Kinetics and Mechanism of the Oxidation of Iminodiacetate, Nitrilotriacetate and Ethylenediaminetetraacetate by *trans*-Cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetatomanganate(III) in Aqueous Media[†]

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Kinetic studies of the oxidation of iminodiacetate (ida), nitrilotriacetate (nta) and ethylenediaminetetraacetate (edta) by *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetatomanganate(III), $[Mn^{III}(cdta)]^-$, have been made in aqueous solution in the range pH 3.0–10.0 with varying reductant concentrations at constant ionic strength, $I = 0.50$ mol dm^{-3} ($NaClO_4$), and temperature, 30 °C. All the reactions are first order both in complex and reductant concentration, and follow the general rate law $-d[Mn^{III}]/dt = k_{obs}[Mn^{III}] = (k_d + k_s[R])[Mn^{III}]$, where k_d denotes the autodecomposition rate of the complex, k_s the electron-transfer rate and R is the reductant irrespective of the nature and type of the reacting species. The complex $[Mn^{III}(cdta)]^-$ showed an interesting behaviour in acidic and alkaline media. For ida oxidation both the aqua- and hydroxo-forms of the complex are reactive and an inner-sphere mechanism has been proposed. However, for nta and edta oxidations, the aqua form is the sole reacting species and an outer-sphere mechanism has been proposed. The rate parameters and proton equilibrium constants of the complex and reductants were obtained by fitting of the experimental data by appropriate rate equations using computer-fit programs. Thus the reactivities of all the species of the polycarboxylates available in the reaction solutions have been evaluated individually. The reactivity orders are $Hida^- < ida^{2-}$, $H_2nta^- < Hnta^{2-} < nta^{3-}$ and $H_3edta^- < H_2edta^{2-} < Hedta^{3-} < edta^{4-}$.

The redox chemistry of manganese(III) complexes has been the subject of intensive research over the past few decades.[1,2] Among the several complexes reported, *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetatomanganate(III), $[Mn^{III}(cdta)]^-$, has drawn special attention by kineticists owing to its moderate stability in aqueous medium. This complex is known to exist in two forms in aqueous solution, *viz.* $[Mn(cdta)(H_2O)]^-$ in acidic media and $[Mn(cdta)(OH)]^{2-}$ in alkaline media.[3] In the oxidation of several inorganic and organic substrates by this complex in acidic media both inner-[4–12] and outer-sphere[13–15] mechanisms have been encountered. However, comparatively little is known about the redox behaviour of the hydroxo-form of this complex. Two recent reports, one from this laboratory[10] and another by Macartney and Thompson[15] narrate the redox chemistry of this complex in alkaline media and these reflect considerable diversity in behaviour towards different reductants.

In view of the above findings, we chose to study the redox interaction of $[Mn(cdta)]^-$ with some amine-N-polycarboxylates, namely iminodiacetate, nitrilotriacetate and ethylenediaminetetraacetate both in acidic and alkaline media. Recently we reported the reactions of these polycarboxylates with a substitutionally inert species, dodecatungstocobaltate(III) in acidic media where an outer-sphere mechanism was proposed.[16] The present study thus provides an opportunity to clarify the oxidation mechanism of amine-N-carboxylates by outer- or inner-sphere pathways. This may have some relevance to amino acid metabolism. Studies covering a wide pH range would also enable us to determine the relative reactivities of the different anionic species of these polycarboxylates available in solution towards the protonated and deprotonated forms of the complex.

Experimental

Materials and Reagents.—The potassium salt of *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetatomanganate(III), $K[Mn(cdta)]\cdot 2.5H_2O$ (hereafter designated as Mn^{III})[‡] was prepared, characterised and standardised as reported earlier.[3] The recrystallised disodium salt of iminodiacetic acid, Na_2ida (Fluka AG), nitrilotriacetic acid, H_3nta (Fluka AG), and the disodium salt of ethylenediaminetetraacetic acid, Na_2H_2edta (BDH, AnalaR) were used in this kinetic investigation.[§] Recrystallised sodium perchlorate was used to maintain the ionic strength of the reaction medium and the pH was adjusted by using perchloric acid, acetic acid–sodium acetate or sodium borate–sodium hydroxide buffers as required. All the solutions were prepared by using doubly distilled water.

Kinetic Measurements.—The kinetic measurements were carried out with a Philips Analytical SP8-150 spectrophotometer equipped with thermostatted cell compartments. Reactions were followed by monitoring the decrease in $[Mn^{III}]$ at 510 nm for the aqua-species ($\varepsilon_{max}^{510} = 345$ dm^3 mol^{-1} cm^{-1}) and at 448 nm for the hydroxo-species ($\varepsilon_{max}^{448} = 329$ dm^3 mol^{-1} cm^{-1}). The pH measurements were done in a digital pH meter (Systronics model 335, India). Dissolved oxygen has no observable effect on the reaction rate.

[†] *Supplementary data available* (No. SUP 56838, 5 pp): observed rate constants at different pH. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

[‡] In general, Mn^{III} represents both the aqua- and hydroxo-forms of the complex but, in particular, aqua- and hydroxo-species are represented as $[Mn^{III}(H_2O)]^-$ and $[Mn^{III}(OH)]^{2-}$ respectively.

[§] Although these formulations have been strictly followed in describing the actual species involved at any certain pH, designations such as, ida, nta and edta have also been used in a general way to describe a particular amine-N-polycarboxylate without emphasising the actual species.

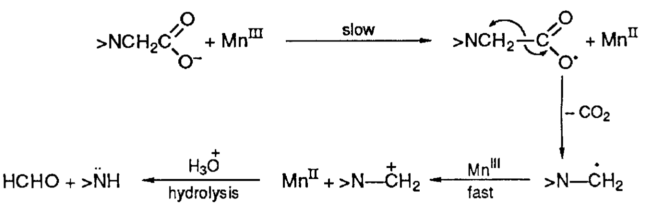
Table 1 Pseudo-first-order rate constants for the oxidation of amine-N-polycarboxylates by Mn^{II} at different acidities with $[Mn^{III}] = 1.0 \times 10^{-3}$ mol dm^{-3} (5.0×10^{-4} mol dm^{-3} when [reductant] = 5.0×10^{-3} mol dm^{-3}), $I = 0.50$ mol dm^{-3}, [acetate] or [borate][a] = 0.02 mol dm^{-3}, 30 °C

Reductant		$10^4k_{obs}/s^{-1}$ pH			
(R)	[R]/mol dm^{-3}	4.0[b]	6.0[c]	7.50[d]	9.19[e]
edta	0.005		19.6	44.30	17.0
	0.007		27.4	63.5	23.2
	0.01	3.48	39.1	87.0	33.5
	0.02		78.1	176	
	0.03				96.0
	0.05	17.5			159
	0.07	24.2			223
	0.10	34.3			
	0.125	43.0			
nta	0.005			11.2	
	0.007			13.0	
	0.01	0.50		19.5	15.2
	0.03	1.22	1.35	55.5	44.2
	0.05	2.02	2.10	91.2	73.5
	0.07	2.57	2.85		103
	0.10	3.81	3.85		145
	0.125		5.08		
ida	0.01		1.38		3.47
	0.03		3.95	3.96	7.80
	0.05		6.15	5.70	12.8
	0.07		8.90	8.20	16.9
	0.10		12.5	10.9	24.1
	0.20			20.7	

[a] The reaction rates (k_{obs}) increase by *ca.* 2–3% on addition of 0.02 mol dm^{-3} acetate buffer compared to the unbuffered condition and this falls well within the limit of experimental error (≈5–6%). However on increasing [O_2CMe^-] at a certain pH, the rate increases further (*e.g.* 0.05 mol dm^{-3} [O_2CMe^-] causes 8–10% increase in rate). [b] For nta, pH 3.50. [c] For nta, pH 5.0 and for ida, pH 6.04. [d] For nta, pH 7.50 and for ida, pH 7.53. [e] For nta, pH 9.67 and for ida, pH 9.25.

Polymerisation Study.—The reactions proceed through the generation of free radicals and this was tested by the polymerisation of acrylonitrile as described earlier.[16]

Stoichiometry and Reaction Products.—The stoichiometries for the oxidation of ida, nta and edta were determined by allowing a large excess of oxidant (12:1 for ida and nta and 20:1 for edta) to react with the respective amine-N-polycarboxylates until the manganese(III) complex had reached a steady concentration. Respective blank solutions were also prepared to measure the amount of complex undergoing autodecomposition. The amount of oxidant left was estimated spectrophotometrically and the net oxidant reacted was calculated by considering the amount undergoing autodecomposition. For each of the reductants three separate experiments using different quantities of reductants at pH 5.5 showed that 2.1 ± 0.20 and 4.02 ± 0.10 mol of Mn^{III} reacted per mol of ida and nta respectively. For the oxidation of edta a time-dependent stoichiometry was obtained which becomes constant at complex:reductant = 14:1. Thus the stoichiometry under reaction conditions with an excess of edta was determined. For this purpose the contents of three vials, with large excesses of edta, 0.01, 0.03 and 0.05 mol dm^{-3} at pH 5.50, were treated with 5.0×10^{-3} mol dm^{-3} [Mn^{III}] and the unreacted edta was then estimated by complexometric titration using murexide as indicator; these experiments were repeated twice. In each case a 2.10 ± 0.05:1 stoichiometry with respect to the complex was obtained. Thus, under these conditions only one carboxylate group is decarboxylated as shown in Scheme 1. This scheme also seems to be appropriate for nta oxidation leading to a 2:1 stoichiometry with respect to the complex. Similar stoichiometric results were also obtained in the oxidation of edta with dodecatungstocobaltate(III).[16] The triacid thus produced might hamper the estimation of edta but repeated experiments offered the same results and it can be assumed that the triacid did not interfere in the titration.



Scheme 1

The product analyses for these oxidations were carried out carefully. To analyse the organic product in the oxidation of ida, nta and etda, [Mn(cdta)]$^-$ was treated in the ratio Mn^{III}:reductant 12:1, 12:1 and 1:1 respectively at pH 5.5. The metal ions were separated by means of ion exchange and the eluents were then subjected to paper electrophoresis at 1 mA per strip for 1 h at 400 V. The dried paper strips were briefly (2 s) immersed in a 0.5% solution of ninhydrin in butanol and developed in an oven at 75 °C for 10 min. For comparison, high-purity analytical grade samples of glycine, ethylenediaminediacetic acid (H_2edda), iminodiacetic acid (H_2ida) and formaldehyde were run concurrently as reference standards. The results indicate that in the oxidation of ida and nta the organic products were glycine and formaldehyde, whereas in edta oxidation the products were H_2edda and formaldehyde. Unreacted edta does not interfere in this estimation. Carbon dioxide has been detected as one of the oxidation products for all the acids.

Results and Discussion

The kinetics of the redox interactions of [Mn^{III}(cdta)]$^-$ with the amine-N-polycarboxylates was studied in the range pH 3.0–10.0 with variable reductant concentrations at constant ionic strength, 0.50 mol dm^{-3} ($NaClO_4$), and temperature, 30 °C. Typical spectral scanning both in acidic and alkaline media for these reductants did not indicate the formation of any stable intermediate. The kinetics was followed under pseudo-first-order conditions with excess of reductant over the complex. Plots of $-\log(A_t - A_\infty)$ *vs.* t (where A_t, A_∞ and t have their usual significance) are all linear up to *ca.* 90% completion of reaction indicating a first-order dependence of the rate on the complex concentration. The reductant concentrations were varied at different pH. Plots of k_{obs} *vs.* [R] (R represents the reductant, irrespective of the nature of actual reacting species) are all linear with a positive intercept on the rate axis and the corresponding data are listed in Table 1. This indicates a first-order dependence of the rate on the reductant concentration, and the corresponding rate law may be emphasised as in equation (1) where [Mn^{III}] denotes the complex concentration

$$-d[Mn^{III}]/dt = k_{obs}[Mn^{III}] = (k_d + k_s[R])[Mn^{III}] \quad (1)$$

either in acidic or alkaline media, k_d is the self-decomposition rate of the complex and k_s is the corresponding electron-transfer rate.

The effect of pH on the reaction rates was studied individually for the three polycarboxylates. Interestingly, the reaction of ida with Mn^{III} differs considerably from that of nta and edta. For the oxidation of ida, both the aqua- and hydroxo-forms of the complex are reactive whereas for nta and edta oxidation the aqua-form is the sole reactive species. The experimental conditions were so adjusted that the reactivities of different

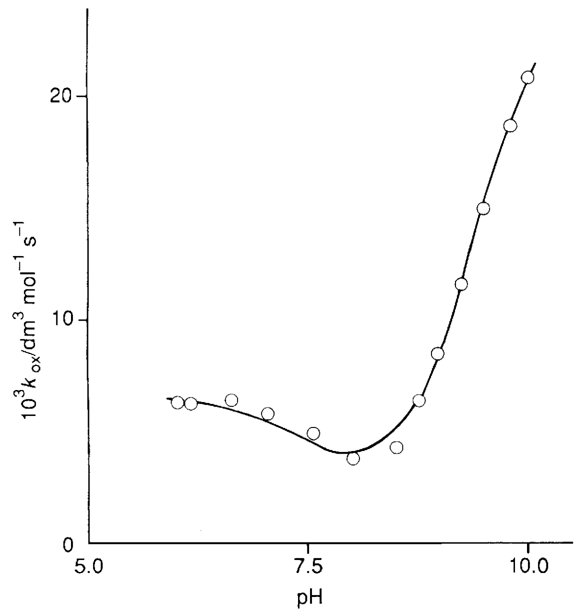


Fig. 1 Variation of k_{ox} $\{= (k_{obs} - k_d)/2[R]_T\}$ as a function of pH for the oxidation of iminodiacetate at 30 °C with $[Mn^{III}] = 1.0 \times 10^{-3}$ mol dm^{-3} and $I = 0.50$ mol dm^{-3} ($NaClO_4$). The solid line represents the theoretical and the experimental values are shown by points

reacting species can be determined. The proton dissociation constants of H_2ida are reported to be[17] $K_1 = 1.12 \times 10^{-3}$ mol dm^{-3} and $K_2 = 4.17 \times 10^{-10}$ mol dm^{-3} and that of the complex[3] is $K_m = 7.76 \times 10^{-9}$ mol dm^{-3}. In the range pH 6.04–10.0 both the aqua- and hydroxo-forms of the complex exist, and Hida$^-$ and ida^{2-} are the reactive species towards the complex. The ionisation of the complex and reductant can be represented as in equations (2) and (3). The pH-rate profile

$$[Mn^{III}(H_2O)]^- \xrightleftharpoons{K_m} [Mn^{III}(OH)]^{2-} + H^+ \qquad (2)$$

$$Hida^- \xrightleftharpoons{K_2} ida^{2-} + H^+ \qquad (3)$$

shows that the rate remains constant in the range pH 6.04–6.66, decreases reaching a minimum at pH ≈8.0, and then increases steeply with pH (Fig. 1). In the range pH 6.06–8.0 both $[Mn^{III}(H_2O)]^-$ and $[Mn^{III}(OH)]^{2-}$ react with Hida$^-$ which is the only reactive species and the decrease in rate with pH indicates the lower reactivity of $[Mn^{III}(OH)]^{2-}$ towards Hida$^-$ than of $[Mn^{III}(H_2O)]^-$. Beyond pH 8.5 $[Mn^{III}(OH)]^{2-}$ mainly exists and the steep increase in rate manifests the greater reactivity of ida^{2-} with $[Mn^{III}(OH)]^{2-}$.

The foregoing observations lead us to formulate the following outer-sphere reaction Scheme 2 where Mn^{II} represents $[Mn^{II}(cdta)]^{2-}$.

$$[Mn^{III}(H_2O)]^- + Hida^- \xrightarrow{k_H} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^- + ida^{2-} \xrightarrow{k'_H} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(OH)]^{2-} + Hida^- \xrightarrow{k_{OH}} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(OH)]^{2-} + ida^{2-} \xrightarrow{k'_{OH}} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^-/[Mn^{III}(OH)]^{2-} + \text{free radical} \xrightarrow{\text{fast}} Mn^{II} + \text{products}$$

Scheme 2

Considering the stoichiometry for the oxidation of ida by Mn^{III} as 2:1, the theoretical rate expression corresponding to Scheme 2 is (4) where $[ida]_T$ denotes the total ida concentration.

$$k_{ox} = \frac{k_{obs} - k_d}{2[ida]_T} = \frac{k_H[H^+]^2 + (k'_H K_2 + k_{OH}K_m)[H^+] + k'_{OH}K_2K_m}{(K_2 + [H^+])(K_m + [H^+])} \qquad (4)$$

Experimental data were fitted by this equation using an optimisation program following the Simplex algorithm[18] and the best fit was obtained by varying K_2 and K_m. The values of the rate parameters and proton equilibrium constants of H_2ida and complex thus obtained are: $k_H = (6.49 \pm 0.20) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, $k'_H = (4.45 \pm 0.13) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $k_{OH} = (1.53 \pm 0.03) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, and $k'_{OH} = (2.53 \pm 0.07) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}; $K_2 = (3.98 \pm 0.10) \times 10^{-10}$ mol dm^{-3} and $K_m = (2.11 \pm 0.06) \times 10^{-8}$ mol dm^{-3}. There is excellent agreement between the experimental and calculated k_{ox} values (Fig. 1). There is also reasonable agreement between the reported and kinetically determined values of K_2, but there is an increase in the K_m value. It is well known that a shift in the proton-dissociation constant of a complex takes place only when an inner-sphere intermediate is formed between the complex and ligands.[19,20] If this is so an alternative mechanism leading to an inner-sphere reaction for the oxidation of ida by Mn^{III} can be postulated as in Scheme 3. The corresponding rate

$$[Mn^{III}(H_2O)]^- + Hida^- \xrightleftharpoons{K_3} [Mn^{III}(Hida)]^{2-} \xrightarrow{k_{H1}} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^- + ida^{2-} \xrightleftharpoons{K_4} [Mn^{III}(ida)]^{3-} \xrightarrow{k'_{H1}} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(OH)]^{2-} + Hida^- \xrightleftharpoons{K_5} [Mn^{III}(Hida)(OH)]^{3-} \xrightarrow{k_{OH1}} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(OH)]^{2-} + ida^{2-} \xrightleftharpoons{K_6} [Mn^{III}(ida)(OH)]^{4-} \xrightarrow{k'_{OH1}} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^-/[Mn^{III}(OH)]^{2-} + \text{radical} \xrightarrow{\text{fast}} Mn^{II} + \text{products}$$

Scheme 3

equation is (5). Since K_3, K_4, K_5 and K_6 are very small, terms like $K_3[H^+][Mn^{III}(H_2O)^-]$, $K_5[H^+][Mn^{III}(OH)^{2-}]$, $K_2K_4[Mn^{III}(H_2O)^-]$ and $K_2K_6[Mn^{III}(OH)^{2-}]$ are insignificant compared to K_2 or $[H^+]$ and can be neglected. Thus equation (5) reduces to (6). Equations (4) and (6) are identical with $k_H = k_{H1}K_3, k'_H = k'_{H1}K_4, k_{OH} = k_{OH1}K_5$ and $k'_{OH} = k'_{OH1}K_6$.

According to the above mechanism, an inner-sphere intermediate complex is formed through the replacement of the coordinated water molecule by Hida$^-$/ida^{2-} or through partial unwrapping of the carboxylate arms of the cdta ligand in the aqua-complex.[21,22] However, for the hydroxo-species, displacement of the hydroxo-group is rather difficult and the second process is most likely to be operative. No spectral evidence could be obtained for the existence of such species. The reason for this may be the very small value of the formation constants, resulting in a negligible change in optical density, or the ε of these species are very close to those of the original manganese(III) complex. Thus the proposed outer-sphere (Scheme 2) and inner-sphere (Scheme 3) mechanism leading to identical rate equations could not be distinguished on the kinetic grounds.

The other two amine-N-polycarboxylates, nta and edta, with multiple dissociable protons would have different reactive species in the experimental range of pH (3.0–9.90). The pH–rate profiles are bell-shaped curves with peaks in the region pH 8.30–8.80 [Fig. 2(*a*)] and 7.0–7.75 (Fig. 2(*b*)] for nta and edta

$$k_{ox} = \frac{k_{H1}K_3[H^+]^2 + (k'_{H1}K_2K_4 + k_{OH1}K_mK_5)[H^+] + k'_{OH1}K_2K_mK_6}{\{[H^+] + K_3[H^+][Mn^{III}(H_2O)^-] + K_5[H^+][Mn^{III}(OH)^{2-}] + K_2 + K_2K_4[Mn^{III}(H_2O)^-] + K_2K_6[Mn^{III}(OH)^{2-}]\}(K_m + [H^+])} \tag{5}$$

$$k_{ox} = \frac{k_{H1}K_3[H^+]^2 + (k'_{H1}K_2K_4 + k_{OH1}K_mK_5)[H^+] + k'_{OH1}K_2K_mK_6}{(K_2 + [H^+])(K_m + [H^+])} \tag{6}$$

respectively. This indicates that $[Mn^{III}(OH)]^{2-}$ is unreactive towards the electron-transfer process. The decrease in rate with increase in pH is associated with a decrease in reduction potential on deprotonation of the complex[23] which causes the hydroxo-species of the complex to be unreactive.[15]

The reported acid-dissociation constants for H_3nta[17] are $K'_1 = 2.0 \times 10^{-2}$, $K'_2 = 3.98 \times 10^{-3}$ and $K'_3 = 2.14 \times 10^{-10}$ mol dm^{-3}. In the above range of pH (3.0–9.9) the reactive species would be H_2nta^-, $Hnta^{2-}$ and nta^{3-}. Considering the proton-dissociation constants of H_3nta as well as that of $[Mn^{III}(H_2O)]^-$ (the only reactive species), the outer-sphere reaction sequence in Scheme 4 may be postulated. This leads to a general rate

$$[Mn^{III}(H_2O)]^- \overset{K_m}{\rightleftharpoons} [Mn^{III}(OH)]^{2-} + H^+ \tag{2}$$

$$H_2nta^- \overset{K'_2}{\rightleftharpoons} Hnta^{2-} + H^+$$

$$Hnta^{2-} \overset{K'_3}{\rightleftharpoons} nta^{3-} + H^+$$

$$[Mn^{III}(H_2O)]^- + H_2nta^- \xrightarrow{k_1} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^- + Hnta^{2-} \xrightarrow{k_2} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^- + nta^{3-} \xrightarrow{k_3} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^- + \text{free radical} \xrightarrow{\text{fast}} Mn^{II} + \text{product}$$

Scheme 4

expression (7). A convenient way to get the rate parameters is to

$$k_{ox} = \frac{k_{obs} - k_d}{2[nta]_T} = \frac{(k_1[H^+]^2 + k_2K'_2[H^+] + k_3K'_2K'_3)[H^+]}{([H^+]^2 + K'_2[H^+] + K'_2K'_3)(K_m + [H^+])} \tag{7}$$

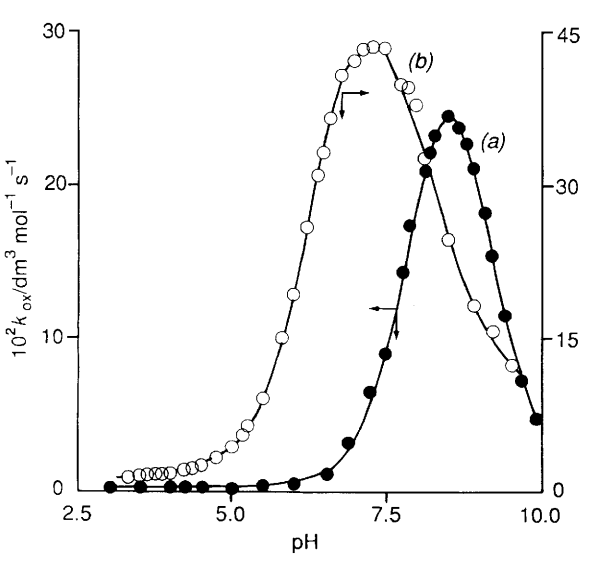


Fig. 2 Variation of k_{ox} as a function of pH for the oxidation of (*a*) nitrilotriacetate and (*b*) ethylenediaminetetraacetate. Other details as in Fig. 1

choose a certain pH region from which certain rate parameters can be extracted. Thus, in the region pH 3.0–5.0 the reactive species are $H_2nta^-(k_1)$ and $Hnta^{2-}(k_2)$ and the corresponding rate equation is (8). The values of the rate parameters and

$$k_{ox} = \frac{k_1[H^+] + k_2K'_2}{[H^+] + K'_2} \tag{8}$$

equilibrium constant as extracted by fitting the experimental data by equation (8) by means of a computer-fit program are: $k_1 = (5.32 \pm 0.06) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, $k_2 = (1.93 \pm 0.01) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and $K'_2 = (3.89 \pm 0.01) \times 10^{-3}$ mol dm^{-3}. Again, in the region of pH 6.9–9.9, the reductant species are $Hnta^{2-}$ and nta^{3-} but beyond pH 6.9 the hydroxo-form of the complex starts to prevail. The rate equation corresponding to the pertinent reactions in the above pH range is (9).

$$k_{ox} = \frac{(k_2[H^+] + k_3K'_3)}{([H^+] + K'_3)}\left(\frac{[H^+]}{K_m + [H^+]}\right) \tag{9}$$

Equation (9) was solved by employing a Simplex optimisation program[18] where a best fit of the experimental data was obtained by varying K'_3 and K_m and keeping the other parameters constant. The evaluated parameters are: $k_2 = (1.93 \pm 0.06) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and $k_3 = (3.62 \pm 0.10)$ dm^3 mol^{-1} s^{-1}; $K'_3 = (1.01 \pm 0.03) \times 10^{-9}$ mol dm^{-3} and $K_m = (8.27 \pm 0.25) \times 10^{-9}$ mol dm^{-3}.

The reported values of K'_2, K'_3 and K_m are very close to the kinetically extracted values. Considering all the rate parameters (k_1, k_2 and k_3) and equilibrium constants (K'_2, K'_3 and K_m), the k_{ox} values were calculated at each pH using the general rate equation(7). An excellent agreement between the calculated and experimental values of k_{ox} [Fig. 2(*a*)] justifies the proposed reaction scheme.

Similarly, the reactivities of all the species of edta present in the experimental pH range (3.3–9.5) were evaluated. The acid-dissociation constants of H_4edta[17] are $K''_1 = 1.02 \times 10^{-3}$, $K''_2 = 2.14 \times 10^{-3}$, $K''_3 = 6.92 \times 10^{-7}$ and $K''_4 = 5.50 \times 10^{-11}$ mol dm^{-3}. Assuming $[Mn^{III}(H_2O)]^-$ as the sole oxidant, the possible reaction pathways are as given in Scheme 5. This leads

$$H_3edta^- \overset{K''_2}{\rightleftharpoons} H_2edta^{2-} + H^+$$

$$H_2edta^{2-} \overset{K''_3}{\rightleftharpoons} Hedta^{3-} + H^+$$

$$Hedta^{3-} \overset{K''_4}{\rightleftharpoons} edta^{4-} + H^+$$

$$[Mn^{III}(H_2O)]^- \overset{K_m}{\rightleftharpoons} [Mn^{III}(OH)]^{2-} + H^+ \tag{2}$$

$$[Mn^{III}(H_2O)]^- + H_3edta^- \xrightarrow{k'_1} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^- + H_2edta^- \xrightarrow{k'_2} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^- + Hedta^{3-} \xrightarrow{k'_3} Mn^{II} + \text{free radical}$$

$$[Mn^{III}(H_2O)]^- + edta^{4-} \xrightarrow{k'_4} Mn^{II} + \text{free radical}$$

Scheme 5

to a generalised rate equation (10). In the range pH 3.3–4.0 the k'_1 and k'_2 paths are operative and corresponding rate equation takes the form (11). Equation (11) was solved by the same

Table 2 Comparison of kinetic data for the oxidation of iminodiacetate, nitrilotriacetate and ethylenediaminetetraacetate with $[Mn^{III}(cdta)]^-$ [a] and $[Co^{III}W_{12}O_{40}]^{5-}$ [b]

			$(dm^3\ mol^{-1}\ s^{-1})$				
Reductant	Oxidant	E°/V	k_0	k_1	k_2	k_3	k_4
edta	$[Mn^{III}(cdta)(H_2O)]^-$	0.81	—	4.42×10^{-3}	1.81×10^{-2}	0.52	14.41
	$Co^{III}W$	1.0	6.80×10^{-3}	4.80×10^{-2}	0.21	1.71	—
nta	$[Mn^{III}(cdta)(H_2O)]^-$	0.81	—	5.32×10^{-4}	1.93×10^{-3}	3.62	
	$Co^{III}W$	1.0	1.10×10^{-3}	7.00×10^{-3}	7.20×10^{-3}	—	
ida	$[Mn^{III}(cdta)(H_2O)]^-$	0.81	—	6.49×10^{-3}	4.45×10^{-2}		
	$Co^{III}W$	1.0	—	4.70×10^{-5}	—		

[a] All the reactions of $[Mn^{III}(cdta)(H_2O)]^-$ were carried out at 30 °C. [b] The reactions of $[Co^{III}W_{12}O_{40}]^{5-}$ with edta, nta and ida were carried out at 15, 30 and 50 °C respectively.

$$k_{ox} = \frac{k_{obs} - k_d}{2[edta]_T} = \frac{(k'_1[H^+]^3 + k'_2K''_2[H^+]^2 + k'_3K''_2K''_3[H^+] + k'_4K''_2K''_3K''_3)[H^+]}{([H^+]^3 + K''_2[H^+]^2 + K''_2K''_3(H^+] + K''_2K''_3K''_4)(K_m + [H^+])} \qquad (10)$$

$$k_{ox} = \frac{k'_1[H^+] + k'_2K''_2}{[H^+] + K''_2} \qquad (11)$$

procedure as for (8) and values thus obtained are: $k'_1 = (4.42 \pm 0.4) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, $k'_2 = (1.81 \pm 0.01) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $K''_2 = (1.22 \pm 0.01) \times 10^{-3}$ mol dm^{-3}. In the range pH 5.0–6.80 the reactivities of H_2edta^{2-} and $Hedta^{3-}$ are to be considered ($pK''_3 = 6.16$), but the complex remains mainly in the aqua-form. The rate equation corresponding to the k'_2 and k'_3 paths is (12) and computed values for the parameters are:

$$k_{ox} = \frac{k'_2[H^+] + k'_3K''_3}{[H^+] + K''_3} \qquad (12)$$

$k'_2 = (1.82 \pm 0.10) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $k'_3 = (0.52 \pm 0.01)$ dm^3 mol^{-1} s^{-1} and $K''_3 = (5.42 \pm 0.04) \times 10^{-7}$ mol dm^{-3}.

Now considering the reactions of $Hedta^{3-}$ and $edta^{4-}$ ($pK''_4 = 10.26$) and the proton dissociation of the complex ($pK_m = 8.11$), the theoretical rate expression in the range pH 7.5–9.5 takes the form (13). Equation (13) was solved in the

$$k_{ox} = \frac{(k'_3[H^+] + k'_4K''_4)}{([H^+] + K''_4)}\left(\frac{[H^+]}{K_m + [H^+]}\right) \qquad (13)$$

same way as for (9) by varying the values of K''_4 and K_m and the parameters thus extracted are: $k'_3 = (0.52 \pm 0.01)$ dm^3 mol^{-1} s^{-1} and $k'_4 = 14.41 \pm 0.42$ dm^3 mol^{-1} s^{-1}; $K''_4 = (6.74 \pm 0.20) \times 10^{-11}$ mol dm^{-3} and $K_m = (7.21 \pm 0.20) \times 10^{-9}$ mol dm^{-3}. There is an excellent agreement between the reported and experimentally obtained values of all the proton-dissociation constants of the reductant and the complex. Taking these values of the equilibrium constants and the rate parameters, k_{ox} was calculated at each experimental pH. There is also an excellent agreement between the experimental and calculated values of k_{ox} [Fig. 2(*b*)] and this strongly supports the proposed mechanism.

The present study thus provides a systematic approach to the evaluation of the reactivities of the different species of the multiply protonated acids having overlapping dissociation constants. The most striking feature is the difference in behaviour of $[Mn^{III}(cdta)]^-$ in acidic and alkaline media towards the different amine-N-polycarboxylates. In the case of ida oxidation, both the aqua- and hydroxo-forms of the complex are reactive, with the aqua more reactive, and this can be explained by considering that deprotonation of the oxidant results in a decrease in reduction potential.[23] The reactivity of the hydroxo-form of this complex was also observed in the oxidation of some *N*-substituted thioureas.[10] However, in that case the reactivity of the hydroxo-species was higher than that of the aqua-form and was explained by considering a ligand-bridged inner-sphere mechanism. In the present case, the reactivity of $[Mn^{III}(OH)]^{2-}$ towards ida led us to assume an inner-sphere mechanism where the intermediate complex would be formed by partial unwrapping of the carboxylate arms of the co-ordinated hexadentate cdta moiety.[21,22] In the oxidation of nta and edta, steric hindrance exerted by the bulky reductants might lead the reaction to proceed *via* an outer-sphere pathway. Additional support in favour of the proposed mechanism comes from a comparison of the rates (Table 2) of oxidation of these polycarboxylates with $[Mn^{III}(cdta)]^-$ and $[Co^{III}W_{12}O_{40}]^{5-}$,[16] where for the latter an outer-sphere mechanism was proposed. The much greater (10^2 times) reactivity of $Hida^-$ towards $[Mn^{III}(H_2O)]^-$ ($E^\circ = 0.81$ V)[3] than that of $[Co^{III}W_{12}O_{40}]^{5-}$ ($E^\circ = 1.0$ V),[24] though the latter has a higher reduction potential, lead us to suggest an inner-sphere mechanism. On the other hand, an outer-sphere mechanism for nta and edta seems to be more reasonable due to the slower rate of reaction of any particular species of nta/edta with $[Mn^{III}(H_2O)]^-$ than that with $[Co^{III}W_{12}O_{40}]^{5-}$ (both having similar electron self-exchange rate constants),[15,25] which is in accordance with their reduction potentials. It is further supported by the inactivity of $[Mn^{III}(OH)]^{2-}$ towards nta and edta. A similar observation was made by Macartney and Thompson[15] in the oxidation of some inorganic complexes with this complex.

An estimate for the self-decomposition rates of $[Mn^{III}(cdta)(H_2O)]^-$ ($k_{d(H)}$) and $[Mn^{III}(cdta)(OH)]^{2-}$ [$k_{d(OH)}$] can be made from the intercept of plots of k_{obs} *vs.* [R] in acidic and alkaline media respectively (Table 1): $(k_{d(H)})_{av} = (1.58 \pm 1.15) \times 10^{-5}$ s^{-1} in the range pH 3.50–6.04, $(k_{d(OH)})_{av} = (1.12 \pm 0.50) \times 10^{-4}$ s^{-1} in the range pH 7.50–9.67. In the range pH 3.5–6.04 the rate is found to be constant at a particular ionic strength and temperature and agrees quite well with reported values.[3] Again in the region pH 7.5–9.67 $k_{d(OH)}$ is constant and higher than $k_{d(H)}$. There is no report of $k_{d(OH)}$ in the literature.

A comparison of the reactivity of the acid species showed that the protonated species are less reactive than the corresponding deprotonated species and follow the orders: $Hida^- < ida^{2-}$; $H_2nta^- < Hnta^{2-} < nta^{3-}$; and $H_3edta^- < H_2edta^{2-} < Hedta^{3-} < edta^{4-}$. A similar increase in reactivity upon deprotonation was observed for other organic reductants as a result of the change in their oxidation potentials[12,26] and the same trend was also followed in the reduction of $[Co^{III}W_{12}O_{40}]^{5-}$ by these reductants.[16]

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