. However, hydroxylamine has a record low self-exchange rate constant, and outer-sphere reactions occur very rarely with NH_2OH in spite of its moderately low $E°$ value. We observed that **1** does not oxidize $[Fe(CN)_6]^{4-}$,

Fig. 3. Effect of phenanthroline on rate constants at a fixed pH (4.50), c_R (0.05 mM), and I (1.0 M); $p = ([H^+] + K_{a1})[phen] + K_d[H^+]$; $f = K_a c_R/(K_a + [H^+])$. The solid line is drawn using least-squares slope and intercept.



indicating for **1** a reduction potential less than that for the $[Fe(CN)_6]^{4-/3-}$ couple (0.46 V). Calculations using simple Marcus relation ($k_{12} = (k_{11}k_{22}K_{12})^{1/2}$) for outer-sphere reactions with k_iK_i used as k_{12} values imply impossibly high self-exchange rate constants ($k_{11} > 10^{10}$) for the $\{Fe_2O\}^{4+}$ complexes. The calculations refute an outer-sphere mechanism in the present system.

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