Mechanisms of Reduction of *trans*-Cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetatomanganate(III) by Hydrazine, Hydroxylamine, and Substituted Benzene-1,2-diols †

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The kinetics and mechanism of reduction of *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetatomanganate(III), $[Mn^{III}(cdta)(H_2O)]^-$, by hydrazine, hydroxylamine, and a series of substituted benzene-1,2-diols $C_6H_3(OH)_2R$ (R = H, 4-Me, 4-CO_2H, or 3-CO_2H) have been investigated by the stopped-flow technique. Simple first-order dependence on Mn^{III} complex and reductant concentrations has been observed for hydrazine, which shows a rate with $[H^+]^{-1}$ dependence. For hydroxylamine, complex kinetic dependences on reductant and hydrogen-ion concentration suggest a composite inner-sphere mechanism. Also, in the case of the diols an inner-sphere mechanism, through intermediate association, is proposed; for these substrates experimental rates, higher than those computed with the Marcus cross relation, and limiting kinetics are in agreement with the lability of the oxidizing complex.

The chemistry of Mn^{III} as oxidant has received much attention both as aqua-ion [1] or as complex species.[2] A number of kinetic studies using aquamanganese(III) in perchloric acid medium have been published and both inner- and outer-sphere mechanisms have been found to be operative in oxidation reactions of inorganic species as well as in organic compounds, such as, for example, hydrazine,[3] hydroxylamine,[4] nitrous acid,[4] hydrogen peroxide,[5] hydrazoic acid,[6] catechols and quinols.[7,8] Also in the case of stable Mn^{III} complexes with polyaminopolycarboxylic ligands, such as $[Mn^{III}(edta)]^-$ or $[Mn^{III}(cdta)]^-$ (edta = ethylenediaminetetra-acetate; cdta = *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate), outer-sphere electron transfer reactions, as well as inner-sphere, have been described, in agreement with the labile behaviour of these complexes.[9] In the case of the oxidation of benzene-1,4-diol to the corresponding quinone by $[Mn^{III}(edta)]^-$, a complex kinetic behaviour has been observed due to the presence of a simultaneous precursor complex formation step and the redox process.[9] Also, the oxidation of nitrite ion by $[Mn^{III}(cdta)]^-$ [10] showed a complex behaviour with second-order dependence on each reagent and this has been interpreted in terms of 1 : 1 inner-sphere complex formation followed by reductant dimerization during intermediate radical formation. These oxidizing complexes have been described as seven-co-ordinate in aqueous solution with the ligands acting as sexidentate and a labile water molecule occupying the last co-ordination site.[11] Moreover, the carboxylate 'arms' of the ligand may well be rapidly [12] unwrapped so that precursor mixed complexes may play important roles in redox reactions of these oxidants.[9]

In this paper, the results of a study of the stoicheiometry and kinetics of the oxidation of a series of reductants, namely hydrazine, hydroxylamine, and a series of substituted benzene-1,2-diols by $[Mn^{III}(cdta)]^-$, have been reported. These substrates provide different co-ordinating abilities, giving an opportunity for clarifying the oxidation mechanism of these Mn^{III} complexes; among them, $[Mn^{III}(cdta)]^-$ is the most resistant to decomposition ($k_{dec.} \simeq 7 \times 10^{-6}$ s^{-1} at 25.0 °C in acid medium).[13]

Experimental

Solutions of $[Mn^{III}(cdta)]^-$ were freshly prepared according to three different procedures:[9,13] (*i*) from $KMnO_4$, after reduction by EtOH in the presence of H_4cdta, and by oxidation of $[Mn^{II}(cdta)]^{2-}$ with (*ii*) PbO_2 in H_2SO_4 medium and (*iii*) at a platinum anode. The same kinetic behaviour was observed in the kinetic runs for the oxidant prepared by each method, therefore the clean oxidation at an inert anode was then preferred.

The concentration of $[Mn^{III}(cdta)]^-$ was determined either iodometrically or spectrophotometrically at 510 nm (ε = 345 dm^3 mol^{-1} cm^{-1} at pH <6).[13] Solutions of $[Mn^{II}(cdta)]^{2-}$ complex were prepared by mixing appropriate amounts of $Mn[ClO_4]_2$ and H_4cdta and bringing the pH to *ca.* 4 (a slight excess of ligand, *ca.* 1%, was added in order to avoid the presence of free Mn).

Reaction rates were monitored with a Durrum–Gibson stopped-flow spectrophotometer at 510 nm by following the decrease of $[Mn^{III}(cdta)]^-$, the only absorbing species at this wavelength; an excess of reductant (> ten-fold) was used in all runs in order to ensure pseudo-first-order conditions.

Ionic strength was adjusted to 0.20 mol dm^{-3} by using $NaClO_4$. Solutions were buffered to 2.50 < pH < 4.50 with 2×10^{-2} mol dm^{-3} trichloroacetate and acetate. Measurements were performed at different temperatures in order to evaluate activation parameters. In the investigated conditions, hydrazine (pK_1A *ca.* 8.0) [14,15] and hydroxylamine (pKA *ca.* 6.2) [15] have been considered as protonated, namely $N_2H_5^+$ and NH_3OH^+ respectively.

Also, the Mn^{III} complex, which undergoes one-proton dissociation at pH *ca.* 8,[13] has a labile water molecule in its co-ordination sphere: $[Mn^{III}(cdta)(H_2O)]^-$, giving either seven-co-ordinate Mn or with one arm of the ligand detached from the metal centre.

Results and Discussion

Oxidation of Hydrazine.—By mixing equimolar solutions of the pink $[Mn^{III}(cdta)]^-$ complex and hydrazine in acidic solution (pH 2—5) a very fast bleaching is observed. In order to estimate the reaction stoicheiometry, increasing portions of a solution of hydrazine were added to solutions of $[Mn^{III}(cdta)]^-$ until a complete disappearance of the complex occurred. Plots of absorbance at 510 nm *versus* the ratio R = $[Mn^{III}(cdta)^-]/[\text{hydrazine}]$ showed that the molar stoicheiometric quotient between the reagents is $n = 1.0 \pm 0.1$. At $R > 1$, the unreacted Mn^{III} complex disappeared slowly thus showing that primary products of reaction give rise to further redox steps with excess oxidant.

This stoicheiometric ratio has been previously observed in other oxidations of hydrazine by one-electron oxidants such

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† *Non-S.I. unit employed:* 1 cal = 4.184 J.

Table 1. Pseudo-first-order ($k_{obs.}$/s^{-1}) and second-order (k_{II}/dm^3 mol^{-1} s^{-1}) rate constants for the oxidation of hydrazine by [Mn^{III}(cdta)(H$_2$O)]$^-$ under different experimental conditions *

pH	2.50	3.00	3.50	4.00	4.50
10^3[N$_2$H$_5$$^+$]/mol dm^{-3}	$k_{obs.}$/s^{-1} (20.0 °C)				
0.50	0.46	0.92	2.07	5.38	15.8
1.00	0.95	1.83	4.33	10.7	29.1
1.50	1.34	2.57	6.63	14.2	40.2
2.00	1.81	3.57	8.82	20.3	53.3
2.50	2.31	4.89	10.4	23.2	69.8
T/°C	10^{-3}k_{II}/dm^3 mol^{-1} s^{-1}				
9.7	0.67	1.30	2.70	6.60	18.7
20.0	0.92	1.80	4.40	9.90	28.0
30.0	1.22	2.70	7.00	16.4	61.3

* [Mn^{III}(cdta)(H$_2$O)$^-$] = (5—10) × 10^{-5} mol dm^{-3}.

as Mn^{III}(aq),[3] [Co^{III}(nta)(H$_2$O)$_2$] (nta = nitrilotriacetate),[16] while increasing values for n were found when, at increased R values, stronger oxidants were used such as [IrCl$_6$]$^{2-}$ and related Ir^{IV} complexes ($n = 4$),[16,17] [Fe(CN)$_6$]$^{3-}$ ($n = 4$),[16] [MnO$_4$]$^-$ ($n = 4$),[16] [Cu(NH$_3$)$_4$]$^{2+}$ (n = *ca.* 5),[16] [Mo(CN)$_8$]$^{3-}$ (n = *ca.* 5),[16] and I$_2$ ($n = 2$).[18] Since the kinetic measurements were performed also with hydrazine in large excess over Mn^{III} ($R \ll 1$), further oxidation of the primary product was avoided and the condition $n = 1$ could be retained. The overall reaction can be expressed therefore as in equation (1). Since [Mn^{III}(cdta)(H$_2$O)]$^-$ is a one-electron oxidant, the first reaction step is an intermediate radical formation, equation (2),

$$2\,[\mathrm{Mn^{III}(cdta)(H_2O)}]^- + 2\,\mathrm{N_2H_5}^+ \longrightarrow 2\,[\mathrm{Mn^{II}(cdta)(H_2O)}]^{2-} + 2\,\mathrm{NH_4}^+ + 2\,\mathrm{H}^+ + \mathrm{N_2} \quad (1)$$

$$\mathrm{N_2H_5}^+ \longrightarrow \mathrm{N_2H_4}^{\cdot +} + \mathrm{H}^+ + e^- \quad (2)$$

which then rearranges rapidly to give the final product according to the overall reaction (1) above: 2 N$_2$H$_4$$^{\cdot+}$ ⟶ N$_2$ + 2 NH$_4$$^+$.

Kinetic runs were performed with [Mn^{III}(cdta)(H$_2$O)]$^-$ (5.0—10) × 10^{-5} mol dm^{-3} and hydrazine (5.0—25) × 10^{-4} mol dm^{-3}. The reaction was first order with respect to the oxidant (linear plots of lnA_t *versus* time for at least three half-lives; A_t is the absorbance due to Mn^{III} complex at 510 nm, where no other species absorbs). The dependence of $k_{obs.}$ (the observed pseudo-first-order rate constant derived from the slope of the above plots) on [N$_2$H$_5$$^+$] was linear (data are in Table 1), showing that the reaction is first order also on the oxidized substrate. The overall second-order specific rate constant (k_{II}) showed a dependence on acidity of the form in equation (3) as shown in Figure 1.

$$k_{II} = k + k'[\mathrm{H}^+]^{-1} \quad (3)$$

Kinetic measurements, performed at 9.7, 20.0, and 30.0 °C and between pH 2.5 and 4.5, agree with the observed kinetic law (4). The reaction sequence shown by equations (5)—(8)

$$\text{Rate} = -\mathrm{d}[\mathrm{Mn^{III}(cdta)^-}]_{tot.}/\mathrm{d}t = k_{obs.}[\mathrm{Mn^{III}(cdta)^-}]_{tot.} = (k + k'[\mathrm{H}^+]^{-1})\,[\mathrm{Mn^{III}(cdta)^-}][\mathrm{N_2H_5}^+] \quad (4)$$

can then be advanced. From this sequence can be derived equation (9) which represents the observed behaviour of equation (4) with the conditions: $K_{ass.}$[N$_2$H$_5$$^+$] and $K_{ass.}$.K_H[N$_2$H$_5$$^+$][H$^+$]$^{-1}$ $\ll$ 1 and those in (10).

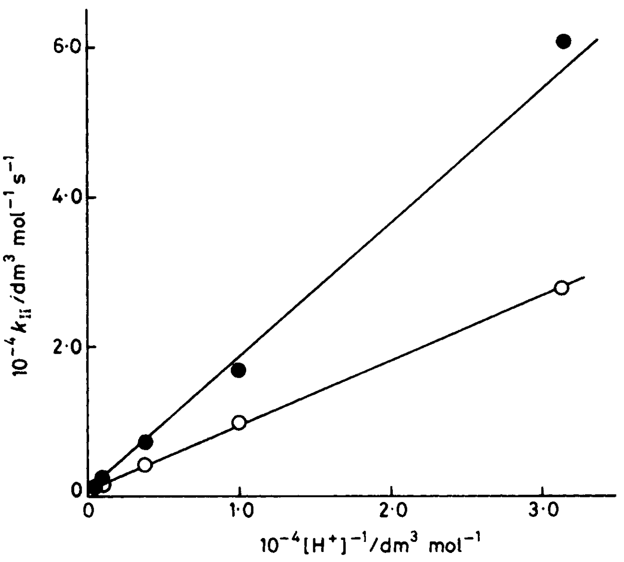


Figure 1. Variation of the second-order rate constant k_{II} as a function of [H$^+$]$^{-1}$ for the oxidation of hydrazine at 20.0 (○) and 30.0 °C (●)

$$[\mathrm{Mn^{III}(cdta)(H_2O)}]^- + \mathrm{N_2H_5}^+ \underset{}{\overset{K_{ass.}}{\rightleftharpoons}} [\mathrm{Mn^{III}(cdta)(N_2H_5)}] \quad (5)$$

$$[\mathrm{Mn^{III}(cdta)(N_2H_5)}] \overset{K_H}{\rightleftharpoons} [\mathrm{Mn^{III}(cdta)(N_2H_4)}]^- + \mathrm{H}^+ \quad (6)$$

$$[\mathrm{Mn^{III}(cdta)(N_2H_5)}] \xrightarrow{k_1} [\mathrm{Mn^{II}(cdta)(H_2O)}]^{2-} + \mathrm{N_2H_5}^{\cdot 2+} \quad (7)$$

$$[\mathrm{Mn^{III}(cdta)(N_2H_4)}]^- \xrightarrow{k_2} [\mathrm{Mn^{II}(cdta)(H_2O)}]^{2-} + \mathrm{N_2H_4}^{\cdot +} \quad (8)$$

$$\text{Rate} = \frac{k_1K_{ass.} + k_2K_{ass.}.K_H[\mathrm{H}^+]^{-1}}{1 + K_{ass.}.[\mathrm{N_2H_5}^+] + K_{ass.}.K_H[\mathrm{H}^+]^{-1}[\mathrm{N_2H_5}^+]} \times [\mathrm{Mn^{III}(cdta)^-}]_{tot.}.[\mathrm{N_2H_5}^+] \quad (9)$$

$$k = k_1K_{ass.} \text{ and } k' = k_2K_{ass.}.K_H \quad (10)$$

It must be noted that the main path is the one with k' rate constant (inverse acid dependence) therefore a proton release equilibrium such as (6) is considered, with deprotonation of the reductant after co-ordination to the metal centre. An outer-sphere mechanism could be alternatively considered with participation of N$_2$H$_4$ unprotonated species in the main path. However in this case the ion-pair precursor species for N$_2$H$_5$$^+$ would be stabilized by the opposite charges of the reactants so that a higher relative contribution of the k term [see equation (3) and Figure 1] would be expected. Other reactions of hydrazine have been found to be either outer- or inner-sphere such as in the case of Mn^{III} (aq) (o.s.)[3] or Tl^{III} (i.s.).[19] Support for the proposed inner-sphere mechanism comes from the activation parameters. The low $\Delta H^\ddagger$, as in the case of Tl^{III} can be again ascribed to an inner-sphere interaction. Other considerations will be reported below.

Table 2 contains all the derived parameters obtained from the variation of k_{II} as a function of [H$^+$]$^{-1}$ at each temperature, together with the activation parameters for both paths.

Table 2. Kinetic and activation parameters for the oxidation of hydrazine by $[Mn^{III}(cdta)(H_2O)]^-$

T/°C	9.7	20.0	30.0
$k_1K_{ass.}$/dm^3 mol^{-1} s^{-1}	$(4 \pm 1) \times 10^2$	$(7 \pm 2) \times 10^2$	$(10 \pm 2) \times 10^2$
$\Delta H^‡$/kcal mol^{-1}		7 ± 4	
$\Delta S^‡$/cal K^{-1} mol^{-1}		-22 ± 10	
$k_2K_{ass.}K_H$/s^{-1}	0.58 ± 0.05	0.90 ± 0.07	1.90 ± 0.10
$\Delta H^‡$/kcal mol^{-1}		9 ± 1	
$\Delta S^‡$/cal K^{-1} mol^{-1}		-27 ± 3	

Table 3. Pseudo-first-order ($k_{obs.}$/s^{-1}) and a and b terms [equation (13)] for the oxidation of hydroxylamine by $[Mn^{III}(cdta)(H_2O)]^-$ under different experimental conditions *

pH	2.50	3.00	3.50	4.00	4.50
$10^2[NH_3OH^+]$/ mol dm^{-3}	$k_{obs.}$/s^{-1} (20.0 °C)				
0.50	0.0193	0.0420	0.129	0.767	5.26
1.00	0.0403	0.0928	0.324	1.95	16.4
1.50	0.0615	0.145	0.595	3.57	31.6
2.00	0.0886	0.218	0.896	5.60	46.7
2.50	0.109	0.292	1.24	7.95	75.0
T/°C	a/dm^3 mol^{-1} s^{-1}				
9.7		3.8	8.0	30	125
20.0	3.7	7.5	21.0	110	400
30.0	6.3	13.8	46.0	180	580
	$10^{-3}b$/dm^6 mol^{-2} s^{-1}				
9.7		0.140	0.890	6.10	42.5
20.0	0.03	0.170	1.13	8.35	98.0
30.0	0.18	0.42	1.70	17.0	120

* $[Mn^{III}(cdta)(H_2O)^-] = (5—10) \times 10^{-5}$ mol dm^{-3}.

Oxidation of Hydroxylamine.—This reaction has been investigated in pseudo-first-order conditions also (large excess of reductant) so that no Mn^{III} complex remained at the end of each run and the progress could be followed at 510 nm. The reaction stoicheiometry could not be investigated in these conditions. A procedure similar to the one described for hydrazine was unsuccessful since the lower rate did not allow, around $R = 1$, a distinction between primary disappearance of Mn^{III} complex and further steps: a complete disappearance of the complex was observed for up to $R = 5$ showing additional secondary steps between excess $[Mn^{III}(cdta)]^-$ and primary oxidation products of the reductant. These steps are absent in the conditions investigated in the kinetic experiments; such an increase of the stoicheiometric ratio as a function of excess oxidant has been previously observed for the oxidation of hydroxylamine by other one-electron oxidants.[20] A stoicheiometry $n = 1$ has been assumed in our conditions since further oxidation steps were surely absent; the first interaction gives a radical, equation (11), which then, in the absence of excess oxidant, rapidly gives the products in

$$NH_3OH^+ \longrightarrow NH_2OH^{\cdot+} + H^+ + e^- \quad (11)$$

$$2\,NH_2OH^{\cdot+} \longrightarrow N_2 + 2\,H_2O + 2\,H^+ \quad (12)$$

equation (12). The mechanism involved in step (11) is complex, as shown by the kinetic results. The rate of reaction is first order with respect to the Mn^{III} complex, since log plots were linear for at least three half-lives (the observed pseudo-first-order rate constants for different experimental conditions are collected in Table 3).

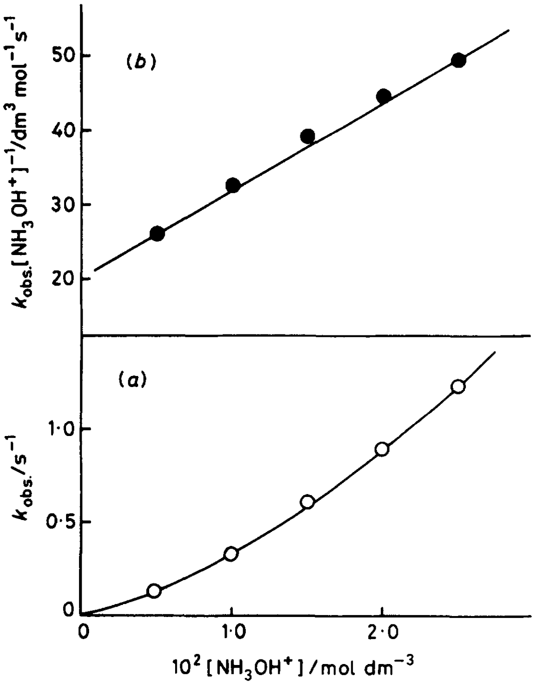


Figure 2. Variation of (*a*) $k_{obs.}$ and (*b*) $k_{obs.}/[NH_3OH^+]$, for the oxidation of hydroxylamine at 20.0 °C and at pH 3.5, as a function of reductant concentration

A dependence higher than first order on hydroxylamine concentration has been observed as can be seen in Figure 2(*a*), where a plot of $k_{obs.}$ *versus* $[NH_3OH^+]$ is reported. The observed behaviour can be interpreted in terms of two competing pathways: one first order and another second order on reductant concentration, according to equation (13), which can be rewritten as equation (14). Plots of $k_{obs.}/[NH_3OH^+]$ as a function of $[NH_3OH^+]$ were linear [see Figure 2(*b*)] and intercepts and slopes gave the values of a and b at the investigated acidities.

$$k_{obs.} = a[NH_3OH^+] + b[NH_3OH^+]^2 \quad (13)$$

$$k_{obs.}/[NH_3OH^+] = a + b[NH_3OH^+] \quad (14)$$

The dependences of a and b on acidity are given respectively by equations (15) and (16) as shown in Figures 3 and 4. The

$$a = k[H^+]^{-1} \quad (15)$$

$$b = k'[H^+]^{-1} + k''[H^+]^{-2} \quad (16)$$

first of the two competitive contributions in equation (13) is formally similar to the one for the oxidation of hydrazine and consequently can be interpreted through an inner-sphere mechanism where addition of NH_3OH^+ into the labile and non-saturated co-ordination sphere of $[Mn^{III}(cdta)(H_2O)]^-$ involves the proton release responsible for the inverse acidity dependence of equation (15) [equations (17)—(20)].

$$[Mn^{III}(cdta)(H_2O)]^- + NH_3OH^+ \xrightleftharpoons{K_{ass.}} [Mn^{III}(cdta)(NH_3OH)] \quad (17)$$

$$[Mn^{III}(cdta)(NH_3OH)] \xrightleftharpoons{K_H} [Mn^{III}(cdta)(NH_2OH)]^- + H^+ \quad (18)$$

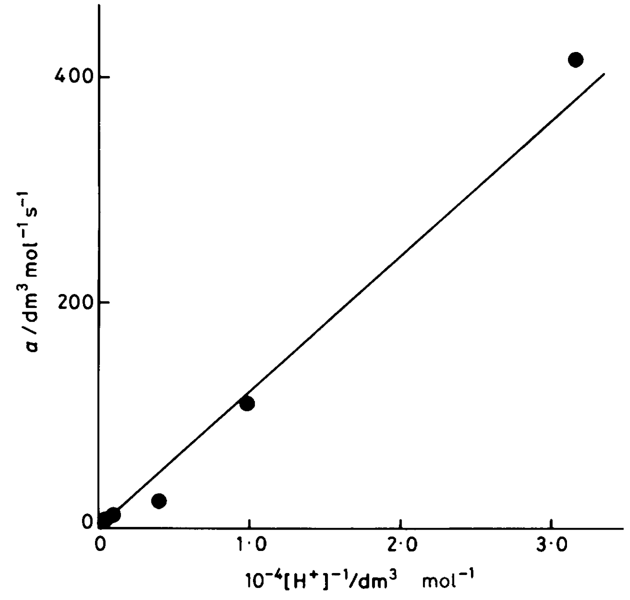


Figure 3. Variation of a [equations (14) and (15)] as a function of $[\mathrm{H^+}]^{-1}$ for the oxidation of hydroxylamine at 20.0 °C

$$[\mathrm{Mn^{III}(cdta)(NH_2OH)}]^- \xrightarrow{k_3} [\mathrm{Mn^{II}(cdta)(H_2O)}]^{2-} + \mathrm{NH_2OH^{\cdot+}} \quad (19)$$

$$2\,\mathrm{NH_2OH^{\cdot+}} \xrightarrow{\text{fast}} \mathrm{N_2} + 2\,\mathrm{H_2O} + 2\,\mathrm{H^+} \quad (20)$$

From this sequence, under the condition $K_{\mathrm{ass.}}K_{\mathrm{H}}[\mathrm{NH_3OH^+}][\mathrm{H^+}]^{-1} \ll 1$, $k = k_3K_{\mathrm{ass.}}K_{\mathrm{H}}$ is obtained. Alternatively, an outer-sphere mechanism cannot be ruled out, but in this case protonation of $\mathrm{NH_3OH^+}$ would make more favourable the reactant approach before the electron transfer and the inverse acid dependence should not occur. The ambiguity of the nature of the first-order step is however overcome in the case of the second-order step. In fact, the second-order dependence on the reductant clearly shows an inner-sphere interaction to be operative, and the two terms in equation (16) are given by equations (21)—(24). Again, under the previously described conditions, the observed dependences can be accounted for with the equations in (25).

$$[\mathrm{Mn^{III}(cdta)(NH_2OH)}]^- + \mathrm{NH_3OH^+} \xrightleftharpoons{K_{\mathrm{ass.}}} [\mathrm{Mn^{III}(cdta)(NH_2OH)(NH_3OH)}] \quad (21)$$

$$[\mathrm{Mn^{III}(cdta)(NH_2OH)(NH_3OH)}] \xrightleftharpoons{K'_{\mathrm{H}}} [\mathrm{Mn^{III}(cdta)(NH_2OH)_2}]^- + \mathrm{H^+} \quad (22)$$

$$[\mathrm{Mn^{III}(cdta)(NH_2OH)(NH_3OH)}] \xrightarrow{k_4} [\mathrm{Mn^{II}(cdta)(NH_2OH)}]^{2-} + \mathrm{NH_2OH^{\cdot+}} + \mathrm{H^+} \quad (23)$$

$$[\mathrm{Mn^{III}(cdta)(NH_2OH)_2}]^- \xrightarrow{k_5} [\mathrm{Mn^{II}(cdta)(NH_2OH)}]^{2-} + \mathrm{NH_2OH^{\cdot+}}$$

$$\text{followed by } 2\,\mathrm{NH_2OH^{\cdot+}} \xrightarrow{\text{fast}} \mathrm{N_2} + 2\,\mathrm{H_2O} + 2\,\mathrm{H^+} \quad (24)$$

$$k' = k_4K_{\mathrm{ass.}}K'_{\mathrm{ass.}}K_{\mathrm{H}} \quad \text{and} \quad k'' = k_5K_{\mathrm{ass.}}K'_{\mathrm{ass.}}K_{\mathrm{H}}K'_{\mathrm{H}} \quad (25)$$

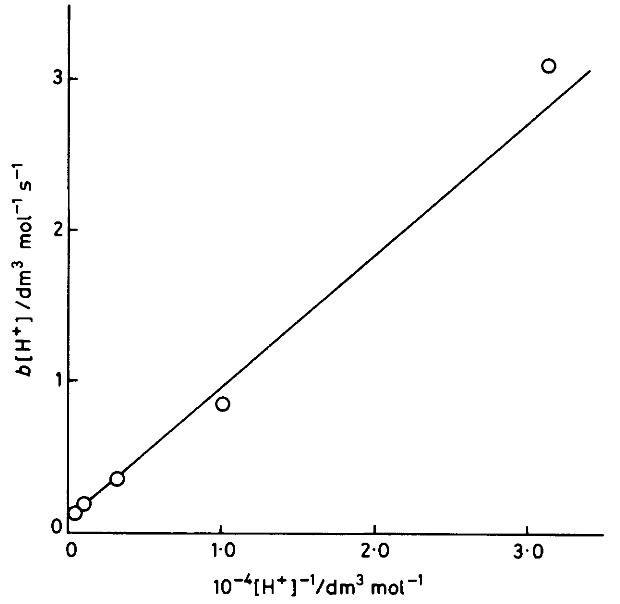


Figure 4. Variation of $b[\mathrm{H^+}]$ [equations (14) and (16)] as a function of $[\mathrm{H^+}]^{-1}$ for the oxidation of hydroxylamine at 20.0 °C

Table 4. Kinetic and activation parameters for the oxidation of hydroxylamine by $[\mathrm{Mn^{III}(cdta)(H_2O)}]^-$

T/°C	9.7	20.0	30.0
$k_3K_{\mathrm{ass.}}K_{\mathrm{H}}$/s^{-1}	0.003 ± 0.001	0.011 ± 0.001	0.018 ± 0.002
$\Delta H^‡$/kcal mol^{-1}		14 ± 4	
$\Delta S^‡$/cal K^{-1} mol^{-1}		−18 ± 10	
$k_4K_{\mathrm{ass.}}K'_{\mathrm{ass.}}K_{\mathrm{H}}$ /dm^3 mol^{-1} s^{-1}	0.13 ± 0.07	0.10 ± 0.07	0.30 ± 0.10
$\Delta H^‡$/kcal mol^{-1}		7 ± 5	
$\Delta S^‡$/cal K^{-1} mol^{-1}		−35 ± 15	
$k_5K_{\mathrm{ass.}}K'_{\mathrm{ass.}}K_{\mathrm{H}}K'_{\mathrm{H}}$/ s^{-1}	(5 ± 1) × 10^{-5}	(9 ± 1) × 10^{-5}	(11 ± 1) × 10^{-5}
$\Delta H^‡$/kcal mol^{-1}		6 ± 2	
$\Delta S^‡$/cal K^{-1} mol^{-1}		−55 ± 6	

Therefore the competition indicated by equation (13) involves the oxidation of a first or of a second hydroxylamine molecule entering the co-ordination sphere of $\mathrm{Mn^{III}}$. The inner-sphere type of interaction which is suggested by this composite reductant dependence as well as composite acid dependence is supported also for these reactions by the low value of the enthalpies of activation computed for the observed pathways (see Table 4 which contains all the kinetic parameters for the oxidation of hydroxylamine).

Generally, the behaviour of hydroxylamine in reactions with mono- and bi-electron acceptors has been found to be similar to that of hydrazine with the same oxidants. Also, this analogy, observed for a wide series of reactions, implies, together with the other arguments, that the present reaction of hydrazine should be considered as inner sphere.

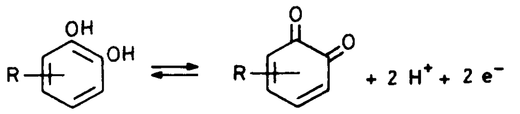
*Oxidation of Benzene-*1,2*-diols.*—An excess of organic reductant with respect to $[\mathrm{Mn^{III}(cdta)}]^-$ was used also for these reactions and the reactions were found to proceed with pseudo-first-order kinetics for all the investigated derivatives, namely benzene-1,2-diol ($\mathrm{H_2L^1}$), 4-methylbenzene-1,2-diol ($\mathrm{H_2L^2}$), 3,4-dihydroxybenzoic acid ($\mathrm{H_2L^3}$), and 2,3-dihydroxybenzoic acid ($\mathrm{H_2L^4}$). These substrates undergo a reversible

Table 5. Summary of equilibrium and standard data for the investigated reactants

Compound	$E°/V$ [a,b]	$E°'/V$ [b,c]	pKA [b,d]	$k_{self-ex}$ [e]$/s^{-1}$
H_2L^1	0.792	1.17	10	1×10^8
H_2L^2	0.739	1.12	11	1×10^8
H_2L^3	0.885	1.265	9	1×10^8
H_2L^4	0.870	1.25	9	1×10^8
$[Mn(cdta)]^{-/2-}$	0.81 [f]			1.2 [g]

[a] For the couple : quinone + 2 H^+ + 2 e^- $\rightleftharpoons$ benzenediol. [b] Ref. 21 and E. Pelizzetti, E. Mentasti, and C. Baiocchi, *J. Phys. Chem.*, 1976, **80**, 2979 and refs. therein. [c] For the couple: (semiquinone)$^\cdot$ + H^+ + e^- $\rightleftharpoons$ benzenediol. [d] For the dissociation of the first phenolic ^-OH group. [e] Ref. 23. [f] Ref. 13. [g] See Y. A. Im and D. H. Bush, *J. Am. Chem. Soc.*, 1961, **83**, 3357.

two-electron oxidation step with formation of the corresponding *o*-quinone according to equation (26) through intermediate semiquinone radical formation.



(26)

The oxidation of these substrates by $[Mn^{III}(cdta)]^-$ proceeds with different mechanisms depending on the different reduction potential, co-ordination ability, and dissociation constants of the potentially co-ordinating groups of the benzene diols (H_2L). Table 5 shows the variation of the reduction potential for the quinone/diol couple, semiquinone/diol couple and dissociation constant pK_1A for $H_2L \rightleftharpoons HL^- + H^+$. Table 6 reports the observed pseudo-first-order rate constants for the oxidation of H_2L^1, H_2L^2, and H_2L^3. At different substrate concentrations, the variation of $k_{obs.}$ as a function of the concentration of H_2L^1, H_2L^2, and H_2L^3 shows a linear behaviour and from the slopes the second-order rate constants reported in Table 7 were evaluated.

A very different dependence of the rate of oxidation of H_2L^1, H_2L^2, or H_2L^3 on acidity is shown by the data in Tables 6 and 7; in particular, H_2L^2 shows an independence of k_{II} on acidity, while an inverse dependence on acidity is present for H_2L^3 (see Figure 5); an intermediate behaviour is observed for H_2L^1. This different behaviour can be accounted for if the increased acidity of the substituted derivatives, $L^2 < L^1 < L^3$, is taken into account on one side and the parallel increasing tendency to co-ordination (*cf.* increased co-ordinating ability, for example, of disodium 4,5-dihydroxy-1,3-benzenedisulphonate, pK_1A 7, towards Fe^{III} with respect to benzene-1,2-diol, pK_1A *ca.* 10).[22] Therefore the behaviour of 4-methylbenzene-1,2-diol (H_2L^2) can be represented by equations (27)—(30); equation (30) reduces to the observed behaviour, *i.e.* $k_{II} = 2\,k_{et}K_{ass.}$, under the condition $K_{ass.}[H_2L^2] \ll 1$.

$$[Mn^{III}(cdta)(H_2O)]^- + H_2L^2 \xleftarrow{K_{ass.}} [Mn^{III}(cdta)(H_2L^2)]^- \quad (27)$$

$$[Mn^{III}(cdta)(H_2L^2)]^- \xrightarrow{k_{et}} [Mn^{II}(cdta)]^{2-} + (H_2L^2)^{\cdot +} \quad (28)$$

$$[Mn^{III}(cdta)]^- + (H_2L^2)^{\cdot +} \xrightarrow{\text{fast}} o\text{-quinone} + 2\,H^+ + [Mn^{II}(cdta)]^{2-} \quad (29)$$

Table 6. Pseudo-first-order rate constants for the oxidation of benzenediols by $[Mn^{III}(cdta)(H_2O)]^-$ at different acidities and at 20.0 °C

Compound	pH	2.50	3.00	3.50	4.00	4.50
	10^3[diol]/ mol dm^{-3}	$k_{obs.}/s^{-1}$				
H_2L^1	0.50	3.14	3.43	3.88		4.15
	1.00	5.59	6.00	7.11	8.12	8.52
	1.50	7.30	8.92	9.54	9.83	13.5
	2.00	10.2	11.9	13.7	16.2	16.9
	2.50	10.8	14.9	18.5	21.8	23.5
H_2L^2	0.50	6.38	5.47	5.13	5.75	6.64
	1.00	9.17	10.9	9.65	10.7	11.4
	1.50	17.1	14.6	15.1	14.8	15.9
	2.00	23.7	23.1	19.4	21.2	20.0
	2.50	25.8	25.1	24.7	25.3	24.0
H_2L^3	0.50	0.048	0.089	0.193	1.07	2.73
	1.00	0.102	0.191	0.450	2.23	5.26
	1.50	0.137	0.294	0.841	3.99	8.86
	2.00	0.188	0.375	1.30	6.13	11.4
	2.50	0.262	0.480	2.15		13.8
H_2L^4	0.50	0.180	0.235	0.194	0.199	0.281
	1.00	0.328	0.345	0.306	0.386	0.482
	1.50	0.477	0.439	0.360	0.515	0.688
	2.00	0.520	0.454	0.443	0.639	0.795
	2.50	0.583	0.459	0.467	0.663	1.02

Table 7. Second-order rate constants ($k_{II}/dm^3\ mol^{-1}\ s^{-1}$), for the oxidation of H_2L^1, H_2L^2, and H_2L^3 by $[Mn^{III}(cdta)(H_2O)]^-$ at different acidities and temperatures

		pH				
Compound	T/°C	2.50	3.00	3.50	4.00	4.50
		$10^{-3}k_{II}/dm^3\ mol^{-1}\ s^{-1}$				
H_2L^1	10.0	4.1	4.9	5.2	7.5	9.1
	20.0	5.2	6.2	7.2	7.8	8.5
	30.0	4.7	5.2	6.5	6.3	6.6
H_2L^2	10.0	10.7		8.6	10.8	13.1
	20.0	11.0	10.8	10.3	11.3	10.4
	30.0	10.5	9.1	9.3	10.0	11.6
H_2L^3	20.0	0.095	0.19	0.59	2.8	5.7
	30.0	0.19	0.36	0.96	3.6	6.5
	38.0	0.25	0.42	1.2	4.0	6.9

$$\text{Rate} = \frac{2k_{et}K_{ass.}[Mn^{III}(cdta)^-]_{tot.}[H_2L^2]}{1 + K_{ass.}[H_2L^2]} \quad (30)$$

In the case of H_2L^3, the sequence of equations (31)—(34) may be proposed, which, again, reduces to the observed kinetic law, *i.e.* $k_{II} = 2k_{et}K_{ass.}$, under the condition $K_{ass.}[H^+]^{-1}[H_2L^3] \ll 1$.

$$[Mn^{III}(cdta)(H_2O)]^- + H_2L^3 \xrightarrow{K_{ass.}} [Mn^{III}(cdta)(HL^3)]^{2-} + H^+ \quad (31)$$

$$[Mn^{III}(cdta)(HL^3)]^{2-} \xrightarrow{k_{et}} [Mn^{II}(cdta)]^{2-} + (HL^3)^\cdot \quad (32)$$

$$[Mn^{III}(cdta)]^- + (HL^3)^\cdot \xrightarrow{\text{fast}} o\text{-quinone} + H^+ + [Mn^{II}(cdta)]^{2-} \quad (33)$$

$$\text{Rate} = \frac{2k_{et}K_{ass.}[H^+]^{-1}[Mn^{III}(cdta)^-]_{tot.}[H_2L^3]}{1 + K_{ass.}[H^+]^{-1}[H_2L^3]} \quad (34)$$

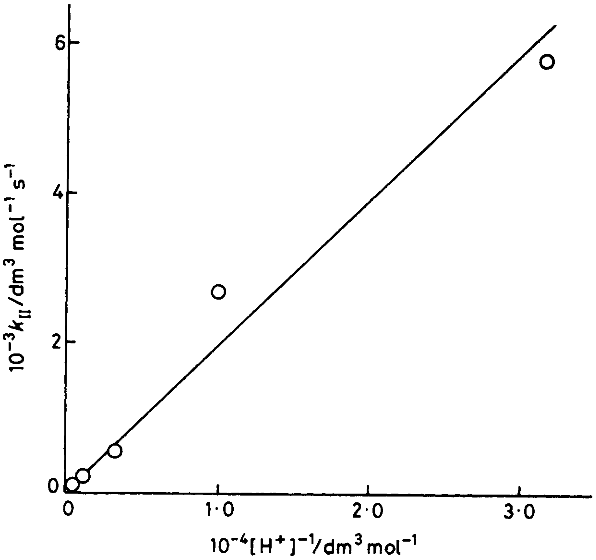


Figure 5. Variation of the second-order rate constant k_{II} as a function of $[H^+]^{-1}$, for the oxidation of H_2L^3 at 20.0 °C

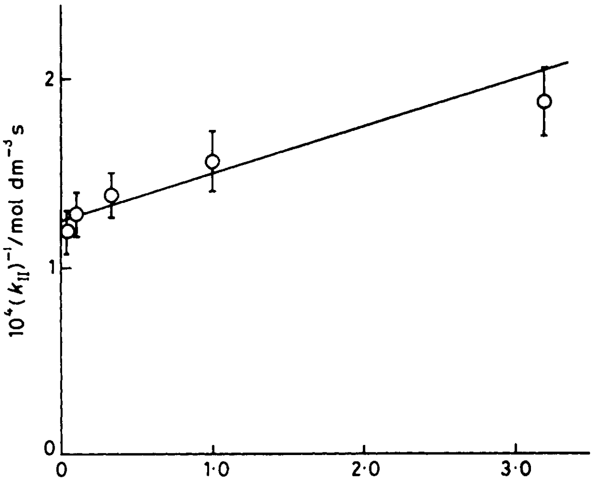


Figure 6. Variation of the second-order rate constant on acidity for the oxidation of benzene-1,2-diol [equation (35)]

In the case of benzene-1,2-diol (H_2L^1) a complex dependence of rate on acidity was found; this variation could not be unambiguously rationalized, due to the reduced variation (1.5 times increase over two orders of magnitude of $[H^+]$ decrease). However the simplest functional form which appeared to give a satisfying fit with the experimental data (see Figure 6) was of the form in equation (35). The experimental data in the Figure seem to show a non-linear downward trend, but the reported 10% uncertainty on the single second-order rate constants allows the data, within the experimental uncertainty, to agree with the linear behaviour represented by equation (35). The above dependence indicates that benzene-1,2-diol has a dependence intermediate between the inverse first order for H_2L^3 and the independence for H_2L^2.

$$k_{II} = 2k[H^+]^{-1}/(1 + K[H^+]^{-1}) \qquad (35)$$

This intermediate tendency parallels the one based on acidity of these substrates as shown in Table 5. Therefore, again, precursor co-ordination with different proton release ability appears to be of great importance. This consideration is strengthened by the behaviour of H_2L^4; the oxidation of this substrate showed limiting kinetics as can be seen from Figure 7 and from the data reported in Table 6, thus suggesting a strong interaction before the redox process. An inner-sphere precursor complex is favoured for H_2L^4 by the presence of the *o*-hydroxy–carboxylic moiety (salicylic acid type) centred on the redox site of the substrate, while an outer-sphere interaction would be unfavourable due to the presence of the acidic $-CO_2H$ group (p*K* 3.0 – 3.5) which would create a repulsion with the anionic oxidizing complex. Thus the operative reaction sequence may be represented by equations (36)—(38).

Table 8. Kinetic and activation parameters for the oxidation of benzene-1,2-diols by $[Mn^{III}(cdta)(H_2O)]^-$ [a]

(*a*) Benzene-1,2-diol

T/°C	k [b]/s^{-1}	10^3K [b]/mol dm^{-3}
10.0	13 ± 5	3 ± 1
20.0	17 ± 5	5 ± 2
30.0	20 ± 7	6 ± 2
$\Delta H^‡$/kcal mol^{-1}	4 ± 3	
$\Delta S^‡$/cal K^{-1} mol^{-1}	−45 ± 10	

(*b*) 4-Methylbenzene-1,2-diol

T/°C	$10^{-3}k_{et}K_{ass.}$ [c]/ $dm^3\ mol^{-1}\ s^{-1}$
10.0	5.4 ± 0.9
20.0	5.4 ± 0.9
30.0	5.1 ± 0.5
$\Delta H^‡$/kcal mol^{-1}	−1 ± 2
$\Delta S^‡$/cal K^{-1} mol^{-1}	−45 ± 6

(*c*) 3,4-Dihydroxybenzoic acid

T/°C	$10k_{et}K_{ass.}$ [d]/s^{-1}
20.0	1.0 ± 0.2
30.0	1.4 ± 0.4
38.0	1.7 ± 0.5
$\Delta H^‡$/kcal mol^{-1}	5 ± 3
$\Delta S^‡$/cal K^{-1} mol^{-1}	−45 ± 10

(*d*) 2,3-Dihydroxybenzoic acid

pH	2.50	3.00	3.50	4.00	4.50	
k_{et} [e]/s^{-1}	1.4	0.63	0.67	2.0	2.5	(20.0)
	2.5	1.8	0.64	1.1	5.0	(30.0)
	2.5	1.9	0.83	1.3	2.5	(38.0)
$10^{-2}K_{ass.}$ [e]/$dm^3\ mol^{-1}$	2.8	12	8.0	2.3	2.5	(20.0)
	2.7	4.3	16	6.1	1.7	(30.0)
	3.5	5.7	18	6.3	3.8	(38.0)

[a] Temperatures (°C) in parentheses. [b] See equation (35). [c] See equation (30). [d] See equation (34). [e] See equation (40).

$$[Mn^{III}(cdta)(H_2O)]^- + H_2L^4 \xrightleftharpoons{K_{ass.}} \text{Intermediate} \qquad (36)$$

$$\text{Intermediate} \xrightarrow{k_{et}} [Mn^{II}(cdta)]^{2-} + \text{semiquinone} \qquad (37)$$

$$\text{semiquinone} + [Mn^{III}(cdta)]^- \xrightarrow{\text{fast}} [Mn^{II}(cdta)]^{2-} + o\text{-quinone} \qquad (38)$$

$$\text{Rate} = \frac{2k_{et}K_{ass.}[Mn^{III}(cdta)^-]_{tot.}[H_2L^4]}{1 + K_{ass.}[H_2L^4]} \qquad (39)$$

From the sequence the rate law (39) can be derived which explains the experimental behaviour reported in Figure 7. $K_{ass.}$

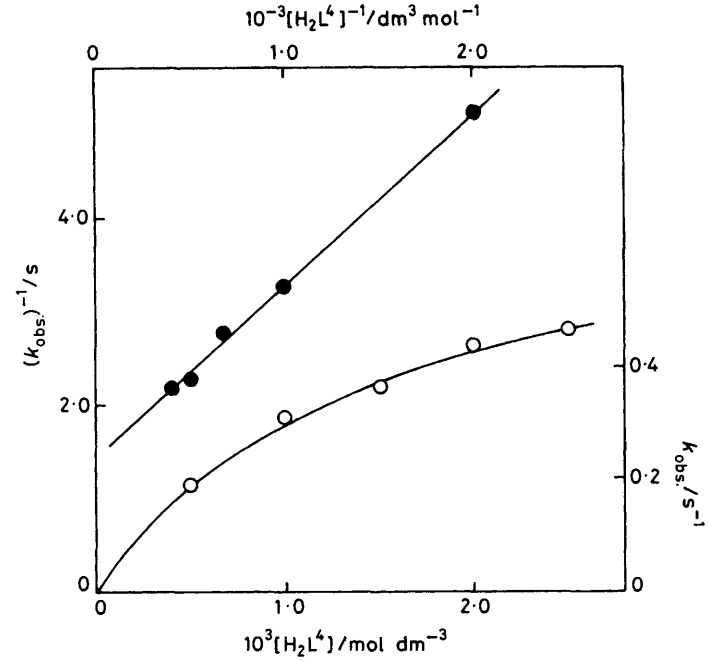


Figure 7. Variation of $k_{obs.}$ as a function of reductant concentration (○) and of $(k_{obs.})^{-1}$ as a function of inverse reductant concentration (●), for the oxidation of H_2L^4 at 20.0 °C and pH 3.5

and k_{et} have been evaluated from plots of $(k_{obs.})^{-1}$ *versus* $[H_2L^4]^{-1}$ according to equation (40).

$$(k_{obs.})^{-1} = (2k_{et})^{-1} + (2k_{et}K_{ass.}[H_2L^4])^{-1} \qquad (40)$$

Table 8 collects the derived parameters together with those for the other investigated diols. Again, as for the parent compound, the very limited and complex variation of k_{et} and $K_{ass.}$ with acidity between pH 2.5 and 4.5 did not allow clarification of the details of the co-ordination taking place in equation (36). The main variation concerns $K_{ass.}$ which increases from pH 2.5 to pH 3.5, then again reduces at the higher pH limit investigated. The dissociation of the $-CO_2H$ group of H_2L^4 (p*K*A 3.0—3.5) stabilizes the association in step (36) (increase of $K_{ass.}$ from pH 2.5 to 3.5), while the deprotonation of CO_2H groups of $cdta^{4-}$ (which at the higher acidities must detach from Mn^{III} in order to accommodate the reductant) will reduce the association at the higher pH values. The numerical values obtained for $K_{ass.}$ confirm a high covalent contribution to this precursor association.

The independence of k_{11} from acidity for 4-methylbenzene-1,2-diol may well be interpreted, for this substrate only, in terms of a purely outer-sphere interaction. In this case the reaction rate should be comparable to the one computed with the Marcus cross relation,[9,23] equations (41) and (42), where Z

$$k = (k_{11}k_{22}K_{12}f)^{0.5} \qquad (41)$$

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (42)$$

is the collision frequency in solution ($10^{11}\ s^{-1}$), k_{11} and k_{22} (see Table 5) are the self-exchange rates for the single redox couples involved in the rate-determining step (Mn^{III}/Mn^{II} complex and semiquinone/diol couples), and K_{12} is the equilibrium constant for the one-electron transfer rate-determining step (43). The equilibrium constant for equation (43) can be

$$[Mn^{III}(cdta)(H_2O)]^- + H_2L^2 \longrightarrow [Mn^{II}(cdta)(H_2O)]^{2-} + (HL^2)^{\cdot} + H^+ \qquad (43)$$

computed to be $K_{12} = 4.5 \times 10^{-6}$, while $k_{outer\text{-}sphere}$ is computed with equation (41) to be 13 s^{-1} at 20.0 °C (work terms to bring reactants and products to the reaction distance have been neglected due to the high investigated ionic strength and one of the reagents being uncharged). The much higher experimental value $k_{et}K_{ass.} = 5.4 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ suggests that the inner-sphere route is favoured for these redox reactions, through a lower activation energy profile.*

Taking into account all the present results as a whole, some general considerations can be advanced on the kinetic behaviour of the investigated oxidant, also with reference to the free uncomplexed aquametal ion. In the data collected by Davies *et al.* on the oxidation of several molecules like hydrazine,[3] hydroxylamines,[4] nitrous acid,[4] thioureas,[26] hydroquinone,[27] in general no spectrophotometric evidence for complex formation has been gained. In some cases, *e.g.* in the oxidation of hydrazoic acid, both spectroscopic as well as kinetic evidence for intermediate complex formation has been observed.[6,28] Competition between Mn^{3+} and $Mn(OH)^{2+}$ reactive species has been observed and in some cases, such as the oxidation of thioureas, benzene-1,2-diol, substituted benzene-1,2-diols, and catecholamines, a substitution-controlled mechanism has been found in the case of the $Mn(OH)^{2+}$ oxidant.[7,8]

In reactions involving Mn^{III} complexed to non-oxidizable ligands, it would appear that the reaction may proceed *via* an outer-sphere mechanism. For example, the reactions of Mn^{III} pyrophosphate with various substituted Fe^{II}–phenanthroline complexes conform to the outer-sphere Marcus theory.[29] This

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* A lower $E°$ value for the $[Mn^{III}/Mn^{II}(cdta)]$ couple has been recently reported;[24] this value would give a lower calculated $k_{outer\text{-}sphere}$ value. $K_{ass.}$ also, in the case of an outer-sphere mechanism, should be $\leqslant 1$,[25] the diol being uncharged, so that the experimental k_{et} value would be $\geqslant 5.4 \times 10^3\ s^{-1}$.

behaviour cannot, however, be generalized since the present results indicate that also in the case of very stable aminopolycarboxylato-complexes an inner-sphere mechanism is operative, through the partial unwrapping of the ligand and free co-ordination sites of the complex. This behaviour is particularly evident in the case of substrates with higher co-ordinating capability as in the case of H_2L^4.

No substitution-controlled mechanism has been observed here since the reactivities are not high enough; in a previous paper[9] it was proposed that water substitution at Mn^{III} should be similar for $Mn(OH)^{2+}$ (aq) species to that for Mn^{III} aminopolycarboxylato-complexes (k *ca.* 10^4 s^{-1}).

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