DALTON
FULL PAPER

The kinetics and mechanism of oxidation of hydroxylamine by iron(III)

Gösta Bengtsson,†[a] **Sture Fronæus**[a] **and Lars Bengtsson-Kloo**[b]

[a] *Inorganic Chemistry, Chemical Center, Lund University, P.O.Box 124, S-221 00 Lund, Sweden*
[b] *Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden*

Received 12th February 2002, Accepted 18th March 2002
First published as an Advance Article on the web 3rd May 2002

The kinetics of oxidation of hydroxylamine by iron(III) have been studied spectrophotometrically. The effects of pH, reactant and product concentrations led to two experimental rate expressions. The results obtained are consistent with a mechanism dependent on the relative iron(III)-to-hydroxylamine concentrations; an excess of iron(III) gives a stoichiometry of 2 : 1 for the total reaction and N_2O as the oxidation product, whereas at equal amounts or excess of hydroxylamine the stoichiometry reduces to 1 : 1 with N_2 as the main product . In the latter case the rate expression $-d[Fe(III)]/dt = k[Fe(III)]^2[NH_2OH]^2/[Fe(II)]^2[H^+]^4$ is obtained. The consistent mechanism identifies two pre-equilibria and the reaction of two different nitrogen-containing intermediates as the rate-determining step depending on the reactant ratios. The proposed mechanism does also involve the metal hydroxide complex $Fe(OH)^{2+}$, in agreement with previous results.

1 Introduction

The quest to understand the process of nitrogen fixation has received much attention. Such efforts have intensified following reports about the structure of the FeMo-cofactor of dinitrogenase in 1992.[1] Nitrogen as an element is rather unique in its ability to form (relatively) stable molecules in formal oxidation states from −III to +V, and it is obvious that there are many intermediates in the nitrogen fixation process from N_2 to NH_4^+. There are many recent studies exploring the role of iron in biological systems or model systems in the redox reactions of hydroxylamine.[2–4] The role of vanadium(V) as an oxidising agent has also been investigated for similar purposes.[5–6]

In an early study,[7] the main features of the mechanism of the oxidation of hydroxylammonium ion by iron(III) were determined. The rate expression was found to be complex, being second-order with respect to both iron(III) and the hydroxylammonium ion and inversely dependent on the square of the iron(II) concentration. The reaction was also found to be strongly inhibited by hydrogen ions. Reactions with similar rate expressions have been published. Barney, in his study of plutonium(IV) with hydroxylamine, has even suggested that the mechanism postulated for this reaction would also be applicable to the reaction of hydroxylamine with iron(III).[8] A key step in the proposed mechanism involves the reaction between hydroxylamine and a hydrolysed metal ion, $M(OH)^{(m-1)+}$. This idea has also been exploited in more recent work involving iron(III) as an oxidising agent or catalyst.[9–10] Therefore, it seemed worthwhile to perform a more detailed study of the iron(III) hydroxylamine system with the objective of either supporting or contradicting the mechanism proposed by Barney.

2 Experimental

The chemicals used in this study were all of analytical reagent grade. All solutions were prepared with triply distilled water. The iron(III) and iron(II) salts used were the perchlorates (G.F. Smith, Chemical Co., Columbus, OH). However, iron(II) stock solutions were mainly prepared by dissolving pure iron metal thread in 2.00 M air-free perchloric acid with gentle heating to obtain a reasonable reaction rate. The perchloric acid solution was previously freed from dissolved air by evacuation. The freshly prepared solution was diluted with air-free water and stored in a flask with minimum air present under the cap. With these precautions, the iron(II) solutions were only slowly oxidized. The iron(III) concentrations given in this paper include the small contributions from any iron(II) solution added. The iron stock solutions were standardized for iron(III) either spectrophotometrically or by titration with permanganate solution, after passage through a column of finely grained cadmium. The spectrophotometric determination of iron(III) was carried out at a wavelength of 240 nm. The molar absorption coefficient of iron(III) in 0.100 M $HClO_4$ + 0.90 M $NaClO_4$ [$(4.25 \pm 0.02)\ 10^3\ M^{-1}\ cm^{-1}$] was determined by dissolving an accurately weighed amount of iron metal thread in perchloric acid solution, boiling the solution with a large excess of hydrogen peroxide and measuring the absorbance after dilution to give measurable absorbances. The two methods gave consistent results within narrow limits.

Hydroxylamine stock solutions were prepared from hydroxylammonium chloride (Riedel de Haën) or hydroxylammonium sulfate (Merck). In most experiments, hydroxylammonium perchlorate solutions were used in order to avoid the complications arising with chloride or sulfate ions present. Hydroxylammonium perchlorate solutions were prepared by adding an equivalent amount of $Ba(ClO_4)_2{\cdot}3H_2O$ (Fluka) to hydroxylammonium sulfate solutions and filtering out the barium sulfate precipitation formed. The concentrations of these hydroxylamine solutions were checked bromatometrically,[11] and were found to agree within very narrow limits (<0.5%) with those calculated from the weight of the salt in question. The solutions, including those of hydroxylammonium perchlorate, were found to be stable for at least a week.

Initial rates of reaction were evaluated from A *vs.* t or $1/A$ *vs.* t plots; the latter normally having a more gentle curvature [$-(\Delta A/\Delta t)_o = A_o^2\ (\Delta\{1/A\}/\Delta t)$]. This evaluation was confined to the region $A_t/A_o \geq 0.95$, except for a few cases with very rapid reaction or low initial absorbance. Every initial rate given in this paper represents the mean value of at least three separate determinations. Whenever possible, linear relationships were

---

† Deceased 1984.

DOI: 10.1039/b201602h

deduced and a least-squares fit was applied to the experimental values. The error limits given represent a confidence level of 99.9%. The temperature was (25.0 ± 0.1) °C and the ionic strength 1.0 M. The spectrophotometric measurements were carried out using a Zeiss PMQ II and a Perkin Elmer 330 recording spectrophotometer.

3 Measurements and results

3.1 Absorption curves

The absorption curves within the wavelength range 220–320 nm [where the charge-transfer band of iron(III) appears] were recorded for the following four solutions: 1, 0.223 mM Fe^{3+}; 2, 0.223 mM Fe^{3+} + 0.273 mM Fe^{2+}; 3, 0.223 mM Fe^{3+} + 0.273 mM Fe^{2+} + 50.0 mM $[NH_3OH]ClO_4$; 4, 0.223 mM Fe^{3+} + 0.273 mM Fe^{2+} + 50.0 mM $[NH_3OH]Cl$. All these solutions were 0.100 M in $HClO_4$ and contained $NaClO_4$ to yield the ionic strength 1.00 M. The absorption curves for the solutions containing NH_3OH^+ were obtained by recording a series of curves at intervals of 2.00 minutes after mixing the reactant solutions and extrapolating the absorbance at a few evenly spaced wavelengths to $t = 0$.

The absorption curves of the first three solutions mentioned above were identical, within experimental error, showing a single, broad band with a maximum at 240 nm and the emergence of another band below at about 230 nm. The absorption curve obtained with hydroxylammonium chloride had, however, a slightly different appearance, exhibiting slightly higher absorbance for wavelengths above 260 nm. The observations described here were supported by the fact that in the wavelength range 280–300 nm A_o was independent of C_L ‡ for hydroxylammonium perchlorate but increased with increasing C_L for hydroxylammonium chloride. This effect seems to be due to the formation of chloroiron(III) complexes, such as $FeCl^{2+}$. Hydroxylammonium sulfate seemed to behave in a similar way as the chloride. The first formation constant for the chloride complex at 25 °C and the ionic strength 1.0 M is $\beta_1 = 2.9\ M^{-1}$. Other chloroiron(III) complexes seem to be negligible at the C_{Cl} ‡ values used in this study.

3.2 Stoichiometry

The stoichiometry of this reaction would perhaps seem to be well established by the use of the reaction for quantitative determination of hydroxylamine according to Raschig (*cf.* ref. 11). However, this method requires at least a three-fold excess of iron(III) and the boiling of the mixture. Otherwise, too low amounts are obtained with respect to the expected $\Delta C_{Fe3}/\Delta C_L = 2$.‡ This, together with the observation that most oxidations of hydroxylamine have variable stoichiometry, mainly depending on the relative concentrations of the reactants, made us determine the stoichiometry at different ratios C_L/C_{Fe3} ranging from 0.1 to 5. The reactions were not complete even after more than a week, so both residual iron(III) and hydroxylamine had to be determined in all cases. However, the reaction proceeded so slowly a couple of days after mixing the reactants that no appreciable change of the iron(III) concentration could be observed during the time required to carry out the complete analysis. The following procedure was applied: aliquots were extracted from the reaction mixtures, which had been kept at 25 °C for at least 100 hours. Residual iron(III) was determined spectrophotometrically after suitable dilution with the ionic medium. Residual NH_3OH^+ was determined bromatometrically after removal of iron ions as hydroxide precipitates by the addition of a slight excess of sodium hydroxide solution (0.10 M). A faint smell of ammonia could be noticed after the addition of sodium hydroxide, indicating disproportionation of hydroxylamine. A calibration curve was constructed with solutions containing a known amount of hydroxylamine and about the same concentration of iron(II) as the solutions to be analysed. By rigorously controlling the conditions at which the analyses were carried out, it was possible to reduce the scatter between repeated determinations of the same hydroxylamine concentration to less than 1%, although there was a decrease of about 10% of the actual hydroxylammonium concentration during the analytical procedure. The results shown in Table 1 imply a variable stoichiometry also in this system. With an excess of NH_3OH^+ the stoichiometry may be represented by the formula

$$Fe^{3+} + NH_3OH^+ \longrightarrow Fe^{2+} + 1/2N_2 + 2H^+ + H_2O \quad (1)$$

and with at least a five- to ten-fold excess of iron(III)

$$2Fe^{3+} + NH_3OH^+ \longrightarrow 2Fe^{2+} + 1/2N_2O + 3H^+ + 1/2H_2O \quad (2)$$

3.3 Polymerisation tests

The oxidation of hydroxylamine by one-equivalent of oxidants is usually assumed to proceed *via* free radical intermediates. The possible occurrence of free radicals in this reaction was tested by the addition of acrylonitrile (15% by volume) to the following solutions: 1, 0.10 M Fe^{3+}; 2, 0.200 M $[NH_3OH]ClO_4$; 3, 0.05 M Fe^{3+} + 10 mM $[NH_3OH]ClO_4$; 4, 10 mM Fe^{3+} + 0.05 M $[NH_3OH]ClO_4$; all in 0.100 M $HClO_4$ + 0.90 M $NaClO_4$. Solutions 3 and 4 became turbid on addition of acrylonitrile, whereas solutions 1 and 2 remained perfectly clear. In order to test the procedure on other systems, one of which has been shown to proceed *via* a free radical mechanism, it was applied also to the systems Ce(IV) + NH_3OH^+ and V(V) + NH_3OH^+.[5,12,13] These reacting systems gave rise to polymerisation, but the individual reactants [*i.e.* Ce(IV), V(V) and NH_3OH^+] did not.

3.4 Rate expression

The rate law was determined by the method of initial rates using solutions initially containing comparable concentrations of iron(III) and iron(II) together with a large excess of hydroxylammonium. Under these conditions, the change in reaction rate becomes sufficiently slow for reliable values of v_o to be obtainable. Figs. 1–4 show the dependence of v_o on C_{Fe3}, C_{Fe2}, C_L and $[H^+]$, respectively. ‡ The quantities shown on the ordinate axes have been chosen such as to, as clearly as possible, show the dependence on the variables shown on abscissa. The values shown in Figs. 1–2 have been obtained with hydroxylammonium chloride (*i.e.* $C_{Cl} = C_L$ = 20.0 mM). Fig. 3 shows, in principle, two sets of data; obtained with and without chloride ions present ($C_{Cl} = C_L$). The values of v_o in this figure have been recalculated to equivalent values of C_{Fe3} and C_{Fe2} through multiplication with the quotient $(C_{Fe3}/C_{Fe2})^2$. A third set of values was obtained by making allowance for the iron(III) being present as $FeCl^{2+}$ in the presence of Cl^- [$C_{Fe3}corr = C_{Fe3}/(1 + \beta_1 C_{Cl})$, where $\beta_1 = 2.89\ M^{-1}$; the stability constant of $FeCl^{2+}$]. After this correction the data coincide within experimental

---

‡ Symbols, notations and equations used: C_{Fe3} overall initial concentration of iron(III) (mol L^{-1}). C_{Fe2} overall initial concentration of iron(II) (mol L^{-1}). C_L overall initial concentration of hydroxylamine (mol L^{-1}). C_{Cl} overall concentration of chloride ions (mol L^{-1}). [Fe(III)] total concentration of iron(III), including complexes, at time *t*. [Fe(II)] total concentration of iron(II), including complexes, at time *t*. *A* absorbance. *b* path length (cm). ε_X molar absorption coefficient of the species indicated ($M^{-1}\ cm^{-1}$). ε formal molar absorption coefficient of a solution containing both iron(III) and a suitable complex-forming agent, such as the chloride ion ($M^{-1}\ cm^{-1}$); $\varepsilon = A/bC_{Fe3}(1 + \Sigma\beta_n[\text{Ligand}]^n)$. λ wavelength (nm). *t* time after mixing of the reactant solutions (s). $v_o$initial reaction rate ($M\ s^{-1}$); $v_o = -(\Delta A/b\varepsilon\Delta t)_{t=0} = -(\Delta C_{Fe3}/\Delta t)_{t=0}$. μ ionic strength (mol L^{-1}). Indices 0, *t* and ∞ denote the times 0, *t* and eternity (*i.e.* complete reaction) after mixing of the reactant solutions.

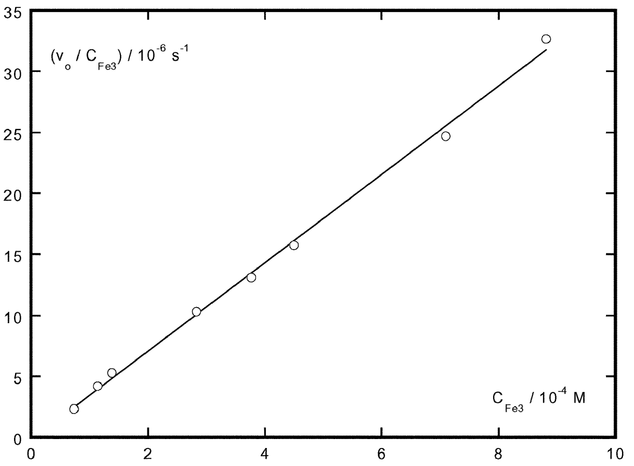

Fig. 1 v_o/C_{Fe3} *vs.* C_{Fe3}. C_{Fe2} = 0.259 mM, C_L = 0.200 mM, C_{Cl} = C_L, $[H^+]$ = 0.100 M.

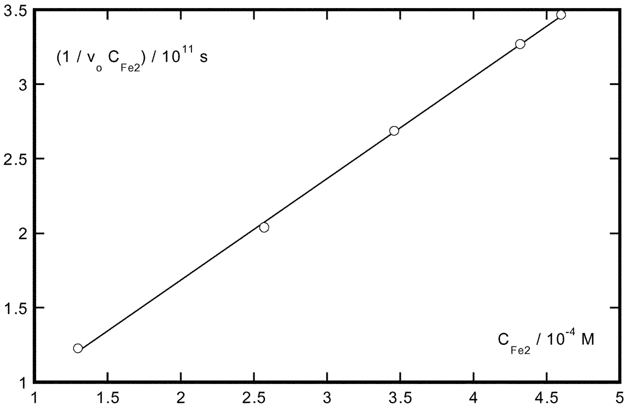

Fig. 2 $1/(v_o\ C_{Fe2})$ *vs.* C_{Fe2}. C_{Fe3} = 0.450 mM, C_L = 20.0 mM, C_{Cl} = C_L, $[H^+]$ = 0.100 M.

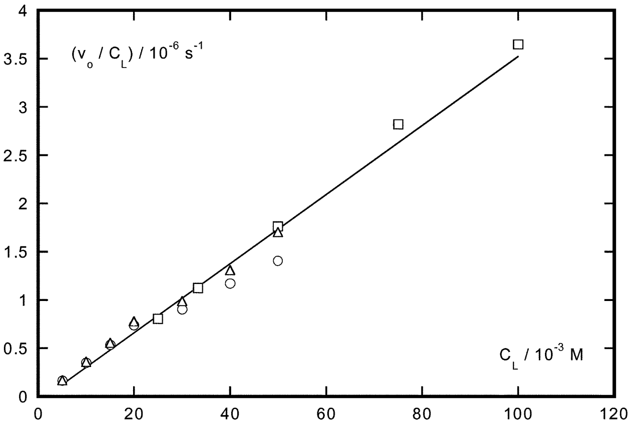

Fig. 3 v_o/C_L *vs.* C_L. C_{Fe3} = 0.224 mM, C_{Fe2} = 0.507 mM, C_{Cl} = 0 or C_L, $[H^+]$ = 0.099 M. Triangles and squares represent two separate but overlapping series of experiments with L = ClO_4; Rings represent L = Cl.

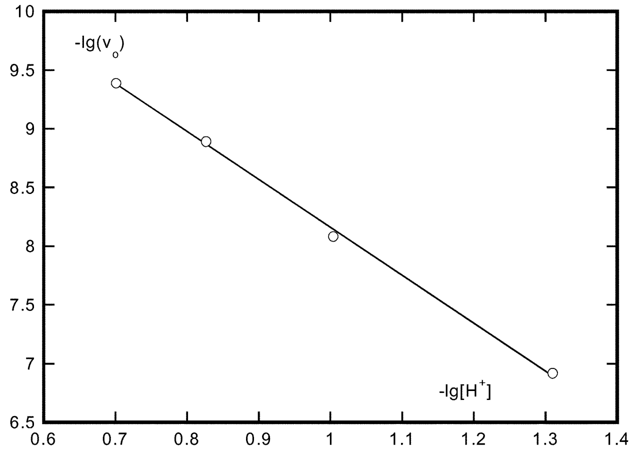

Fig. 4 $-\lg(v_o)$ *vs.* $-\lg[H^+]$. C_{Fe3} = 0.227 mM, C_{Fe2} = 0.500 mM, C_L = 50.0 mM, C_{Cl} = 0.

errors. Other chloro complexes were neglected. No allowance was made for iron(III) present as $FeOH^{2+}$ (about 2% at $[H^+]$ = 0.100 M). The results shown in Fig. 4 were obtained with hydroxylammonium perchlorate.

The results represented in Figs. 1–4 can (corrected for the presence of chloride ions, thus formally in the absence of these) be summarized in the empirical rate law

$$v_o = kC_{Fe3}^2 C_L^2/C_{Fe2}^2[H^+]^4 \quad (3)$$

or, since there is a low concentration of the complex of iron(III) with hydroxylamine

$$-d[Fe^{3+}]/dt = k[Fe^{3+}]^2[NH_3OH^+]^2/[Fe^{2+}]^2[H^+]^4 \quad (4)$$

A mean value of the experimental rate constant k = (1.85 ± 0.07) 10^{-9} M^3 s^{-1} was obtained from the data shown in Figs. 1–3.

The rate expression can be integrated, and if $[H^+]$ and C_L are much greater than C_{Fe3} and C_{Fe2} = 0 at t = 0, the integrated rate law can be written in the form

$$A_o/A_t - A_t/A_o - 2\ln(A_o/A_t) = k_{obs}\, t \quad (5)$$

where

$$k_{obs} = k[NH_2OH]^2/[Fe^{3+}]_0[H^+]^4 \quad (6)$$

Fig. 5 shows the left-hand side of eqn. (5) (Z *vs.* t) for a series of measurements at different C_L. The quantity Z is, in principle, a minute difference between two much larger quantities, and is consequently very sensitive to small experimental errors. This is particularly important at the beginning of a run. When the absorbance has decreased to low values (<0.2), the values of Z also become very sensitive to experimental errors. The lines in Fig. 5 have therefore been confined to the region where $0.2 \le A_t/A_o \le 0.6$, where the magnification of the experimental errors is less than a factor of 10. The curves in Fig. 5 are linear and pass almost through the origin. The average value of k obtained from these measurements is (1.2 ± 0.2) 10^{-9} M^3 s^{-1} in acceptable agreement with that obtained from initial rates (see section 4.3).

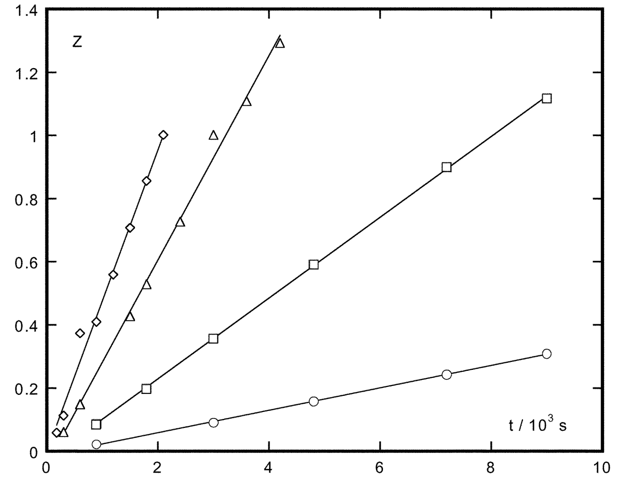

Fig. 5 Application of the integrated rate equation. The quantity Z *vs.* t. C_{Fe3} = 0.219 mM, C_{Fe2} = 0, C_{Cl} = 0, and C_L = 25.0 (○), 50.0 (□), 75.0 (△) and 100.0 (◇) mM, respectively.

4 Discussion

4.1 General

The results of this study show a similarity with those obtained by Barney for the reduction of plutonium(IV) by hydroxylammonium ion.[8]

The stoichiometry is dependent on the proportions between the reactants; with an excess of hydroxylamine nitrogen gas and with a five- to ten-fold excess of iron(III) dinitrogen oxide is formed. The formation of gas bubbles can be observed, if the reactant concentrations are high enough. In an intermediate region of C_L/C_{Fe3} a mixture of N_2 and N_2O should be obtained.

The polymerisation tests with acrylonitrile indicate the participation of free radicals, just as has been observed in the oxidation of hydroxylamine by cerium(IV), hexachloroplatinate(IV) and hexachloroiridate(IV).

4.2 Mechanism

The occurrence of $[Fe^{2+}]$ in the rate equation implies a rapid reversible redox reaction prior to the rate-limiting step. In the latter, two nitrogen-containing intermediates, produced in the pre-equilibrium, seem to be involved. This accounts for the second-order dependence on both $[Fe^{3+}]$ and $[NH_3OH^+]$. Barney suggested a dimerisation of the radical $NH_2O^{\bullet}$ as the rate-limiting step.

The initial absorbance at 300 nm for a constant value of $[Fe^{3+}]$ increases markedly at increasing values of $[NH_2OH]$, whereas at the maximum of the absorption curve of iron(III) at 240 nm no change could be observed. A probable interpretation is that the initial step of the reaction is a rapid formation of a precursor complex $Fe(NH_2OH)^{3+}$ that may be formed from NH_3OH^+ and Fe^{3+} or $Fe(OH)^{2+}$. In the latter case the rate constant is presumably the highest, since no H^+ has to be released. This is in agreement with Barney's theory.[8] The complex formed should be an intermediate of low concentration that decomposes in the first step of the oxidation of NH_2OH. The observation that the stoichiometry of the reaction is different for low and high values of C_{Fe3}/C_L indicates that iron(III) can participate in two steps of the oxidation of hydroxylamine. In addition to the equilibria shown in eqn. (7) and (8)

$$NH_3OH^+ \rightleftharpoons NH_2OH + H^+, \text{ acid constant } K_a \qquad (7)$$

$$Fe^{3+} + NH_2OH \rightleftharpoons Fe(NH_2OH)^{3+}, \text{ stability constant } \beta_1' \qquad (8)$$

we suggest the following reaction scheme:

$$Fe(NH_2OH)^{3+} \rightleftharpoons Fe^{2+} + H_2NO^{\bullet} + H^+ \qquad (9)$$

$$Fe^{3+} + H_2NO^{\bullet} \rightleftharpoons Fe^{2+} + HNO + H^+ \qquad (10)$$

$$2\,H_2NO^{\bullet} \longrightarrow N_2 + 2\,H_2O \qquad (11)$$

$$2\,HNO \longrightarrow N_2O + H_2O \qquad (12)$$

If the steady-state approximation is applied to the intermediates $H_2NO^{\bullet}$ and HNO, the following relationships are obtained, where r_j denotes the rate of reaction (j) and r_{-j} the rate of the reverse reaction.

$$r_9 - r_{-9} - r_{10} + r_{-10} - 2r_{11} = 0 \qquad (13)$$

$$r_{10} - r_{-10} - 2r_{12} = 0 \qquad (14)$$

$$-d[NH_2OH]/dt = r_{11} + 2r_{12} \qquad (15)$$

$$-d[Fe^{3+}]/dt = 2r_{11} + 4r_{12} \qquad (16)$$

Table 1 Stoichiometries

C_{Fe3}/mM	C_L/mM	$\Delta C_{Fe3}/\Delta C_L$
43.9	5.00	1.98
43.9	10.00	1.48
17.51	50.0	1.03
8.75	50.0	1.02

Stoichiometry:

$$d[Fe^{3+}]/d[NH_2OH] = (r_{11} + 2r_{12})/(r_{11} + r_{12}) \qquad (17)$$

Now, let us consider two limiting cases:

A. $[Fe^{3+}] < [NH_3OH^+]$, some Fe^{2+} also added. As it has been found from the measurements that the stoichiometry is 1 : 1 in this case and only N_2 is formed, we must have $r_{12} = 0$. Then, eqn. (16) yields $-d[Fe^{3+}]/dt = 2r_{11}$. Furthermore, eqn. (13) and (14) yield $r_9 - r_{-9} = 2r_{11}$, and since the rate r_9 of the intramolecular electron transfer most likely is much higher than that of the bimolecular reaction (11), it follows that $r_9 \approx r_{-9}$. By inserting the expressions for r_j (with k_j as the corresponding rate constants) and eliminating $[H_2NO^{\bullet}]$, $[NH_2OH]$ and $[Fe(NH_2OH)^{3+}]$ by combination of the equations obtained for $-d[Fe^{3+}]/dt$ and r_9 and the equilibria (7) and (8) we get the rate law of eqn. (18).

$$-d[Fe^{3+}]/dt = B[Fe^{3+}]^2[NH_3OH^+]^2/[Fe^{2+}]^2[H^+]^4 \qquad (18)$$

where $[Fe^{3+}] \approx [Fe(III)]$, $[Fe^{2+}] = [Fe(II)]$ and

$$B = 2k_9^2 k_{11}\,(\beta_1')^2 K_a^2/k_{-9}^2 \qquad (19)$$

By adding the reaction steps (7), (8), (9) and (11) we arrive at the total reaction (20).

$$Fe^{3+} + NH_3OH^+ \longrightarrow Fe^{2+} + 1/2N_2 + 2H^+ + H_2O \qquad (20)$$

In case **A** reaction (11) is the rate-determining step

B. $[Fe^{3+}] \gg [NH_3OH^+]$. If measurements of the stoichiometry (Table 1) indicate that $d[Fe^{3+}]/d[NH_2OH] = 2$, and only N_2O is formed, we have $r_{11} = 0$. Then, eqn. (16) yields $-d[Fe^{3+}]/dt = 4\,r_{12}$ and from eqn. (13) and (14) we get $r_9 - r_{-9} = 2r_{12}$ and $r_{10} - r_{-10} = 2r_{12}$. For high values of $[Fe^{3+}]$ it is likely that $r_{10} \gg r_{-10}$ and thus it follows that $2r_{12} \approx r_{10}$ and $r_9 \approx r_{-9} + r_{10}$. Inserting the expressions for r_9, r_{-9} and r_{10} and making use of eqn. (7) and (8), we obtain the rate law (21) at elimination of $[H_2NO^{\bullet}]$.

$$-d[Fe^{3+}]/dt = B'[Fe^{3+}]^2[NH_3OH^+]/([Fe^{2+}]\,[H^+]^2 + C'[Fe^{3+}][H^+]) \qquad (21)$$

where $[Fe^{3+}] \approx [Fe(III)]$, $[Fe^{2+}] = [Fe(II)]$ and

$$B' = 2k_9\,k_{10}\,(\beta_1')\,K_a/k_{-9} \text{ and } C' = k_{10}/k_{-9} \qquad (22)$$

Addition of the reaction steps (7), (8), (9), (10) and (12) yields the total reaction (23).

$$2Fe^{3+} + NH_3OH^+ \longrightarrow 2Fe^{2+} + 1/2N_2O + 3H^+ + 1/2H_2O \qquad (23)$$

In case **B**, reaction (12) is the rate-determining step.

4.3 Conclusions

It is clear from the measurements that the ratio C_{Fe3}/C_L has a large influence on the stoichiometry of the redox reaction and also on the rate law, which has been deduced only for the two limiting values 1 : 1 and 2 : 1 of Δ[Fe(III)]/Δ[NH_2OH]. Consequently, other measurements giving a stoichiometry between these limits can give an empirical rate law that is quite different from both eqn. (18) and (21). From the description in section 3.2 of the Measurements and results it is evident from the high ratios of C_{Fe3}/C_L and the boiling of the solution required to obtain the stoichiometry 2 : 1 that it is practically impossible to determine an empirical rate law.

There is also another difficulty. At high [Fe(III)] the formation of dinuclear, mixed-valence hydroxo complexes of Fe(III) and Fe(II) is a possibility that cannot be ruled out. It is known, *e.g.* for manganese,[12] that the formation of such complexes might accelerate the electron transfer from a ligand to the oxidant. In the present case, both k_9 and k_{10} could increase and influence the empirical rate law. As the integration in eqn. (5) refers to the condition [Fe(II)] = 0 at $t = 0$, mixed-valence complexes are not present at short times t. On the other hand, the results summarized in the empirical rate law might be influenced by such complexes and explain the somewhat higher k value obtained as compared to that from eqn. (5) and (6).

References

1 See for instance J. Kim and D. C. Rees, *Science*, 1992, **257**, 1677; J. Kim and D. C. Rees, *Nature*, 1992, **360**, 553; A. E. Shilov, *Pure Appl. Chem.*, 1992, **64**, 1409; H. Deng and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1062.
2 P. Bar-On, M. Mohsen, R. Zang, E. Feigin, M. Chevion and A. Samuni, *J. Am. Chem. Soc.*, 1999, **121**, 8070.
3 B. Chaudhuri and R. Banerjee, *Can. J. Chem.*, 1998, **76**, 350.
4 J. W. B. Moir, J.-M. Wehrfritz, S. Spiro and D. J. Richardson, *Biochem. J.*, 1996, **319**, 823.
5 G. Bengtsson, *Acta Chem. Scand., Ser. A*, 1983, **37**, 639.
6 G. Ramababu, P. V. S. Rao, K. Ramakrishna, P. Syamala and A. Satyanarayana, *J. Indian Chem. Soc.*, 2001, **78**, 237.
7 G. Bengtsson, *Acta Chem. Scand.*, 1973, **27**, 1717.
8 G. S. Barney, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1677.
9 B. Chaudhuri and R. Banerjee, *Can. J. Chem.*, 1998, **76**, 350.
10 Y. Chen, B. Zhou and X. Ren, *Ganguang Kexue Yu Guang Huaxue*, 1991, **9**, 76.
11 A. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1961.
12 J. W. Gutch and W. A. Waters, *J. Chem. Soc. A*, 1965, 751.
13 P. K. Sen, S. Maiti and K. S. Gupta, *Indian J. Chem., Ser. A*, 1980, **19**, 865.
14 S. Fronæus, J. Berglund and L. Elding, *Inorg. Chem.*, 1998, **37**, 4939.