Reduction of the bis(pentane-2,4-dionato)diaquo manganese(III) complex by hydroxylamine and L-ascorbic acid in aqueous solution

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Abstract

The kinetics and mechanisms of the reduction of bis(pentane-2,4-dionato)diaquo manganese(III), $[Mn(pd)_2(H_2O)_2]^+$ by hydroxylamine and L-ascorbic acid have been investigated in aqueous solution at 25 °C and ionic strength 0.5 mol dm^{-3}. Mechanisms are proposed which account satisfactorily for the kinetic data. Inner-sphere mechanisms appear to be operative for both reductants. In the case of hydroxylamine, the complex dependency of k_{obs} on the reductant concentration strongly supports this view.

Introduction

The electron transfer reactions of aquated manganese(III) and its complexes have been the subject of a number of previous investigations [1–11]. These investigations have demonstrated that electron transfer reactions involving manganese(III) proceed by a variety of mechanistic pathways. Both inner-, outer- and mixed inner–outer-sphere mechanisms have been found to be operative. Some of the reactions were relatively complex involving multiple reaction steps. In addition, the possible role of a range of manganese(III) complexes as reaction mimics for the water-oxidation cofactor in green plant photosystem II has been investigated [12]. More recently, manganese(II) catecholate complexes have been shown to catalyse the production of hydrogen peroxide from hydroxylamine and hydrazine [13].

The tris manganese(III) complex of pentane-2,4-dione (Hpd) has been well characterised [14, 15]. In aqueous solution, this complex dissociates according to eqn. (1).

$$[Mn(pd)_3] + H^+ + 2H_2O \rightleftharpoons [Mn(pd)_2(H_2O)_2]^+ + Hpd \quad (1)$$

In the presence of 0.025 mol dm^{-3} Hpd, aqueous solutions of $[Mn(pd)_2(H_2O)_2]^+$ are stable in the pH range 4–6. The pK of $[Mn(pd)_2(H_2O)_2]^+$ has been estimated to be approximately 7.3 [14, 15]. Consequently, in the pH range 5–6 the major species present in solutions containing 0.025 mol dm^{-3} Hpd is the diaquo species together with relatively small amounts of $[Mn(pd)_3]$ and the $[Mn(pd)_2(H_2O)(OH)]$ species formed on hydrolysis of $[Mn(pd)_2(H_2O)_2]^+$.

We have now investigated the kinetics and mechanisms of the oxidation of hydroxylamine and L-ascorbic acid by this complex. Kinetic investigations of the electron transfer reactions of metal complexes of β-diketones are sparse and this is one of the few studies of such reactions using simple reductants.

Experimental

The complex $[Mn(pd)_3]$ was prepared as previously described [16]. Pentane-2,4-dione (Riedel de Haën) was distilled prior to use. Perchloric acid was used as the source of hydrogen ions and all solutions were adjusted to an ionic strength of 0.5 mol dm^{-3} by the addition of $NaClO_4$.

L-Ascorbic acid (BDH) and hydroxylamine (BDH) were used as supplied.

pH measurements were made using a PTI6 pH meter equipped with a Russell combination electrode. The filling solution of the reference section was a 3 mol dm^{-3} aqueous solution of sodium chloride. The pH meter was calibrated to read hydrogen ion concentration directly by titrating solutions of perchloric acid (0.001–0.005 mol dm^{-3}) with standard sodium hydroxide solution.

The stoichiometry of the reactions was investigated by spectrophotometric titration of 2.5 ml of a 2.0×10^{-4} mol dm^{-3} solution of the complex with aliquots of a 0.01 mol dm^{-3} solution of the reductant.

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Kinetic measurements were made at 340 nm with the reductant in sufficient excess (>ten-fold) to drive the reaction to completion. The total manganese concentration was 1.0×10^{-4} mol dm^{-3}. In order to provide stable solutions [14, 15] sufficient Hpd was added to the manganese(III) solutions to give a concentration of 0.05 mol dm^{-3}. Initially, Hpd was added to both the manganese(III) and the reductant solutions. However, it was found that over a period of minutes a reaction occurred between Hpd and hydroxylamine. Rate constants were measured with a HiTech SF-20 stopped-flow apparatus which was interfaced to a BBC microcomputer. Pseudo-first-order rate constants were calculated by fitting the absorbance data (70–100 data points) to eqn. (2) using a three-parameter curve-fitting routine in which the absorbance at time zero, A_0, the absorbance at infinity time, A_∞, and the rate constant, k, were treated as variables. Data for from three to four half-lives were utilised in these calculations.

$$A = A_\infty[1-\exp(-kt)] + A_0\exp(-kt) \quad (2)$$

The reported rate constants are the average of at least three determinations. The standard deviation in individual runs was usually less than 1%.

2,6-Lutidine-3-sulfonic acid* and 3-acetyl-2,4-6-collidiniumtetrafluoroborate* buffers were used to control hydrogen ion concentrations during the kinetic runs. During initial experiments using acetate as buffer, it was found that the k_{obs} values exhibited a high dependence on the concentration of acetate used.

In order to confirm the previously reported values of the pK of $[Mn(pd)_2(H_2O)_2]^+$ and the equilibrium constant of the reaction shown in eqn. (1), solutions containing $[Mn(pd)_3]$ and 0.05 mol dm^{-3} Hpd were titrated with both perchloric acid and sodium hydroxide. The titration data were refined using SUPERQUAD [17].

In the non-linear least-squares fitting of the kinetic data, the parameter R, eqn. (3), together with the standard deviations of the final parameters, was used as a measure of the goodness of fit.

$$R = 100\left(\frac{\sum(k_{obs}-k_{calc})^2}{\sum k_{obs}^2}\right)^{1/2} \quad (3)$$

Results

The pK of $[Mn(pd)_2(H_2O)_2]^+$ was found to be 7.30($\pm$0.06) while log β_3 for its reaction with pd$^-$ was found to be 3.87($\pm$0.05). These are in good agreement with the previously reported values of 7.2 and 3.91, respectively.

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Oxidation of hydroxylamine

Due to the fact that at ratios of $[Mn(pd)_2(H_2O)_2]^+$/$[NH_2OH]$ of less than one, the reactions did not go to completion, the stoichiometry of the oxidation of $[Mn(pd)_2(H_2O)_2]^+$ by hydroxylamine could not be measured. However, previous work has shown that oxidation of hydroxylamine proceeds according to eqns. (4) and (5). Accordingly, a stoichiometry of one has been assumed for reduction of $[Mn(pd)_2(H_2O)_2]^+$ by hydroxylamine.

$$NH_3OH \longrightarrow NH_2OH^{\cdot+} + H^+ + e^- \quad (4)$$

$$2NH_2OH^{\cdot+} \longrightarrow N_2 + 2H_2O + 2H^+ \quad (5)$$

The kinetic data are shown in Table 1. While the reaction is first-order in the Mn^{III} complex as indicated by the good first-order behaviour of the reactions, the order with respect to the reductant is complex. This is obvious from Fig. 1 where plots of k_{obs} against hydroxylamine concentration show distinct upward curvature. The observed behaviour can be interpreted in terms of two competing pathways, one of which is first-order in reductant while the other is second-order. In addition, the k_{obs} values exhibit a strong hydrogen ion dependence. The details of the mechanism proposed are shown in Scheme 1.

TABLE 1. Observed and calculated first-order rate constants for reactions of hydroxylamine with $[Mn(pd)_2(H_2O)_2]^+$ at 25 °C and I=0.5 mol dm^{-3} $NaClO_4$

10^2[Hydroxylamine] (mol dm^{-3})	pH	k_{obs} (s^{-1})	k_{calc}[a] (s^{-1})
1.00	5.02	6.65	7.52
2.00	5.02	15.7	16.9
3.00	5.02	26.0	28.3
4.00	5.02	39.2	41.6
5.00	5.02	52.2	56.8
1.00	5.32	10.2	13.2
2.00	5.32	30.6	29.6
3.00	5.32	52.8	49.1
4.00	5.32	79.7	71.8
5.00	5.32	102	97.5
1.00	5.57	18.3	19.7
2.00	5.57	45.2	43.6
3.00	5.57	73.8	71.7
4.00	5.57	108	104
5.00	5.57	140	140
1.00	5.70	20.8	23.3
2.00	5.70	51.7	51.4
3.00	5.70	84.5	83.9
4.00	5.70	117	121
5.00	5.70	158	163

[a]Based on eqn. (12).

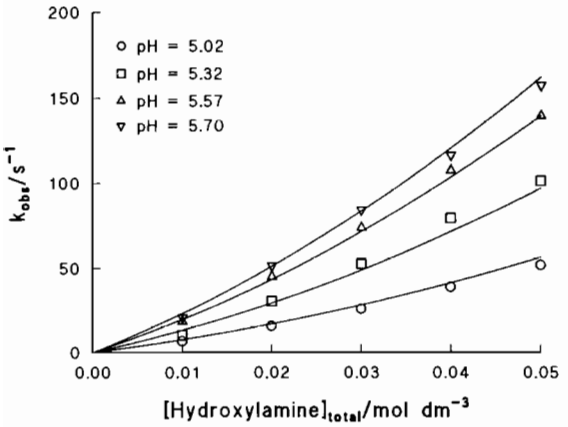

Fig. 1. Plot of k_{obs} for reaction of $[Mn^{III}(pd)_2(H_2O)_2]^+$ with hydroxylamine in aqueous solution at 25 °C and ionic strength 0.5 mol dm^{-3} $NaClO_4$. pH=5.02; ○; 5.32, △; 5.57, ▽; 5.72, ◇.

$$NH_3OH^+ \overset{K_a}{\rightleftharpoons} NH_2OH + H^+ \quad (6)$$

$$[Mn(pd)_2(H_2O)_2]^+ \overset{K_h}{\rightleftharpoons} [Mn(pd)_2(H_2O)(OH)] + H^+ \quad (7)$$

$$[Mn(pd)_2(H_2O)_2]^+ + NH_2OH \overset{K_1}{\rightleftharpoons} [Mn(pd)_2(H_2O)(NH_2OH)]^+ + H_2O \quad (8)$$

$$[Mn(pd)_2(H_2O)(NH_2OH)]^+ + NH_3OH^+ \overset{K_2}{\rightleftharpoons} [Mn(pd)_2(NH_2OH)(NH_3OH)]^{2+} + H_2O \quad (9)$$

$$[Mn(pd)_2(H_2O)(NH_2OH)]^+ \xrightarrow{k_1} Mn^{II} + \text{products} \quad (10)$$

$$[Mn(pd)_2(NH_2OH)(NH_3OH)]^{2+} \xrightarrow{k_2} Mn^{II} + \text{products} \quad (11)$$

Scheme 1.

For the mechanism in Scheme 1, k_{obs} will have the form of eqn. (12) where $[NH_2OH]=[NH_2OH]_0/(1+[H^+]/K_a]$, $[NH_3OH^+]=[NH_2OH]_0(1+K_a/[H^+])$, $[NH_2OH]_0$ is the total hydroxylamine concentration

$$k_{obs}=\frac{k_1K_1[NH_2OH]+k_2K_1K_2[NH_2OH][NH_3OH^+]}{(1+K_1[NH_2OH]+K_1K_2[NH_2OH][NH_3OH^+])\left(1+\frac{K_h}{[H^+]}\right)} \quad (12)$$

present and $K_a=10^{-6.00}$ [18]. In the event that $1 \gg (K_1[NH_2OH]+K_1K_2[NH_2OH][NH_3OH^+]$, eqn. (12) reduces to eqn. (13).

$$k_{obs}=\frac{k_1K_1[NH_2OH]+k_2K_1K_2[NH_2OH][NH_3OH^+]}{\left(1+\frac{K_h}{[H^+]}\right)} \quad (13)$$

Fitting the kinetic data to eqn. (13) results in values of $7.08(\pm0.41)\times10^3$ mol^{-1} dm^3 s^{-1}, $1.15(\pm0.13)\times10^5$ mol^{-2} dm^6 s^{-1} and 4.3% for k_1K_1, $k_2K_1K_2$ and R, respectively. Various other reaction schemes were also investigated. For example, a mechanism involving two molecules of NH_2OH in the second-order pathway gave a distinctly inferior fit. It should also be noted that reaction (8) can also be formulated as a reaction in which NH_3OH^+ reacts with $[Mn(pd)_2(H_2O)OH]$. In this event, k_{obs} has the form of eqn. (14). Fitting the kinetic data to this equation gives values of

$$k_{obs}=\frac{k_1K_1K_h[NH_3OH^+]+k_2K_1K_2K_h[NH_3OH^+]^2}{1+\frac{[H^+]}{K_h}} \quad (14)$$

$1.41(\pm0.08)\times10^5$ dm^3 mol^{-1} s^{-1}, $2.30(\pm0.27)\times10^6$ dm^6 mol^{-2} s^{-1} and 4.3% for k_1K_1, $k_2K_1K_2$ and R, respectively. In the fitting procedures above, allowance was madc for thc small quantity (<10%) of $[Mn(pd)_3]$ present which was assumed not to be involved in the electron transfer process.

Figure 1 shows a plot of the data based on the assumption that the reaction proceeds by the mechanism shown in Scheme 1. The solid lines are derived using eqn. (13) together with the reactant concentrations and the fitted values of the parameters. It is clear that this equation gives a good representation of the kinetic data, thus supporting the proposed mechanism.

Oxidation of L-*ascorbic acid*

The stoichiometric measurements for reactions of $[Mn(pd)_2(H_2O)_2]^+$ with L-ascorbic acid (H_2A) indicate that the overall reactions can be represented by eqn. (15).

$$2Mn^{III} + H_2A \longrightarrow 2Mn^{II} + A + 2H^+ \quad (15)$$

The reaction was first-order with respect to the oxidant for at least three half lives. k_{obs} exhibited a linear dependence on L-ascorbic acid concentration and alterations in the hydrogen ion concentration had little effect on the magnitude of k_{obs}. The kinetic data are listed in Table 2 and are consistent with the rate law shown in eqn. (16).

$$d[Mn(pd)_2(H_2O)_2{}^+]/dt = 2k_0[Mn(pd)_2(H_2O)_2][H_2A] \quad (16)$$

The mechanism proposed to account for the kinetic data in Table 2 is shown in Scheme 2 where coordinated waters are omitted in order not to preempt the decision as to whether the reactions proceed by inner- or outer-sphere mechanisms. The mechanism in Scheme 2 predicts that k_0 has the form of eqn. (24).

TABLE 2. Observed and calculated first-order rate constants for reactions of ascorbic acid with $[Mn(pd)_2(H_2O)_2]^+$ at 25 °C and $I=0.5$ mol dm^{-3} $NaClO_4$

10^3[Ascorbic acid] (mol dm^{-3})	pH	k_{obs} (s^{-1})	k_{calc}[a] (s^{-1})
1.00	4.20	61.0	70.0
1.50	4.20	105	105
2.00	4.20	139	140
2.50	4.20	180	175
0.50	4.80	36.0	37.8
1.00	4.80	74.7	75.6
1.50	4.80	114	113
2.00	4.80	155	151
2.50	4.80	194	189
0.50	5.10	35.3	37.8
1.00	5.10	70.0	75.6
1.50	5.10	106	113
2.00	5.10	143	151
2.50	5.10	179	189
0.50	5.50	35.7	35.7
1.00	5.50	75.0	71.5
1.50	5.50	115	107
2.00	5.50	143	143
2.50	5.50	189	179

[a]Calculated using eqn. (24).

$$Mn(pd)_2^+ \overset{K_h}{\rightleftharpoons} Mn(pd)_2(OH) + H^+ \quad (17)$$

$$H_2A \overset{K_a}{\rightleftharpoons} HA^- + H^+ \quad (18)$$

$$Mn(pd)_2 + H_2A \overset{K_1}{\rightleftharpoons} Mn(pd)_2(H_2A)^+ \quad (19)$$

$$Mn(pd)_2^+ + HA^- \overset{K_2}{\rightleftharpoons} Mn(pd)_2(HA) \quad (20)$$

$$Mn(pd)_2(H_2A)^+ \xrightarrow{k_1} Mn^{II} + HA^{\cdot} + H^+ \quad (21)$$

$$Mn(pd)_2(HA) \xrightarrow{k_2} Mn^{II} + HA^{\cdot} \quad (22)$$

$$Mn(pd)_2 + HA^{\cdot} \xrightarrow{fast} Mn^{II} \quad (23)$$

Scheme 2.

$$k_0 = \frac{k_1K_1[H^+] + k_2K_aK_2}{(1 + K_1[H_2A] + K_2[HA^-])(H^+ + K_a)\left(1 + \frac{K_h}{[H^+]}\right)} \quad (24)$$

In the event that $(K_1[H_2A] + K_2[HA^-]) \ll 1$, k_0 reduces to eqn. (25).

$$k_0 = \frac{k_1K_1[H^+] + k_2K_aK_2}{(H^+ + K_a)\left(1 + \frac{K_h}{[H^+]}\right)} \quad (25)$$

Fitting the kinetic data to eqn. (25) gives values of $2.95(\pm 0.19)\times 10^4$ mol^{-1} dm^3 s^{-1}, $4.06(\pm 0.06)\times 10^4$ mol^{-1} dm^3 s^{-1} and 4.5% for k_1K_1, k_2K_2 and R, respectively. The agreement between the calculated values of the rate constants and k_{obs} values is excellent (Table 2) over the range of hydrogen ion and ascorbic acid used in the present investigation and strongly supports the mechanism proposed.

The question arises as to whether the reduction proceeds by an inner- or an outer-sphere mechanism. Previous work has shown that most reductions of metal complexes by L-ascorbic acid proceed by outer-sphere mechanisms although under certain conditions inner-sphere mechanisms have also been observed [19, 20]. The value of $E°$ for $[Mn(H_2O)_6]^{3+}$ is 1.51 V [21] while that for $[Md(pd)_3]$ is 0.11 V [12]. Although the value of $E°$ for $[Mn(pd)_2(H_2O)_2]^+$ could not be directly measured under the experimental conditions using cyclic voltammetry, an approximate value can be calculated by analogy with similar systems. The stabilisation of 1.42 V observed when Co^{3+} is coordinated by three molecules of 1,10-phenanthroline [22] is almost identical to that observed when Mn^{3+} is coordinated by three molecules of Hpd, 1.40 V. The loss of stabilisation on going from $[Co(phen)_3]^{3+}$ to $[Co(phen)_2(H_2O)_2]^{3+}$ is 0.30 V [22]. Applying a similar criteria to the manganese(III) system results in a value of approximately 0.40 V for the $E°$ value of $[Mn(pd)_2(H_2O)_2]^+$. Using this value, together with the values of 0.71 V and 2×10^5 s^{-1} for $E°$ [23] and the self-exchange rate constant [24] for the couple, $HA^{\cdot}/HA^-$ respectively, the self-exchange rate constant for $[Mn(pd)_2(H_2O)_2]^{+/0}$ can be estimated using the Marcus cross relationship, eqn. (26), and is found to be *c.* 10^{10} dm^3 mol^{-1} s^{-1}. Even allowing for the approximate nature of the calculations, this appears to be extremely large for the self exchange reaction of $Mn^{3+/2+}$ complexes. The largest value reported to date is 3.2×10^3 dm^3 mol^{-1} s^{-1} for Mn(tetrakis(4-sulfonatophenylporphyrin)]$^{4-/3-}$ [8]. Thus, on balance, it appears that the oxidation of ascorbic acid by $[Mn(pd)_2(H_2O)_2]^+$ proceeds by an inner-sphere mechanism.

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$

$$\text{where } \log f_{12} = \frac{(\log K_{12})^2}{4 \log k_{11}K_{22}/Z^2} \quad (26)$$

Discussion

This is the first detailed study of the kinetics and mechanisms of the reduction of $[Mn(pd)_2(H_2O)_2]^+$. The reduction reactions with hydroxylamine have been formulated using pathways involving $[Mn(pd)_2(H_2O)_2]^+$. In the pH range used for the investigations, only very small quantities of the hydrolysed species $[Mn(pd)_2(H_2O)OH]$ would be present. In general, hydrated species are considerably more reactive towards

substitution when one of the coordinated water molecules loses a proton but it is only when the pH is considerably less than $-\log K_h$ that the reaction with the unhydrolysed species predominates [25]. In the present instance, the alternative pathways involve reaction of NH_3OH^+ with $[Mn(pd)_2(H_2O)OH]$.

For reduction of $[Mn(pd)_2(H_2O)_2]^+$ by hydroxylamine, an outer-sphere mechanism cannot be completely eliminated for the reaction pathway which is first-order in reductant concentration. However, the second-order dependence of k_{obs} on hydroxylamine clearly demonstrates that two molecules of the reductant are involved in one of the reaction pathways. Such an observation has been previously used as unambiguous proof of an inner-sphere mechanism [4]. In the present investigation, at least one of the hydroxylamine molecules must be coordinated in an inner-sphere fashion. The actual electron transfer could involve prior coordination of one molecule of NH_2OH and one molecule of NH_3OH^+ followed by electron transfer as indicated in Scheme 1 (eqn. (10)) or, alternatively, it could involve an outer-sphere electron transfer between $[Mn(pd)_2(H_2O)(NH_2OH)]^+$ and a molecule of NH_3OH^+. The data clearly show that a molecule of NH_3OH^+ is involved in the second step of this reaction. Reaction schemes involving NH_2OH or which involve release of a proton on coordination of NH_3OH^+ give greatly inferior fits. The presence of a hydrolysed species involving one coordinated hydroxylamine and one hydroxide molecule cannot be completely ruled out. However, the pK of such a species would be greater than 7.2 so that under the experimental conditions used, the concentrations of any such species present would be very small indeed. In this respect the kinetic data appear to resolve the proton ambiguity present.

In a previous investigation, Arselli and Mentasti [4] have studied the reduction of *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetraacetatomanganate(III), $[Mn^{III}(cdta)H_2O]^-$, by hyroxylamine. On the basis of their results they postulated three pathways for the reduction, one involving $[Mn^{III}(cdta)(NH_3OH)]$ (k), one involving $[Mn^{III}(cdta)(NH_3OH)(NH_2OH]$ (k') and one involving $[Mn^{III}(cdta)(NH_2OH)_2]^-$ (k''). This gave the following expression for k_{obs} where k, k' and k'' are collections of rate and equilibrium constants.

$$k_{obs} = k[NH_3OH^+][H^+]^{-1} + \{k'[H^+]^{-1} + k''[H^+]^{-2}\}[NH_3OH^+]^2 \quad (27)$$

They assumed that under their reaction conditions all the hydroxylamine existed in the protonated form. Using this hypothesis and fitting the kinetic data reported by Arselli and Mentasti [4] at 20 °C to eqn. (27) gives values of 1.90×10^{-2}, -6.65×10^{-1}, 1.14×10^{-4} dm^3 mol^{-1} s^{-1} and 3.9% for k, k', k'' and R, respectively. It is apparent that the values reported by Arselli and Mentasti for k (1.1×10^{-2}), k' (0.10) and k' (9.0×10^{-5}) are not a good description of their kinetic data. This is more clearly seen in Fig. 2 where the solid lines are drawn using their published values for k, k' and k''. They give an R value of 11.3%. Fitting the kinetic data using only the k and k'' pathways results in values of 1.27×10^{-2}, 1.03×10^{-4} dm^3 mol^{-1} s^{-1} and 4.9% for k, k'' and R, respectively. It would appear that the k' pathway does not make a significant contribution to the overall reaction. However, the overall results are similar to those obtained in the present study in that the kinetic data are consistent with pathways involving the oxidation of one and two hydroxylamine molecules in an inner-sphere process.

The results with hydroxylamine as reductant also support the inner-sphere mechanism proposed for the ascorbic acid reduction shown in Scheme 2. Although many reductions with ascorbic acid proceed by outer-sphere mechanisms, Xu and Jordan [19] have shown that the reduction of $[Fe(H_2O)_6]^{3+}$ proceeds by an inner-sphere mechanism when the reaction is carried out with excess iron(III). van Eldik and co-workers have recently argued on the basis of their high-pressure studies [20] that the oxidation of L-ascorbic acid by the more inert $[Fe(H_2O)_6]^{3+}$ proceeds by an outer-sphere mechanism while an inner-sphere mechanism operates for the more labile $[Fe(H_2O)_5(OH)]^{2+}$.

The lack of a significant hydrogen ion dependence in the present work is rather unusual and contrasts with the usual behaviour observed during reductions with ascorbic acid where k_{obs} has the form of eqn. (28) where a and b represent reactions pathways involving H_2A and HA^-, respectively.

$$k_{obs} = a + b/[H^+] \quad (28)$$

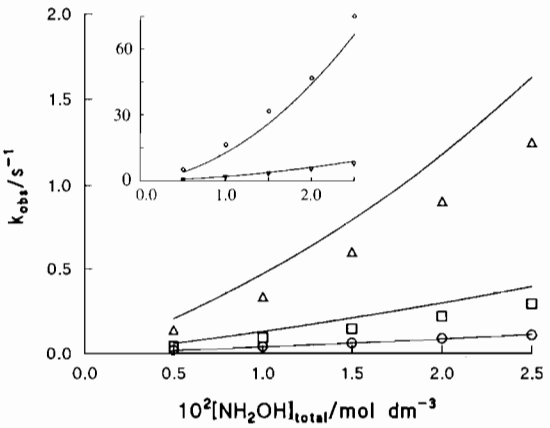

Fig. 2. Plot of k_{obs} for reaction of $M^{III}(cdta)(H_2O)^-$ with hydroxylamine in aqueous solution at 20 °C and ionic strength 0.20 mol dm^{-3} $NaClO_4$. Data from ref. 4. pH = 2.50, ○; 3.00, □; 3.50, △; 4.00, ▽; 4.50, ◇.

Where the metal species is partially hydrolysed, the situation is more complex and this can lead to ambiguities in assigning the reactions' steps [25, 26]. The reactivity of fully protonated ascorbic acid towards $[Mn(pd)_2(H_2O)_2]^+$ might be considered unusual were it not for the work of Xu and Jordan [19] who obtained a value of 5.5×10^3 dm^3 mol^{-1} s^{-1} for reaction of H_2A with $[Fe(H_2O)_6]^{3+}$. Although comparisons are rendered difficult by the fact that substitution reactions of $[Fe(H_2O)_6]^{3+}$ are thought to proceed by an associative mechanism, it does appear that fully protonated ascorbic acid, H_2A is a better nucleophile than might be expected. This may account for its reactivity in the present instance. However, it is only at the lowest pH value that the H_2A path makes a significant contribution to the overall reaction.

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