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SOME ASPECTS OF THE CHEMISTRY OF MANGANESE(III) IN AQUEOUS SOLUTION

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ABBREVIATIONS

CYDTA	*trans*-1,2diaminocyclohexanetetraacetic acid
EDTA	ethylenediaminetetraacetic acid
HEDTA	hydroxyethylenediaminetriacetic acid
acac	acetylacetone
$BiPH_2$	bipyridinium cation
k_o	observed rate constant

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A. INTRODUCTION

The number of possible valence states of manganese makes the chemistry of this element extensive[1]. In this Review we shall consider aspects of the solution chemistry of manganese(III), which is one of the more unstable oxidation states.

The Mn^{III} system is oxidising and is unstable with respect to the simplified disproportionation scheme[2,3]

$$Mn^{III} + Mn^{III} \rightleftharpoons Mn^{IV} + Mn^{II} \tag{1}$$

$$Mn^{IV} + 2H_2O \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} MnO_2(s.) \tag{2}$$

Manganese(III) can be stabilised by (i) increase of acidity, (ii) increase of Mn^{II} concentration, or (iii) complex formation. Since Mn^{II} has a tendency to form weak complexes with anions and common chelating agents, the last mentioned method has most generally been employed for stabilisation of the trivalent state. However, the complexes formed are often unstable in strong acid or alkali, and their oxidising power is reduced by anionic complexation, which makes other reagents, such as Ce^{IV} or Cr^{VI}, preferable as analytical reagents[4].

Recently, Rosseinsky[2] and Diebler and Sutin[3] have shown that by using methods (i) and/or (ii) it is possible to obtain moderately stable solutions of Mn^{III} even in weakly-complexing perchlorate media. Use of high concentrations of Mn^{II} at lower perchloric acid concentrations prevents the precipitation of hydrated manganese oxides[2]. Previously, Adamson[5] had used this precipitation as a separation method in his study of the electron-exchange between Mn^{II} and Mn^{III}. Wells and Davies[6] have made a detailed study of the spectral changes which take place with variation of acidity in perchlorate media. They were able to reach acidities as low as 0.10M $HClO_4$ by adjusting the total ionic strength by addition of Mn^{II}. A number of studies in perchlorate solution have now been published, and we shall discuss these results as a basis for a consideration of the reactions of other complexed species.

It is generally possible to prepare much higher concentrations of Mn^{III} in the form of complexed species than as the aquo complexes in perchlorate, owing

TABLE 1

EQUILIBRIUM DATA FOR THE REACTION $Mn^{II} \rightleftharpoons Mn^{III} + e^-$ IN DIFFERENT MEDIA

Medium	$-E°$ *(volts)*	*Ref.*
perchlorate		
(3M $HClO_4$)	1.56	3
(1M $HClO_4$)	1.51	3, 10
sulphate	1.49	11
pyrophosphate	1.15	12
EDTA, ClO_4^-	0.824	13

to the tendency towards precipitation of hydrated oxides in the latter medium[2,3,5,6]. Some equilibrium data for complexes of Mn^{III} in the form of electrode potentials are collected in Table 1. The potential of the Mn^{III}/Mn^{II} couple generally decreases on complexation. An example of the effect of complexation on the oxidising power of Mn^{III} is the observation that hydrogen peroxide is found as a product of the oxidation of oxalate by *trans*-1,2 diaminocyclohexanetetraacetatomanganate(III) at low pH[7], in sharp contrast to the rapid redox reaction observed between Mn^{III} and H_2O_2 in perchlorate media[8,9].

B. METHODS OF PREPARATION

The trivalent state of manganese has been obtained in solution *via* three routes, namely by oxidation of Mn^{II} or by reduction of Mn^{IV} or Mn^{VII}.

(i) *Oxidation of* Mn^{II}.—Both chemical and electrolytic methods are available for the oxidation of Mn^{II} to Mn^{III}. Among the chemical agents which have been employed are $S_2O_8^{2-}$ (ref. 14), $Cr_2O_7^{2-}$ (ref. 15), Ag_2O (ref. 16), mixtures of H_2SO_5 and H_2O_2 (ref. 17), Co^{III} (ref. 3, 18), Ce^{IV} (ref. 18–20), and Mn^{VII} (ref. 2, 21–23). The kinetics of the latter reaction have been studied in perchlorate media[24]. Electrogeneration of Mn^{III} from Mn^{II} has been carried out in perchlorate[3,6], nitrate[25], sulphate[26–30], phosphate and pyrophosphate media[31], and in acetic acid[32,33]. Among the anode materials which have been used are Pt[3,6], spectroscopic carbon[26], Au[28] and Pb[30,34]. Stirring of the electrolysis mixture, either magnetically[8,28] or using a stream of inert gas such as nitrogen[6,28], often increases the rate of oxidation[35]. High current densities and low Mn^{II} concentrations favour the formation of Mn^{VII}, especially at high acidity under weakly-complexing conditions[21,36]. The formation of an oxide film usually takes place during electrolysis, particularly at low acidity[26,34,36]. A sulphate salt, which is soluble at 50°, is precipitated during electrolysis of Mn^{II} in 7–8M H_2SO_4 using a manganese anode[37]. A high-frequency electrolytic method, which may have applications in the preparation of Mn^{III}, has also been described[38].

Photooxidation of Mn^{II} takes place in aerated pyrophosphate solutions containing a photosensitiser and organic compounds with readily-transferable hydrogen atoms[39].

(ii) *Reduction of* Mn^{IV}.—Reduction of hydrated oxides of Mn^{IV} has chiefly been used in the preparation of polyaminocarboxylate[13] and oxalate[29,40] complexes of Mn^{III}. The use of a volatile reductant (*e.g.* ethanol) facilitates the removal of remaining reductant after reaction[13].

(iii) *Reduction of* Mn^{VII}.—The reduction of Mn^{VII} by Mn^{II} (see above), and by H_2O_2 (ref. 41) yields Mn^{III} complexes under appropriate conditions. Electrolytic reduction methods, for example in sulphate media, have also been described[42].

C. METHODS OF ESTIMATION

As mentioned previously, it is often possible to use standard titrimetric procedures[4] for the estimation of Mn^{III} complexes, since higher concentrations can be produced than are available in the presence of weakly-complexing anions. In perchlorate media the absorption in the ultra-violet region has been characterised[6,36] and can be used as a means of direct estimation. In nitrate media the strong absorption of the anion makes this procedure inapplicable and also interferes with the spectrophotometric estimation of Fe^{III} formed on addition of Mn^{III} to an excess of Fe^{II}, which method is suitable for use in acid perchlorate solution[6].

D. EQUILIBRIA AND KINETICS IN PERCHLORATE SOLUTION

Since the equilibria existing in acidic perchlorate solutions of Mn^{III} containing an excess of Mn^{II} are probably the simplest and best understood at the present time, we shall discuss the results available for perchlorate media and relate them, where appropriate, to data obtained for other trivalent ions in the first transition series. An understanding of prevailing equilibria is fundamental to kinetic studies, and we shall use this information in discussing some of the kinetic results obtained in perchlorate media.

(i) *Equilibria.*—Results obtained some years ago in a study of the solubility of manganese oxides in aqueous perchloric acid indicated to Taube and his co-workers[43] that Mn^{III} is considerably hydrolysed even in moderately strong perchloric acid, and the apparent inverse acidity dependence of the Mn^{III}-catalysed aquation of $CrCl^{2+}$ was discussed in these terms[18]. Since that time[43] three groups of workers[3,6,21] have reported studies of the spectrum of Mn^{III} under conditions of changing acidity, and as a result of this work, there can be little doubt that the hydrolysis of $Mn_{aq}{}^{3+}$ is considerable even at high acidity.

At lower acidities, even in the presence of a very large excess[6] of Mn^{II}, the solutions are quite unstable. At room temperature the apparent extinction coefficient decreases with time[3,6,36]. This leads to too low an estimate of the extinction coefficient of $MnOH^{2+}$, unless account is taken of this change. The net result is that some estimates[3,21] of the acid dissociation constant K_H for the rapid equilibrium

$$Mn_{aq}{}^{3+} + H_2O \overset{K_H}{\rightleftharpoons} MnOH_{aq}{}^{2+} + H_3O^+ \tag{3}$$

are probably too large[6]. It has been shown[6] using freshly-prepared solutions of Mn^{III} and extrapolation of any changes in optical density to zero time that changes in optical density with changing acidity can be quantitatively accounted for in terms of the acid dissociation equilibrium (3). Thus, Beer's Law is obeyed for Mn^{III} solutions in both the ultraviolet and visible regions of the spectrum in acid perchlorate solution containing sufficient Mn^{II} to suppress the formation[6] of Mn^{IV}.

This suggests that the concentration of polymeric species is negligible in these freshly-prepared solutions. The value of K_H has been found to be 0.93 ± 0.03M at $\mu = 4.0$M in perchlorate media[6] at 25.0°. The extinction coefficients of Mn^{III} at various acidities are found to be insensitive, within experimental error, to changes in ionic strength in the range[36] $\mu = 1$–6M.

Identical species are produced by electrolytic[3,6] or chemical (Mn^{VII}) (ref. 2, 21) oxidation of Mn^{II}. The spectra of $Mn_{aq}{}^{3+}$ and $MnOH_{aq}{}^{2+}$ are very similar in both the visible and ultra-violet regions[6] (Fig. 1). An absorption maximum at 470nm for both species may be ascribed[6,21] to the $^5T_{2g} \leftarrow {}^5E_g$ transition, which is the only spin-allowed transition in a spin-free d^4 system with octahedral symmetry. The extinction coefficient of $MnOH_{aq}{}^{2+}$ in the visible region is greater than that of $Mn_{aq}{}^{3+}$ perhaps because of greater 4p–3d mixing in the lower symmetry of $MnOH_{aq}{}^{2+}$. The peak for $Mn_{aq}{}^{3+}$ is somewhat broader than that for $MnOH_{aq}{}^{2+}$ because of the greater influence of the Jahn–Teller effect in the octahedral aquo ion. The spectra of $Mn_{aq}{}^{3+}$ and of $Mn(H_2O)_6{}^{3+}$ in $CsMn(SO_4)_2 \cdot 12H_2O$ (ref. 34) are very similar although the extinction coefficient is about ten times larger in solution than in the solid. Fackler and Chawla[21] have pointed out that the extinction coefficient of $Mn_{aq}{}^{3+}$ is too large to be accounted for in terms of vibronic transitions alone, and have considered the consequences of the so-called dynamical Jahn–Teller effect as discussed by Liehr[45]. It would seem that α, the Jahn–Teller force, is quite large in the aquo complexes, but that the barrier to configurational change is small, resulting in a broad band at 470nm from the superposition of the spectra of at least the three expected distorted configurations of lowest energy. A broad, low energy band near 700nm is presumably due to transitions within the ^5E_g level[21]. The solution spectra of $Cr_{aq}{}^{2+}$ and $Mn_{aq}{}^{3+}$ are very similar and the Dq ratio for the pairs Cr^{2+}–Mn^{3+} (d^4), V^{2+}–Cr^{3+} (d^3) and Mn^{2+}–Fe^{3+} (d^5) are all about the same[21,46]. A similarity of values of Dq for OH^- and H_2O may account for the absence of splitting[6,21] in $MnOH_{aq}{}^{2+}$. However, it is interesting to note that the spectrum of Mn^{III} splits in the presence of an excess of fluoride[21], (see Section E (i)).

Although there are analytical difficulties connected with the spectrophotometric study of the dilute solutions of Mn^{III} which can be produced in nitrate media (see previous section), it is possible to compare the visible spectrum in nitrate with that in perchlorate solution[25]. No differences are apparent at moderate acidities, and this supports the conclusion that only very weak, outer-sphere anionic complexes are present in these two media. Kinetic studies also support these spectrophotometric observations.

The ultra-violet spectrum of Mn^{III} at different acidities[6] is also consistent with a close similarity of σ bonding (and π bonding, if present) in $Mn_{aq}{}^{3+}$ and $MnOH_{aq}{}^{2+}$. The absorption maxima are found in the region 210–220nm, with extinction coefficients of about $4 \times 10^3 M^{-1} cm^{-1}$. The most likely transition in this region is $1t_{1u} \rightarrow 2e_g$, which involves electron transfer from ligand to metal

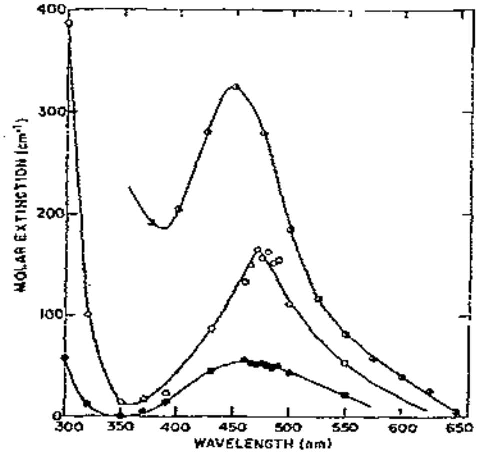

Fig. 1. Spectra of some Mn^{III} complexes in solution at 25°. ○, $MnOH_{aq}^{2+}$, $\mu = 4.0$M in perchlorate (ref. 6); ◐, $Mn(OH)CYDTA_{aq}^{2-}$ (ref. 13a); ●, Mn_{aq}^{3+}, $\mu = 4.0$M in perchlorate (ref. 6).

through σ bonds[6]. These observations also suggest the presence of a dynamic Jahn–Teller effect in the aquo complexes.

Wells[47] has discussed the acid-dissociation parameters of Mn_{aq}^{3+} in relation to those of other trivalent ions in the first transition series. A tendency towards the stable $t_{2g}^3e_g^2$ configuration increases the strength of σ bonds in Mn^{3+}–OH^- as compared to Mn^{3+}–H_2O, and the low enthalpy of dissociation[6] ((4.8 ± 0.8) Kcal · mole^{-1}) is largely responsible for the marked hydrolysis of Mn_{aq}^{3+}, making it one of the strongest acids of the series. It is interesting to note that polyaminocarboxylate complexes of Mn^{III} also behave as weak acids, and that the presence of the conjugate base (*e.g.*, $Mn(OH)CYDTA_{aq}^{2-}$, Fig. 1) also tends to reduce the stability of the system with respect to precipitation[13]. Diebler and Sutin[3] have observed that if the electrolysis of an acidic perchlorate solution of Mn^{II} is continued as far as the precipitation of manganese oxides, then the apparent concentration of Mn^{III} present in solution is proportional to the square root of the initial $[Mn^{II}]$. This leads to an upper limit of 10^{-2} for the equilibrium constant

$$K = [Mn^{II}]\,[Mn^{IV}]/[Mn^{III}]^2$$

for reaction (1) at 23° in 6M $HClO_4$. This estimate[3] is certainly consistent with both the estimate of the corresponding equilibrium constant in acid sulphate media[27] and the conclusions of Wells and Davies[6].

Solutions of Mn^{III} become cloudy on standing, the appearance of cloudiness being accelerated by decrease of acidity or $[Mn^{II}]$, or by increase of temperature or total concentration of Mn^{III}. An irreversible condensation reaction such as that of scheme (4), might account for these observations.

$$2MnOH_{aq}^{2+} \rightarrow MnOMn_{aq}^{4+} + H_2O$$

$$MnOMn_{aq}^{4+} \rightleftharpoons MnO_{aq}^{2+} + Mn^{2+}$$

$$\text{dimer} \rightarrow \text{soluble polymers} \rightarrow \text{precipitation of hydrated oxides} \qquad (4)$$

The dimeric species, written as only one of its possible structures, has an extinction coefficient which is lower than that of $MnOH_{aq}{}^{2+}$ in the visible region. This is not a complete mechanism, however, since, in the absence of any other evidence it is difficult to account for the apparent dependence of the rate on $[Mn^{II}]$. One possibility is, of course, that the first step is reversible[47a].

Analogous dimeric species are believed to exist, for example, in solutions of Co^{III} in perchlorate solution[48], but here the dimerisation equilibrium would seem to be more rapidly reversible (*cf.* the dimerisation equilibrium of Fe^{III} (ref. 49). The formation of soluble higher polymers can, of course, precede the appearance of solid material. Subsequent precipitation may be heterogeneously catalysed by oxides which have already precipitated[47a]. This latter phenomenon greatly complicates studies of these processes, which is unfortunate since our knowledge of the chemistry of Mn^{IV} in solution is lacking.

(ii) *Kinetics.*—Adamson's study[5] of the electron-exchange between Mn^{III} and Mn^{II} was one of the early reactions investigated in acid perchlorate solution. Adamson concluded that, like many other exchange reactions between cations of this charge type in the first transition series, the exchange is not instantaneous. It seems likely from subsequent attempts[3] to measure the rate directly, that separation-induced exchange was occurring in Adamson's system, although there have been indirect estimates[3] of the rate of exchange based on the use of the Marcus theory[50] for outer-sphere reactions. The simplest mechanism for the exchange reaction in the presence of an excess of Mn^{II} would presumably be

$$\begin{aligned} &{}^*Mn_{aq}{}^{3+} + Mn_{aq}{}^{2+} \overset{k_1}{\rightleftharpoons} {}^*Mn_{aq}{}^{2+} + Mn_{aq}{}^{3+} \\ &{}^*MnOH_{aq}{}^{2+} + Mn_{aq}{}^{2+} \overset{k_1'}{\rightleftharpoons} {}^*MnOH_{aq}{}^{+} + Mn_{aq}{}^{3+} \qquad (5) \\ &{}^*MnOH_{aq}{}^{2+} + Mn_{aq}{}^{2+} \overset{k_1''}{\rightleftharpoons} {}^*Mn_{aq}{}^{2+} + MnOH_{aq}{}^{2+} \end{aligned}$$

Exchange between Mn^{II} and Mn^{IV} in a scheme such as (4) above could also contribute. A direct estimate of rates of electron-exchange which are not separation-induced would be extremely useful, for instance, in testing the applicability of the Marcus theory[3,50] as a means of distinguishing between inner- and outer-sphere reaction mechanisms.

The rapid oxidation of Fe^{II} by Mn^{III} has been studied by Rosseinsky[19,51] and by Sutin[3] and their coworkers, using polarographic and spectrophotometric stopped-flow techniques, respectively. The agreement between the results of the two groups is good and leads to the mechanism

$$\begin{aligned} &Mn_{aq}{}^{3+} + Fe_{aq}{}^{2+} \xrightarrow{k_1} Mn_{aq}{}^{2+} + Fe_{aq}{}^{3+} \\ &MnOH_{aq}{}^{2+} + Fe_{aq}{}^{2+} \xrightarrow{k_1'} Mn_{aq}{}^{2+} + FeOH_{aq}{}^{2+} \end{aligned} \qquad (6)$$

Results calculated from the data[3,51] (Table 2) indicate that $k_1' > k_1 \simeq 1\times10^4$ $\text{M}^{-1}\text{sec}^{-1}$ at 25°, although the difference between these two rate constants is not large. Rosseinsky and Nicol[51] have pointed out that the general similarity of this reaction to that of Ce^{IV} with Fe^{II} suggests an outer-sphere mechanism for both reactions, and the estimates[3] of the rate of the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ exchange reaction based

TABLE 2

SOME KINETIC DATA FOR SECOND-ORDER REACTIONS OF Mn^{III} IN PERCHLORATE MEDIA WITH $\mu = 3.90\text{M}$ AND AT 25°.

Reductant	*$10^{-4}\ k_1$*[a] $\text{M}^{-1}\textit{sec}^{-1}$	*$10^{-4}\ k_1'$*[a] $\text{M}^{-1}\textit{sec}^{-1}$	*Ref.*
H_2O_2	7.3	3.2	8
5-Methyl- 1,10 phenanthroline-Fe^{II}	observed rate constants $3.2\times10^3\text{M}^{-1}\text{sec}^{-1}$ (M $HClO_4$) $2.5\times10^4\text{M}^{-1}\text{sec}^{-1}$ (3M $HClO_4$)		3
HNO_2	2.2	4.9	70
1,10 phenanthroline-Fe^{II}	observed rate constants $1.85\times10^3\text{M}^{-1}\text{sec}^{-1}$ (M $HClO_4$) $1.55\times10^4\text{M}^{-1}\text{sec}^{-1}$ (3M $HClO_4$)		3
$p\text{-}C_6H_4(OH)_2$	0.48	3.3	72
$NH_3{}^+OH$	0.14	0.31	70
Fe^{2+}	1.27[b]	2.11[b]	3
	0.74[c]	2.40[c]	51
VO^{2+}	0.01	0.058	55
Hg°	0.3[d]	1.0	2
5-Chloro- 1,10 phenanthroline-Fe^{II}	observed rate constants $3.95\times10^2\text{M}^{-1}\text{sec}^{-1}$ (M $HClO_4$) $2.9\times10^3\text{M}^{-1}\text{sec}^{-1}$ (3M $HClO_4$)		3
$NH_3{}^+NH_2$	≤0.05	1.03	71
$CH_3NH_2{}^+NH_2$	≤0.008	0.30	71
$(CH_3)_2NH^+NH_2$	≤0.01	0.40	71
5-nitro- 1,10 phenanthroline-Fe^{II}	observed rate constants $0.9\times10^2\text{M}^{-1}\text{sec}^{-1}$ (M $HClO_4$) $4.2\times10^2\text{M}^{-1}\text{sec}^{-1}$ (3M $HClO_4$)		3
$CH_3NH_2{}^+NHCH_3$	≤0.004	0.073	71
$(CH_3)_2NH^+NHCH_3$	≤0.002	0.053	71
$(CH_3)_2NH^+N(CH_3)_2$	0.028	≈0.003	71
Br^-	0.001	—	61
$NH_3{}^+OCH_3$	0.00006	0.0006	70
$(CH_3)_2CHOH$, $(CH_3)_2CHOH_2{}^+$(?)	$k_1 = 1.4\times10^{-5}$	$k_1' = 4.4\times10^{-5}$	74

[a] Only data for reactions with an apparent second-order overall concentration dependence are given in the Table. For higher-order reactions see Text. The rate constants k_1 and k_1' refer to the parallel steps

$$\text{Mn}_{\text{aq}}{}^{3+} + \text{reductant} \xrightarrow{k_1} \text{products}$$

$$\text{MnOH}_{\text{aq}}{}^{2+} + \text{reductant} \xrightarrow{k_1'} \text{products}$$

and are obtained from results at various acidities where these can be appropriately assigned.

[b] $\mu = 3.10\text{M}$, measured spectrophotometrically.

[c] Measured polarographically.

[d] Estimated from the data assuming $k_1/k_1' \approx 0.3$ at 50° (see Text).

[e] Estimated from the data assuming $k_1/k_1' \approx 0.3$ at 25°.

on this assumption[50] are in reasonable agreement with those obtained from the reactions of Co^{III} with Mn^{II} (ref. 3) and of Mn^{III} with phenanthroline complexes of Fe^{II} (ref. 3). The rates of the last mentioned reactions increase[3] in going from 1.0 to 3.0M $HClO_4$. The rates of all these reactions are first-order in each reactant and the rate constants are collected in Table 2. From the studies of the oxidation of phenanthroline complexes of Fe^{II}, which are perhaps the most likely outersphere reactions of this group[3,52,53] the value of $2\times10^{-4}\text{M}^{-1}\text{sec}^{-1}$ for the exchange rate constant at 25° has been calculated[3] at 1M and 3M $HClO_4$. The apparent insensitivity of reaction rate to acidity could mean that, if the mechanism (5) is appropriate, then $k_1 > (2k_1'+k_1'')$, since $K_H \approx [H^+]$. This would be in contrast to the increase in rate which occurs with decreasing acidity, for example, in the Fe^{II}/Fe^{III} exchange reaction[54]: however, we must be cautious in drawing any firm conclusion in view of the limited amount of data available.

The oxidation of VO^{2+} by Mn^{III} has been studied at acidities in the range 0.8–3.0M $HClO_4$ at temperatures[55] between 5 and 20°. The acid-dependence of the rate is consistent with the mechanism

$$\begin{aligned} H_2O + {Mn_{aq}}^{3+} + {VO_{aq}}^{2+} &\xrightarrow{k_1} {Mn_{aq}}^{2+} + {VO_{2aq}}^{+} + 2{H_{aq}}^{+} \\ {MnOH_{aq}}^{2+} + {VO_{aq}}^{2+} &\xrightarrow{k_1'} {Mn_{aq}}^{2+} + {VO_{2aq}}^{+} + {H_{aq}}^{+} \end{aligned} \tag{7}$$

with $k_1 = 1.1\times10^2\text{M}^{-1}\text{sec}^{-1}$ and $k_1' = 5.8\times10^2\text{M}^{-1}\text{sec}^{-1}$ at $\mu = 3.90$M and 25°.

The activation parameters[51,55] for the reactions of Mn_{aq}^{3+} and $MnOH_{aq}^{2+}$ with Fe_{aq}^{2+} and VO_{aq}^{2+}, respectively, show that $\Delta H_1^* \approx \Delta H_1^{*\prime}$ and $\Delta S_1^* \approx \Delta S_1^{*\prime}$, with $\Delta S_1^{*\prime}$ generally more negative than ΔS_1^*. The values of the entropies of activation are more positive than those found, for example, in the Fe^{III}–Fe^{II} reaction[56].

The absence of any effect of perchlorate on the reaction rate is typical of the reactions of Mn^{III} which have been studied thus far, which makes it unlikely that the perchlorate ion is a constituent of either activated complex. A close parallelism exists[55] between reactions of V^{IV} and Fe^{II} with the oxidants $V^{V} < Mn^{III} < Co^{III} < < Fe^{III}$ arranged in order of decreasing rate constants for reaction with both reductants. There is thus no parallelism of rates with the electrode potential of the oxidant couple[8], and it is difficult to differentiate between inner and outersphere mechanisms for these reactions. However, the rates of reaction with Fe^{II} are, in general, greater than those with V^{IV}.

The reaction[2] between Mn^{III} and Hg^{I} has been followed titrimetrically at 50° and if we include reactions of $MnOH^{2+}$ then the following mechanism is suggested

$$(Hg^{I})_{2aq} \overset{K'}{\rightleftharpoons} {Hg_{aq}}^{0} + {Hg_{aq}}^{II} \tag{8}$$

$$2{Mn_{aq}}^{III} \overset{K''}{\rightleftharpoons} {Mn_{aq}}^{IV} + {Mn_{aq}}^{II} \tag{9}$$

$${Mn_{aq}}^{3+} + {Hg_{aq}}^{0} \xrightarrow{k_1} {Mn_{aq}}^{II} + {Hg_{aq}}^{I} \tag{10}$$

$$\mathrm{MnOH_{aq}}^{2+} + \mathrm{Hg_{aq}}^{0} \xrightarrow{k_1'} \mathrm{Mn_{aq}}^{\mathrm{II}} + \mathrm{Hg_{aq}}^{\mathrm{I}} \tag{11}$$

$$\mathrm{Mn_{aq}}^{\mathrm{III}} + \mathrm{Hg_{aq}}^{\mathrm{I}} \xrightarrow{\text{rapid}} \mathrm{Mn_{aq}}^{\mathrm{II}} + \mathrm{Hg_{aq}}^{\mathrm{II}} \tag{12}$$

$$\mathrm{Mn_{aq}}^{\mathrm{IV}} + (\mathrm{Hg^{I}})_{2\mathrm{aq}} \xrightarrow{k_2} \mathrm{Mn_{aq}}^{\mathrm{II}} + 2\mathrm{Hg_{aq}}^{\mathrm{II}} \tag{13}$$

with reactions (10), (11) and (13) as the rate-determining steps. This study is an example of the complexity which appears when the disproportionation reaction (9) is not repressed by the presence of a large excess of $\mathrm{Mn^{II}}$. Rosseinsky[2] has estimated that $(k_1[\mathrm{H^+}]+k_1')/([\mathrm{H^+}]+K_\mathrm{H})$ is equal to $5\times10^3\mathrm{M^{-1}sec^{-1}}$ at 50° in 3M $\mathrm{HClO_4}$ and $\mu = 4.5\mathrm{M}$. If we assume that the ratio of rate constants $k_1/k_1' = 0.3$ (a typical value for $\mathrm{Mn^{III}}$ reactions, see following discussion), then we may calculate that $k_1 \approx 3\times10^3\mathrm{M^{-1}sec^{-1}}$ and $k_1' \approx 1\times10^4\mathrm{M^{-1}sec^{-1}}$ at 50° and $\mu = 4.5\mathrm{M}$. The observed[2] increase in the rate constant with decreasing acidity at low $[\mathrm{Hg^I}]_0$ is consistent with these estimates. It would be useful to have some data concerning the variation of k_2 with acidity. Rosseinsky[2] reports that $k_2 \geq 5\times10^1\mathrm{M^{-1}sec^{-1}}$ at 50° in 3M $\mathrm{HClO_4}$ at $\mu = 4.5\mathrm{M}$.

Ogard and Taube[18] have studied the manganese(III)-catalysed aquation of $\mathrm{CrCl^{2+}}$ in perchlorate media at 25°. The suggested mechanism involves the oxidation of $\mathrm{CrCl^{2+}}$ to $\mathrm{CrCl^{3+}}$ as the rate-determining steps:

$$\left.\begin{aligned}
&\mathrm{Mn_{aq}}^{3+} + \mathrm{CrCl_{aq}}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mn_{aq}}^{2+} + \mathrm{CrCl_{aq}}^{3+}\\
&\mathrm{MnOH_{aq}}^{2+} + \mathrm{CrCl_{aq}}^{2+} \underset{k_{-1'}}{\overset{k_1'}{\rightleftharpoons}} \mathrm{MnOH_{aq}}^{+} + \mathrm{CrCl_{aq}}^{3+}\\
&\mathrm{CrCl_{aq}}^{3+} \xrightarrow{k_3} \mathrm{Cr^{IV}} + \mathrm{Cl^-}\\
&\mathrm{Cr^{IV}} + \mathrm{Mn^{II}} \xrightarrow{k_4} \mathrm{Cr^{III}} + \mathrm{Mn^{III}}
\end{aligned}\right. \tag{14}$$

The experimental rate law is

$$\text{rate} = \frac{-\mathrm{d}\,[\mathrm{CrCl_{aq}^{2+}}]}{\mathrm{dt}} = k_0[\mathrm{CrCl_{aq}}^{2+}]\,[\mathrm{Mn^{III}}]$$

where $k_0 = (k_1[\mathrm{H^+}]+k_1'K_\mathrm{H})/([\mathrm{H^+}]+K_\mathrm{H})$; this may be closer to the true acid-dependence of the rate than the simple inverse acidity dependence deduced[18] from the experimental measurements over a limited acidity range. The observed dependence does, however, suggest that $k_1' > k_1$ for this reaction.

$\mathrm{Mn^{III}}$ forms comparatively stable complexes with fluoride[21] and chloride ions[58,59,60] , the bromide complex is unstable and decomposes to give molecular bromine and $\mathrm{Mn^{II}}$ as the products. Wells and Mays[61] have demonstrated the free radical nature of the reaction by infrared identification of the end-groups in the polymer which is formed when the reaction is run in the presence of acrylonitrile. At low concentrations of bromide the mechanism consists of the unimolecular decomposition of the complex, followed by rapid recombination of the bromine atoms which are produced.

$$\begin{aligned}&\mathrm{Mn_{aq}}^{3+}+\mathrm{Br_{aq}}^{-}\overset{K}{\rightleftharpoons}\mathrm{MnBr_{aq}}^{2+}\ \text{(rapid)}\\&\mathrm{MnBr_{aq}}^{2+}\xrightarrow{k_1}\mathrm{Mn_{aq}}^{\mathrm{II}}+\mathrm{Br_{aq}}\\&2\mathrm{Br_{aq}}\xrightarrow{\text{fast}}\mathrm{Br_{2aq}}\end{aligned}\tag{15}$$

At higher concentrations of bromide the reaction becomes second-order in bromide ion concentration, and the mechanism, suggested by analogy with the $\mathrm{Fe^{III}}$–iodide[62] and $\mathrm{Ce^{IV}}$–bromide[63] reactions, is[61]

$$\mathrm{MnBr_{aq}}^{2+}+\mathrm{Br_{aq}}^{-}\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}\mathrm{Mn_{aq}}^{\mathrm{II}}+\mathrm{Br}^{\cdot}_{2\mathrm{aq}}{}^{-}$$

$$\mathrm{Mn_{aq}}^{\mathrm{III}}+\mathrm{Br}^{\cdot}_{2\mathrm{aq}}{}^{-}\xrightarrow{k_3}\mathrm{Mn_{aq}}^{\mathrm{II}}+\mathrm{Br_{2aq}}$$

which gives the rate law

$$\frac{-\mathrm{d}\,[\mathrm{Mn^{III}}]}{\mathrm{d}t}=\frac{2k_2k_3K[\mathrm{Mn^{III}}]^2[\mathrm{Br_{aq}}^-]^2}{k_{-2}[\mathrm{Mn^{II}}]+k_3[\mathrm{Mn^{III}}]}=k_0[\mathrm{Mn^{III}}]\,[\mathrm{Br_{aq}}^-]^2$$

on assumption of a steady state for $\mathrm{Br}^{\cdot}_{2\mathrm{aq}}{}^{-}$ and with $k_{-2}[\mathrm{Mn^{II}}] \ll k_3[\mathrm{Mn^{III}}]$. The decrease of the rate with increasing $[\mathrm{Mn^{II}}]$ is attributed[61] to the removal of bromide in the form of a relatively inert $\mathrm{Mn^{II}}$–bromide complex rather than a reverse reaction between $\mathrm{Mn^{2+}}$ and $\mathrm{Br}^{\cdot}_{2\mathrm{aq}}{}^{-}$ in view of the experimental rate law. This latter assumption is supported by the observation that the addition of oxidatively inert cations such as $\mathrm{Al^{III}}$ and $\mathrm{Zn^{II}}$ also has a retarding effect on the rate. The rate increases with increasing acidity and appreciable contribution from a mixed complex $\mathrm{Mn(OH)Br_{aq}}^{+}$ is discounted on the basis of the kinetic dependencies[61]. Although only the products k_1K and k_2K can be deduced from the data, it is interesting to note that their ratio $k_2/k_1 \approx 4\times10^4$ is certainly large and may be connected with the influence of co-ordinated bromide on the lability of the inner sphere of $\mathrm{Mn^{III}}$ in addition to the greater stability of solvated $\mathrm{Br^{-}}^{\cdot}_{2\mathrm{aq}}$ as compared to that of a solvated bromine atom.

Although the oxidation of hydrazoic acid has no kinetic term which is first-order in both reactants even at low concentrations of azide, the available data[64,65] is consistent with the presence of at least a 1:1 metal azide complex. At low azide concentrations, ($\mathrm{H[N_3]} \leqslant 10^{-3}$M), the reaction between $\mathrm{Mn^{III}}$ and $\mathrm{HN_3}$ is first-order in $[\mathrm{Mn^{III}}]$ and second-order[64] in $[\mathrm{HN_3}]$. A mechanism consistent with this reaction order is a follows.

$$\mathrm{Mn_{aq}}^{3+}+\mathrm{HN_{3aq}}\overset{K}{\rightleftharpoons}\mathrm{MnHN_{3aq}}^{3+}\tag{16}$$

$$\mathrm{MnHN_{3aq}}^{3+} + \mathrm{HN_{3aq}} \xrightarrow{k_1} \mathrm{MnN_{3aq}}^{+} + \mathrm{HN_{3aq}}^{+} + \mathrm{H_{aq}}^{+} \tag{17}$$

$$\xrightarrow{k_1'} \mathrm{Mn_{aq}}^{2+} + \mathrm{H_2N_{6aq}}^{+}$$

$$\mathrm{Mn_{aq}}^{3+} + \mathrm{HN_{3aq}} \overset{K}{\rightleftharpoons} \mathrm{MnN_{3aq}}^{2+} + \mathrm{H_{aq}}^{+} \tag{16'}$$

$$\mathrm{MnN_{3aq}}^{2+} + \mathrm{HN_{3aq}} \xrightarrow{k_2} \mathrm{MnN_{3aq}}^{+} + \mathrm{HN_{3aq}}^{+} \tag{17'}$$

$$\xrightarrow{k_2'} \mathrm{Mn_{aq}}^{2+} + \mathrm{HN_{6aq}}$$

$$\mathrm{Mn_{aq}}^{\mathrm{III}} + \mathrm{H_2N_{6aq}}^{+} \xrightarrow{k_3} \mathrm{Mn_{aq}}^{\mathrm{II}} + 3\mathrm{N_2} + 2\mathrm{H_{aq}}^{+} \tag{18}$$

$$\mathrm{Mn_{aq}}^{\mathrm{III}} + \mathrm{HN_{6aq}} \xrightarrow{k_3'} \mathrm{Mn_{aq}}^{\mathrm{II}} + 3\mathrm{N_2} + \mathrm{H_{aq}}^{+}$$

$$2\mathrm{HN_{3aq}}^{+} \xrightarrow{k_4} 3\mathrm{N_2} + 2\mathrm{H_{aq}}^{+} \tag{18'}$$

with $k_4, k_3, k_3' > k_1, k_1', k_2, k_2'$ and $K[\mathrm{HN_3}], K'[\mathrm{HN_3}] \ll (1+K_\mathrm{H}/[\mathrm{H}^+]_{\mathrm{aq}}.)$

Although $\mathrm{MnOH_{aq}}^{2+}$ is present in these solutions it does not appear to react with $\mathrm{HN_3}$. The parallel paths in (17) and (17′) are kinetically indistinguishable, and there is no independent evidence that steps involving $\mathrm{H_2N_{6aq}}^{+}$ and $\mathrm{HN_{6aq}}$ are significant in this mechanism: indeed, their existence seems less likely than that of $\mathrm{HN_{3aq}}^{+}$ (a protonated azide radical, *cf.* $\mathrm{H_2O_{2aq}}^{+}$), and presumably $k_1 > k_1'$ and $k_2 > k_2'$. The mechanism consisting of steps (16)–(18′) predicts a linear plot of $k_0(1+K_\mathrm{H}/[\mathrm{H}^+])$ *vs.* $1/[\mathrm{H}^+]$, (Fig. 2). We may estimate the acid-independent quantities $k_1'K' = 2.8\times10^3\mathrm{M}^{-1}\mathrm{sec}^{-1}$, and $Kk_1 = 5\times10^3\mathrm{M}^{-2}\mathrm{sec}^{-1}$ from the slope and intercept, respectively. Although no separate study of the dependence of rate on $[\mathrm{Mn^{II}}]$ was carried out, the data[64] are consistent with an irreversibility of steps (17) and/or (17′) and the lack of appreciable $\mathrm{Mn^{II}}$–azide complexation[66].

At much larger excesses of hydrazoic acid the stoichiometry of reaction is unchanged, but the kinetic dependencies become more complex, and Davies *et al.*[65] have proposed the mechanism

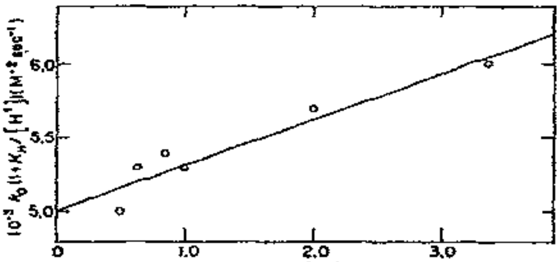

Fig. 2. Plot of $10^{-3}\,k_0\,(1+K_\mathrm{H}/[\mathrm{H}^+])$ *vs.* $1/[\mathrm{H}^+]$ from the data of ref. 64.

$$2\mathrm{MnN_{3aq}}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mn_{aq}}^{2+} + \mathrm{Mn(N_3)_{2aq}}^{2+} \tag{19}$$

$$\mathrm{Mn(N_3)_{2aq}}^{2+} \xrightarrow{k_2} \mathrm{Mn_{aq}}^{2+} + 3\mathrm{N_{2aq}} \tag{20}$$

$$\mathrm{Mn(N_3)_{2aq}}^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{MnN_{3aq}}^{+} + \mathrm{N_{3aq}}^{+} \tag{21}$$

$$\mathrm{HN_{3aq}} + \mathrm{N_{3aq}}^{+} \xrightarrow{k_4} 3\mathrm{N_2} + \mathrm{H_{aq}}^{+} \tag{22}$$

from a study under these conditions, using the stopped-flow method. The equilibrium constants $K = [\mathrm{MnN_{3aq}}^{2+}][\mathrm{H_{aq}}^{+}]/[\mathrm{Mn_{aq}}^{3+}][\mathrm{HN_3}]$ obtained from initial optical densities (89 ± 18) and from kinetic analysis (74 ± 15) are in good agreement, despite the kinetic complexity of the reaction and the possibility of higher-order complexation in a large excess of azide. The absorption spectrum of $\mathrm{MnN_{3aq}}^{2+}$ has been obtained in the wavelength range 440 to 570nm, $\varepsilon_{\max}$ being $\simeq 750\,\mathrm{l\,M^{-1}\,cm^{-1}}$ at 520 nm. The chief features of this mechanism are the reaction of two monoazidomanganese(III) complexes to form $\mathrm{Mn(N_3)_{2aq}}^{2+}$, and the formation of $\mathrm{N_{3aq}}^{+}$. If the reactions of step (19) are limited by the rates of water exchange[57]; in $\mathrm{MnN_{3aq}}^{2+}$ and $\mathrm{Mn_{aq}}^{2+}$, respectively, then $3 \times 10^6 \leq k_1 \leq 9 \times 10^6\,\mathrm{M^{-1}\,sec^{-1}}$ and $k_1 \leq 3 \times 10^8\,\mathrm{M^{-1}\,sec^{-1}}$ at 25° and $\mu = 3.8\,\mathrm{M}$. Independent estimates of $K' = [\mathrm{MnN_{3aq}}^{+}]/[\mathrm{Mn_{aq}}^{2+}][\mathrm{N_{3aq}}^{-}]$ and k_4 would be valuable in throwing more light on the magnitude of the other rate constants in this mechanism. The appearance of step (19) in high excess of azide suggests that azide is acting as a bridging group: if this is the case, then the formulation of the reactive complex as $\mathrm{MnN_{3aq}}^{2+}$ rather than $\mathrm{MnHN_{3aq}}^{3+}$, would seem appropriate[67]. The visible spectrum of $\mathrm{MnN_{3aq}}^{2+}$ is shown in Fig. 3, together with the spectra of $\mathrm{MnCYDTA_{aq}}^{-}$ and $\mathrm{Mn(H_2P_2O_7)_{3aq}}^{3-}$ for comparison.

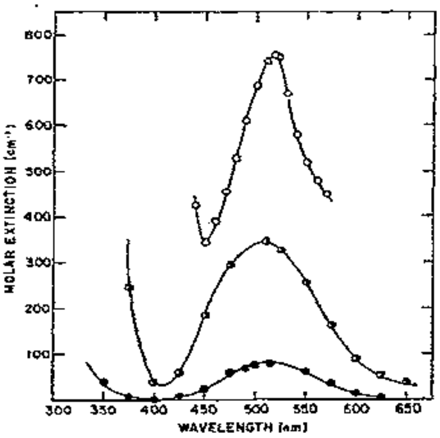

Fig. 3. Spectra of some $\mathrm{Mn^{III}}$ complexes in solution at 25°. ○, $\mathrm{MnN_{3aq}}^{2+}$ (ref. 65); ◐, $\mathrm{MnCYDTA_{aq}}^{-}$ at pH 2-7 (ref. 13a); ●, $\mathrm{Mn(H_2P_2O_7)_{3aq}}^{3-}$ in 0.05 F $\mathrm{H_2SO_4}$ (ref. 3).

Using the average value for the equilibrium constant of reaction (16′) ($K = 82$), one calculates a value of $k_2 = 34\text{M}^{-1}\text{sec}^{-1}$ for the rate of reaction (17′). The ratio of rate constants for reactions (19) and (17′) is estimated at $1\times10^5 \lesssim k_{19}/k_{17}' \lesssim 3\times10^5$, which sould be compared with the value for the corresponding ratio found in the Mn^{III}–Br^- reaction[61] (page 209).

The results of two studies[8,9] of the rapid reaction between Mn^{III} and hydrogen peroxide using the stopped-flow method lead to somewhat different conclusions. Wells and Mays[9] have observed a first-order decay of an intermediate which is rapidly formed and decays with an acid-independent rate constant of 40 sec^{-1} at 25° and $\mu = 4.0\text{M}$. A dependence of the rate on $[\text{Mn}^{\text{II}}]$ cannot be ruled out from these results, however, since the ionic strength was adjusted by addition of Mn^{II} in the acidity range 0.5–3.7M $HClO_4$. Indeed, the results of Davies *et al.*[8] suggest the alternative mechanism

$$\begin{tikzcd}
\text{Mn}_{\text{aq}}{}^{3+} + \text{H}_2\text{O}_{2\text{aq}} \arrow[rr, shift left, "K"] \arrow[dr, shift right, "k_1"'] & & \text{Mn}^{3+}\text{H}_2\text{O}_{2\text{aq}} \arrow[ll, shift left] \arrow[dl, shift left, "k_1'"] \\
& \text{Mn}_{\text{aq}}{}^{2+} + \text{H}_2\text{O}_{2\text{aq}}{}^{+} \arrow[ul, shift right, "k_{-1}"'] \arrow[ur, shift left, "k_{-1'}"] &
\end{tikzcd} \tag{23}$$

$$\begin{tikzcd}
\text{MnOH}_{\text{aq}}{}^{2+} + \text{H}_2\text{O}_{2\text{aq}} \arrow[rr, shift left, "K"] \arrow[dr, shift right, "k_2"'] & & \text{MnOH}^{2+}\text{H}_2\text{O}_{2\text{aq}} \arrow[ll, shift left] \arrow[dl, shift left, "k^2"] \\
& \text{Mn}_{\text{aq}}{}^{2+} + \text{HO}_{2\text{aq}} \arrow[ul, shift right, "k_{-2}"'] \arrow[ur, shift left, "k_{-2'}"] &
\end{tikzcd} \tag{24}$$

$$\text{HO}_{2\text{aq}} + \text{H}_{\text{aq}}{}^{+} \overset{K_a}{\rightleftharpoons} \text{H}_2\text{O}_{2\text{aq}}{}^{+} \qquad \text{(25) (ref. 8)}$$

$$\text{Mn}_{\text{aq}}{}^{3+} + \text{H}_2\text{O}_{2\text{aq}}{}^{+} \xrightarrow{k_3} \text{Mn}_{\text{aq}}{}^{2+} + 2\text{H}_{\text{aq}}{}^{+} + \text{O}_2 \tag{26}$$

$$\text{MnOH}_{\text{aq}}{}^{2+} + \text{H}_2\text{O}_{2\text{aq}}{}^{+} \xrightarrow{k_3'} \text{Mn}_{\text{aq}}{}^{2+} + \text{H}_{\text{aq}}{}^{+} + \text{O}_2 \tag{27}$$

The additional steps (28) are suggested by the observation of a Mn^{III}-catalysed decomposition at high peroxide concentrations

$$\left.\begin{aligned} &\text{H}_2\text{O}_{2\text{aq}}{}^{+} + \text{H}_2\text{O}_{2\text{aq}} \xrightarrow{k_4} \text{OH}_{\text{aq}} + \text{H}_3\text{O}^{+} + \text{O}_2 \\ &\text{OH}_{\text{aq}} + \text{Mn}_{\text{aq}}{}^{\text{II}} \xrightarrow{k_5} \text{Mn}_{\text{aq}}{}^{\text{III}} + \text{OH}_{\text{aq}}{}^{-} \end{aligned}\right. \tag{28}$$

An acid-dependent equilibrium constant of $k_{\text{app}} = [\text{Mn}^{\text{III}}\cdot\text{H}_2\text{O}_2]/[\text{Mn}^{\text{III}}][\text{H}_2\text{O}_2] \approx 1.7\times10^3\text{M}^{-1}$ has been obtained from the kinetic data[8] in the acidity range $[\text{HClO}_4] = 1.00$–3.70M.

However, Davies *et al.*[8] did not find spectrophotometric evidence for the presence of complexes, which suggests that either 1) the extinction coefficients of the complex(es) and the aquo-species are similar at the wavelengths used for observation of the reaction, or 2) that the concentration of the complex is kept low by its rapid decomposition to Mn^{II} and radical species. Thus, the rate of formation of complexed species, which would be limited by the rate of water exchange in $Mn_{aq}{}^{3+}$ and/or $MnOH_{aq}{}^{2+}$, may be a relatively slow step in the overall decomposition process, although a steady state for the complexed species is ruled out by the dependence of the rate constant on $1/[H_2O_2]_0$. A reversible step involving $Mn^{II}{}_{aq}$ might be expected from a comparison with the reversible $Ce^{IV}{}_{aq}+H_2O_{2aq} \rightleftarrows$ $\rightleftarrows Ce^{III}{}_{aq}+H_2O_{2aq}{}^+$ system in $0.8\mathrm{M}$ H_2SO_4 (ref. 69). Indeed, the ratios of k_{-1}/k_2 (*cf.* refs. 8 and 69) are not dissimilar for the two systems. The forward rate constants for the reactions (23) and (24) have been found to be $7.3\times10^4\mathrm{M}^{-1}\mathrm{sec}^{-1}$ and $3.2\times10^4\mathrm{M}^{-1}\mathrm{sec}^{-1}$ at ionic strengths in the range $\mu = 2.23$ to $4.90\mathrm{M}$ and 25° (ref. 8). It is noteworthy that the sum of these two rate constants is not too different from the product of the first-order rate constant of Wells and Mays[9], and the approximate equilibrium constant of Davies *et al.*[8] ($10.5\times10^4\mathrm{M}^{-1}\mathrm{sec}^{-1}$ compared to $6.8\times10^4\mathrm{M}^{-1}\mathrm{sec}^{-1}$, respectively).

In contrast to the complexity of the reactions discussed so far, the reactions of Mn^{III} with $NH_3{}^+OH_{aq}$[70], $NH_3{}^+OCH_{3aq}$[70] HNO_{2aq}[70], $NH_3{}^+NH_{2aq}$[71] protonated methylhydrazine molecules[71] and with hydroquinone[72] are all simple, second-order processes, with no large dependencies on ionic strength and no apparent reversibility in the rate-determining step. In general, there is no spectrophotometric evidence for complex formation in this series of reactions[70–72].

The reaction with hydroxylamine[70] has a stoichiometry of up to six equivalents of Mn^{III} for each molecule of hydroxylamine oxidised, and nitrate has been identified as the major oxidation product in the kinetic range. The results have been analysed[70] in terms of the mechanism

$$Mn_{aq}{}^{3+}+NH_3{}^+OH_{aq} \xrightarrow{k_1} Mn_{aq}{}^{2+}+NH_2\dot{O}_{aq}+2H_{aq}{}^+$$

$$MnOH_{aq}{}^{2+}+NH_3{}^+OH_{aq} \xrightarrow{k_1'} Mn_{aq}{}^{2+}+NH_2\dot{O}_{aq}+H_3O_{aq}{}^+$$

$$2H_2O+5Mn_{aq}{}^{III}+NH_2\dot{O}_{aq} \xrightarrow{k_2} 5Mn_{aq}{}^{II}+NO_{3aq}{}^-+6H_{aq}{}^+$$

with $k_2 \gg k_1, k_1'$. The rate constants for this mechanism are[70] $k_1 = 1.4\times10^3$ $\mathrm{M}^{-1}\mathrm{sec}^{-1}$ and $k_1' = 3.1\times10^3\mathrm{M}^{-1}\mathrm{sec}^{-1}$ at 25°. The results for the oxidation of nitrous acid indicate the following series of reactions[70]:

$$Mn_{aq}{}^{3+}+HNO_{2aq} \xrightarrow{k_1} Mn_{aq}{}^{2+}+NO_{2\dot{a}q}+H_{aq}{}^+$$

$$MnOH_{aq}{}^{2+}+HNO_{2aq} \xrightarrow{k_1'} Mn_{aq}{}^{2+}+NO_{2\dot{a}q}$$

$$H_2O+Mn_{aq}{}^{III}+NO_{2\dot{a}q} \xrightarrow{k_2} Mn_{aq}{}^{2+}+NO_{3aq}{}^-+2H_{aq}{}^+$$

with $k_2 \gg k_1, k_1'$. The rate constants are $k_1 = 2.2\times10^4\mathrm{M}^{-1}\mathrm{sec}^{-1}$ and $k_1' =$ $4.9\times10^4\mathrm{M}^{-1}\mathrm{sec}^{-1}$ at 25°, which, when compared to those for hydroxylamine, suggest[70] that nitrous acid may be an intermediate in the oxidation of hydroxylamine to nitrate.

Methylation of the hydroxyl group in hydroxylamine causes a 500-fold decrease in the rate constant and the reaction consists, within the limits of experimental error, of the steps

$$\mathrm{MnOH_{aq}}^{2+}+\mathrm{NH_3}^{+}\mathrm{OCH_{3aq}} \xrightarrow{k_1'} \mathrm{Mn_{aq}}^{2+}+\dot{\mathrm{N}}\mathrm{HOCH_{3aq}}+2\mathrm{H_{aq}}^{+}$$

$$2\dot{\mathrm{N}}\mathrm{HOCH_{3aq}} \xrightarrow{k_2} \mathrm{N_2H_2(OCH_3)_{2aq}}$$

with $k_2 \gg k_1'$, *i.e.* the species $\mathrm{MnOH_{aq}}^{2+}$ is more reactive towards the methylated species[70] than is $\mathrm{Mn_{aq}}^{3+}$.

The rate-determining step in the reactions with hydrazine and with methylhydrazines results in the formation of a protonated hydrazoyl radical *e.g.*

$$\mathrm{Mn_{aq}}^{3+}+\mathrm{CH_3NH_2}^{+}\mathrm{NHCH_{3aq}} \xrightarrow{k_1} \mathrm{Mn_{aq}}^{2+}+\mathrm{CH_3NH_2}^{+}\dot{\mathrm{N}}\mathrm{CH_{3aq}}+\mathrm{H_{aq}}^{+}$$

$$\mathrm{MnOH_{aq}}^{2+}+\mathrm{CH_3NH_2}^{+}\mathrm{NHCH_{3aq}} \xrightarrow{k_1'} \mathrm{Mn_{aq}}^{2+}+\mathrm{CH_3NH_2}^{+}\dot{\mathrm{N}}\mathrm{CH_{3aq}}+\mathrm{H_2O}$$

followed by faster subsequent steps, dependent on the nature of the hydrazoyl radical, with dimerisation generally favoured over further oxidation[71] by $\mathrm{Mn^{III}}$. The rate constants decrease on methylation of hydrazine through the series, and except for the most highly methylated species, the protonated tetramethylhydrazine molecule $\mathrm{(CH_3)_2NH^+N(CH_3)_2}$, it is generally observed that $k_1' > k_1$, as is the case where the OH group is blocked in the hydroxylaminium ion[70]. The absence of transferable hydrogen atoms in the tetramethyl derivative presumably reduces the rate of reaction with $\mathrm{MnOH_{aq}}^{2+}$ in this, the least rapid, reaction of the series by almost three orders of magnitude. An analysis of the rate data for this series of reactions suggests[71] that oxidative attack takes place at a point furthest from the point of protonation, as found, for example, in the reactions of the hydroxyl radical with protonated amine molecules[73].

In the oxidation of hydroquinone[72] there is effective competition between $\mathrm{Mn_{aq}}^{3+}$ and $\mathrm{MnOH_{aq}}^{2+}$ for reaction with the hydroquinone molecule. Thus, in the mechanism for the reaction in the absence of oxygen

$$\mathrm{Mn_{aq}}^{3+}+p\text{-}\mathrm{HOC_6H_4OH_{aq}} \xrightarrow{k_1} \mathrm{Mn_{aq}}^{2+}+p\text{-}\mathrm{HOC_6H_4\dot{O}_{aq}}+\mathrm{H_{aq}}^{+}$$

$$\mathrm{MnOH_{aq}}^{2+}+p\text{-}\mathrm{HOC_6H_4OH_{aq}} \xrightarrow{k_1'} \mathrm{Mn_{aq}}^{2+}+p\text{-}\mathrm{HOC_6H_4O_{aq}}+\mathrm{H_2O}$$

$$\mathrm{Mn_{aq}}^{3+}+p\text{-}\mathrm{HOC_6H_4\dot{O}_{aq}} \xrightarrow{k_2} \mathrm{Mn_{aq}}^{2+}+p\text{-}\mathrm{OC_6H_4O_{aq}}$$

$$\mathrm{MnOH_{aq}}^{2+}+p\text{-}\mathrm{HOC_6H_4O_{aq}} \xrightarrow{k_2'} \mathrm{Mn_{aq}}^{2+}+p\text{-}\mathrm{OC_6H_4O_{aq}}+\mathrm{H_2O}$$

$$2p\text{-}\mathrm{HOC_6H_4\dot{O}_{aq}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} p\text{-}\mathrm{HOC_6H_4OH_{aq}}+p\text{-}\mathrm{OC_6H_4O_{aq}}$$

the observed rate law

$$\frac{-\mathrm{d}\,[\mathrm{Mn^{III}}]}{2\mathrm{d}t} = k_0[\mathrm{Mn^{III}}]\,[p\text{-}\mathrm{HOC_6H_4OH}]$$

is consistent with $k_3[p\text{-HOC}_6\text{H}_4\text{O}^{\cdot}_{aq}] \ll k_2, k_2'$ and $k_2, k_2' \gg k_1, k_1'$, and an analysis of the kinetic data at eight acidities in the range 0.60–3.60M $HClO_4$ leads to the values[72] $k_1 = (0.48 \pm 0.12) \times 10^4 \text{M}^{-1}\text{sec}^{-1}$ and $k_1' = (3.28 \pm 0.43) \times 10^4 \text{M}^{-1}\text{sec}^{-1}$ at 25°.

Variations of rate with acidity in the reaction between Mn^{III} and isopropanol under anaerobic conditions have been interpreted[74] in terms of the reactions

$$\text{Mn}_{aq}{}^{3+} + (\text{CH}_3)_2\text{CHOH}_{aq} \xrightarrow{k_1} \text{Mn}_{aq}{}^{2+} + (\text{CH}_3)_2\dot{\text{C}}\text{OH}_{aq} + \text{H}_{aq}{}^{+} \tag{29}$$

$$\text{Mn}^{\text{III}} + (\text{CH}_3)_2\dot{\text{C}}\text{OH}_{aq} \xrightarrow{k_2} \text{Mn}_{aq}{}^{2+} + (\text{CH}_3)_2\text{CO}_{aq} + \text{H}_{aq}{}^{+} \tag{30}$$

Alternative slow steps *e.g.*

$$\text{MnOH}_{aq}{}^{2+} + (\text{CH}_3)_2\text{CHOH}_{2aq}{}^{+} \xrightarrow{k_1'} \text{Mn}_{aq}{}^{2+} + (\text{CH}_3)_2\dot{\text{C}}\text{OH}_{aq} + \text{H}_{aq}{}^{+} \tag{31}$$

were eliminated on the basis of the observation that the reaction between $\text{MnOH}_{aq}{}^{2+}$ and the unprotonated alcohol[75] need not be considered in the mechanism. Unlike other alcohols, such as methanol, ethanol and n-propanol[60], the presence of isopropanol does not modify the absorption spectrum[60,74] of Mn^{III}. The isotope effect on replacing the alpha hydrogen atom by deuterium[74] is large ($k_{\text{H}}/k_{\text{D}} = 3.04$ at 25°) for a reaction of this type. Reactions (29) and (31) are kinetically indistinguishable and from the other reactions so far studied, (Table 2), it seems possible that $k_1' \gtrless k_1$ and that reaction (31), in which the α-CH bond may be weakened by the presence of the positive charge on the neighbouring hydroxyl group[75], accounts, at least in part, for the magnitude of the isotope effect in this reaction.

We have collected kinetic data for all the well-documented reactions of Mn^{III} in perchloric acid in Table 2. The data are arranged in order of decreasing rate constant. A number of conclusions are suggested by these results:

1) the $\text{MnOH}_{aq}{}^{2+}$ species is generally more reactive towards a given reductant than is $\text{Mn}_{aq}{}^{3+}$. Exceptions would seem to be cases where strong complex-formation is possible (*e.g.* reactions with $\text{Br}_{aq}{}^{-}$[61] and hydrazoic acid[64,65]).

2) effective competition between $\text{Mn}_{aq}{}^{3+}$ and $\text{MnOH}_{aq}{}^{2+}$ for reaction with a given substrate is observed for reductants which contain suitable sites for co-ordination (*e.g.* H_2O_{2aq}[8], HNO_{2aq}[70], $\text{NH}_3{}^{+}\text{OH}_{aq}$[70], hydroquinone[72]) or no transferable H-atoms (*e.g.* $(\text{CH}_3)_2\text{NH}^{+}\text{N}(\text{CH}_3)_{2aq}$[71]).

The lability of both Mn^{II} and Mn^{III} is a serious stumbling block in a distinction between inner- and outer-sphere mechanisms for reactions of Mn^{III}. However, an interesting possibility exists for the fastest reactions which have been observed. That is, that the rate of water exchange in Mn^{III} limits the rate of reaction, and that the oxidation process (H-atom, or electron transfer) takes place very rapidly, in the inner-sphere, following the co-ordination of the reductant to the metal cation[76]. We may thus envisage each slow step as consisting of the diffusion-controlled formation of an ion-pair ((32) and (32')) followed by formation of an inner-sphere complex by rate-determining water loss, ((33) and (33')). The complex then decomposes very rapidly by electron transfer, (33), or H-atom transfer (33'),

$$\mathrm{Mn_{aq}}^{3+} + \mathrm{B_{aq}} \overset{K_0}{\rightleftharpoons} \mathrm{Mn_{aq}}^{3+}, \mathrm{B_{aq}} \tag{32}$$

$$\mathrm{MnOH_{aq}}^{2+} + \mathrm{B_{aq}} \overset{K_0'}{\rightleftharpoons} \mathrm{MnOH_{aq}}^{2+}, \mathrm{B_{aq}} \tag{32'}$$

$$\mathrm{Mn_{aq}}^{3+}, \mathrm{B_{aq}} \overset{k_0}{\rightleftharpoons} (\mathrm{Mn^{3+}B})_{\mathrm{aq}} \xrightarrow{\text{v. fast}} \text{products} \tag{33}$$

$$\mathrm{MnOH_{aq}}^{2+}, \mathrm{B_{aq}} \overset{k_0'}{\rightleftharpoons} (\mathrm{MnOH^{2+}B})_{\mathrm{aq}} \xrightarrow{\text{v. fast}} \text{products} \tag{33'}$$

For this mechanism we may write $k_1 = K_0 k_0$ and $k_1' = K_0' k_0'$, where

$$K_0 = [\mathrm{Mn_{aq}}^{3+}, \mathrm{B_{aq}}]/[Mn_{\mathrm{aq}}{}^{3+}]\,[\mathrm{B_{aq}}] \text{ and}$$
$$K_0' = [\mathrm{MnOH_{aq}}^{2+}, \mathrm{B_{aq}}]/[\mathrm{MnOH_{aq}}^{2+}]\,[\mathrm{B_{aq}}].$$

We cannot measure K_0 and K_0' directly, and it seems certain that the Eigen-Fuoss equation[77] cannot be used to calculate values at the necessarily high ionic strength. We may, however, approximate the situation by using assumptions suggested by Sutin and his co-workers[78], as follows. We will assume that K_0 and K_0' are the same in the $\mathrm{Mn^{III}}$ and $\mathrm{Co^{III}}$ systems. We then write

$$\frac{k_{0,\mathrm{Mn_{aq}}^{3+}}}{k_{0,\mathrm{Co_{aq}}^{3+}}} = \frac{k_{1,\mathrm{Mn_{aq}}^{3+}}}{k_{1,\mathrm{Co_{aq}}^{3+}}} \tag{34}$$

We have calculated the data shown in Table 3 using Sutin's[78] value for water exchange, $k_{0,\mathrm{Co_{aq}}3+} \leq 1 \times 10^3$ sec^{-1}, and the value of the directly-measured forward rate constant of formation of the $\mathrm{Co_{aq}}^{3+}$-malic acid complex[79a]. Since the acid-dissociation constant of $\mathrm{Co_{aq}}^{3+}$ which was used by Sutin *et al.*[78] has recently been confirmed[79], it seems reasonable to accept the value $k_{0'},_{\mathrm{CoOH_{aq}}}{}^{2+} \approx 3 \times 10^3$ sec^{-1}. We have again used the directly-measured rate constant for formation of the $\mathrm{CoOH_{aq}}^{2+}$-malic acid complex[70a] to calculate the value for $K_0'{}_{\mathrm{MnOH_{aq}}}{}^{2+}$ in Table 3, using eqn. (35).

$$\frac{k'_{0,\mathrm{MnOH_{aq}}^{2+}}}{k'_{0,\mathrm{CoOH_{aq}}^{2+}}} = \frac{k'_{1,\mathrm{MnOH_{aq}}^{2+}}}{k'_{1,\mathrm{CoOH_{aq}}^{2+}}} \tag{35}$$

The variations in $k_{0,\mathrm{Mn_{aq}}^{3+}}$ which are observed are probably a reflection of the greater ligand-dependence of K_0 as compared to K_0' because of the greater charge on the metal. The approximation involved in using eqn. (35) is evidently much smaller, and the average value for water exchange on $\mathrm{MnOH_{aq}}^{2+}$ is found to be approximately 1×10^6 sec^{-1}. This estimate is probably within a factor of two or three of the actual value for the rate of water exchange in $\mathrm{MnOH_{aq}}^{2+}$, despite the ligand dependencies which have been found[79] in rates of complex formation with $\mathrm{CoOH_{aq}}^{2+}$. Data for reactions of $\mathrm{Co^{III}}$ with most of the substrates

TABLE 3

ESTIMATES OF THE RATE OF WATER EXCHANGE IN Mn_{aq}^{3+} AND $MnOH_{aq}^{2+}$ AT 25°[a]

Substrate	*$10^{-6}\,k_0$, Mn_{aq}^{3+} sec^{-1}*	*$10^{-6}\,k_0'$, $MnOH_{aq}^{2+}$ sec^{-1}*
p-$C_6H_4(OH)_2$	$\leqslant$ 0.9	1.4
H_2O_2	$\leqslant$ 13.5	1.4
HNO_2	$\leqslant$ 4.1	2.1

[a] Values based on the data for the reaction $Co^{III} + HMal \xrightarrow{k_f} CoHMal$, where HMal is malic acid, ref. 79a (see Text).

in Table 3 might be useful for further estimates of the rates of water exchange in Mn_{aq}^{3+} and $MnOH_{aq}^{2+}$, since it seems preferable to use the same substrate in the systems which are used in the comparison, especially in using eqn. (34). Although crude, these estimates may be useful in the analysis of other data for Mn^{III} reactions. The presence of a large excess of paramagnetic, labile Mn_{aq}^{2+} ions and the limited concentrations of Mn^{III} which are available in perchlorate media would be expected to make the direct estimation of these constants, *e.g.*, by an NMR technique[57], extremely difficult.

The mechanism of oxidation of a series of hydroquinones by Fe^{III} has been interpreted[80] as involving a rate-determining step of the type

$$Fe_{aq}^{3+} + p\text{-}C_6H_4(OH)O_{aq}^{-} \rightleftharpoons Fe_{aq}^{2+} + p\text{-}C_6H_4(OH)O^{\cdot}_{aq} \tag{36}$$

where p-$C_6H_4(OH)O_{aq}^{-}$ is the hydroquinone anion. The rate constants which are derived on this basis are close to the diffusion-controlled limit. Thermodynamic arguments were used[80] to differentiate between this mechanism and the kinetically indistinguishable reaction

$$FeOH_{aq}^{2+} + p\text{-}C_6H_4(OH)_{2aq} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} Fe_{aq}^{2+} + p\text{-}C_6H_4(OH)O^{\cdot}_{aq} \tag{37}$$

If we interpret the data of Baxendale *et al.*[80] in terms of eqn. (37), then we obtain values of k_1' shown in Table 4. The experimental rate constants are about two orders of magnitude smaller than the estimated rate constant for water exchange[81].

TABLE 4

RATE CONSTANTS FOR THE REACTION OF THE TYPE

$FeOH_{aq}^{2+} + p\text{-}C_6H_4(OH)_{2aq} \xrightarrow{k_1'} Fe_{aq}^{2+} + p\text{-}C_6H_4(OH)O^{\cdot}_{aq} + H_2O$[a] at 25°, $\mu = 0.65$M

Reductant	*$10^{-3}\,k_1'$ $M^{-1}sec^{-1}$*
benzohydroquinone	0.26
toluohydroquinone	1.12
2,6-dichlorobenzohydroquinone	0.60
2,3,5,6,-tetramethylbenzohydroquinone	0.79

[a] Calculated from the data of ref. 80, using the acid dissociation constant of Fe_{aq}^{3+} from R. M. Milburn and W. C. Vosburgh, *J. Amer. Chem. Soc.*, 77 (1955) 1352.

in $FeOH_{aq}^{2+}$, $k_{0}'{}_{,FeOH_{aq}^{2+}} \approx 3\times10^{5}$ sec^{-1}. This suggests that the rate-determining step in this reaction is the redox step rather than complex formation. We should also note that the rate constants in Table 2 are consistent with a dependence of K_0 and K_0' on the charge on the substrate, as predicted for a S_N1 mechanism.

E. OTHER COMPLEXES OF Mn^{III}

The majority of Mn^{III} complexed contain bound oxygen atoms. Most of them are unstable in solution. For example, Mn^{III} slowly oxidises bound chloride[59] and EDTA[13a] ligands. The complexes often precipitate hydrated oxides on standing. Although there is evidence of complex formation *e.g.* from colour formation on adding Mn^{VII} to Mn^{II} in the presence of a given ligand, the number of detailed studies of the equilibria involved is at present small. In most cases it is the instability of the complexes which is a serious setback, and indirect, *e.g.* kinetic[58], methods have to be applied. We have collected stability constants for well-defined complexes in Table 5.

TABLE 5

EQUILIBRIUM CONSTANTS FOR Mn^{III} COMPLEX FORMATION IN PERCHLORATE MEDIA AT 25°

Reaction	*Medium*[a]	*Constant*	*Ref.*
$Mn^{3+} \rightleftharpoons MnOH^{2+} + H^{+}$	$\mu = 4.0$ M	0.93 M	6
$Mn^{3+} + HF \rightleftharpoons MnF^{2+} + H^{+}$	$\mu = 5.35$ M[a]	1.6×10^{3} M^{-1}	82
	$\mu = 2$ M	$\sim3.7\times10^{3}$ M^{-1}	58, 82
$MnOH^{2+} + HF \rightleftharpoons Mn(OH)F^{+} + H^{+}$	$\mu = 5.35$ M[a]	1.9×10^{3} M^{-1}	82
	$\mu = 2$ M	$\sim3.7\times10^{3}$	58, 82
$Mn^{3+} + Cl^{-} \rightleftharpoons MnCl^{2+}$	$\mu = 2$ M	13.5 ± 0.5 M^{-1}	58, 82
$Mn^{3+} + H_2C_2O_4 \rightleftharpoons MnC_2O_4^{+} + 2H^{+}$	$\mu = 2$ M	1.64×10^{5} M	58, 82
$MnC_2O_4^{+} + H_2C_2O_4 \rightleftharpoons Mn(C_2O_4)^{-} + 2H^{+}$	$\mu = 2$ M	45 M	58, 82
$MnC_2O_4^{+} + HF \rightleftharpoons Mn(C_2O_4)F + H^{+}$	$\mu = 2$ M	1.18×10^{2}	58, 82
$Mn^{3+} + HN_3 \rightleftharpoons MnN_3^{2+} + H^{+}$	$\mu = 3.8$ M	82	65
$Mn^{3+} + EDTA^{4-} \rightleftharpoons Mn(EDTA)^{-}$	$\mu = 0.20$ M	7.1×10^{24} M^{-1}	13a, 83
$Mn^{3+} + CYDTA^{4-} \rightleftharpoons Mn(CYDTA)^{-}$	$\mu = 0.20$ M	7.9×10^{28} M^{-1}	13a
$Mn^{3+} + HEDTA^{4-} \rightleftharpoons Mn(HEDTA)^{-}$	$\mu = 0.20$ M	5.0×10^{22} M^{-1}	13a
$MnEDTA^{-} + N_3^{-} \rightleftharpoons Mn(EDTA)N_3^{2-}$	$\mu = 0.25$ M	(32.1 ± 0.3) M^{-1}	84
$Mn^{3+} + 3acac \rightleftharpoons Mn(acac)_3^{3+}$	$\mu = 0.2$ M	7.2×10^{3} M^{-1}	85

[a] Temperature = 23 ± 1°.

(i) *Halide and pseudo-halide complexes*

The decomposition of the bromo-complex[61] has been discussed in the previous section. Estimates of the stability constant of $MnCl_{aq}^{2+}$ are available from a study of the effect of addition of chloride on the Mn^{III}-catalysed oxidation of oxalic acid by bromine[58,82]. A very large excess of chloride produces spectroscopic changes[59,60a] which suggest that the species $MnCl_{aq}^{2+}$ has a similar visible spectrum to those of $MnOH_{aq}{}^{2+}$ and $Mn_{aq}{}^{3+}$ and that the spectrum changes only on formation of higher complexes[82]. Recent spectrophotometric studies[82] have shown that the observed splitting[21,60a] of the spectrum of the aquo-species on addition of an excess of fluoride can be accounted for in terms of the formation of $MnF_{aq}{}^{2+}$ and $Mn(OH)F_{aq}{}^{+}$. The spectrum of the former has its maximum at 470 nm while the latter spectrum is split[82]. Splittings in the visible spectra of other complexes in solution noticed recently by Dingle[86] may also be connected with similar acid dissociation equilibria. It would appear that co-ordination of fluoride has little effect on the acidity of the remaining water molecules of the first co-ordination sphere[82]. The assignment of this complex is supported by the formation of a mixed fluoro-oxalate complex (Table 5). The spectra of the two aquo-fluoro complexes are shown in Figure 4. It is likely that the spectra of the monohalide complexes of $Mn_{aq}{}^{3+}$ are all similar to those of the aquo species[6] in the visible region, with maxima in the region of 470 nm, and that cumulative effects of negative charge are responsible for splitting (*e.g.* for $Mn(OH)F_{aq}{}^{+}$), or a decrease (*e.g.* for $SO_4{}^{2-}$, $N_3{}^{-}$) or increase (*e.g.* in $Mn(CYDTA)OH_{aq}{}^{2-}$) in 10 Dq. In all cases splittings of the ground state ^5E_g level (with smaller splittings of $^5T_{2g}$)[87] can produce broad spectral maxima as a result of distortion from octahedral symmetry[87].

It is noteworthy that pentachloromanganate(III) exists as a monomeric, pentacoordinate distorted complex in the salt[87a] $(BiPH_2)MnCl_5$, (Fig. 5).

The formation of 1:1 complexes between $Mn(EDTA)H_2O_{aq}{}^{-}$ and $N_3{}^{-}$ (ref. 84) and CN^{-} (ref. 88) has been observed and is taken as evidence to support seven-co-ordination of these polyamino systems in solution[89], as is observed in the solid salts[90]. It is noteworthy that no similar kinetic evidence for complex formation is observed between Mn-CYDTA complexes and oxalate under comparable conditions[7]. Wilkins and Yelin[91] have recently identified a five-co-ordinated

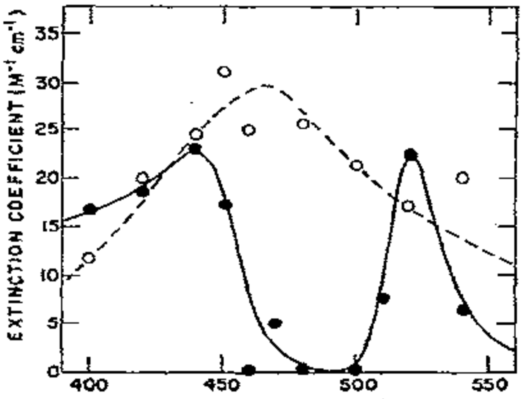

Fig. 4. Spectra of Mn^{III} complexes with fluoride. ○, $MnF_{aq}{}^{2+}$; ●, $Mn(OH)F_{aq}{}^{+}$ from ref. 82 (reproduced by permission of the copyright owner).

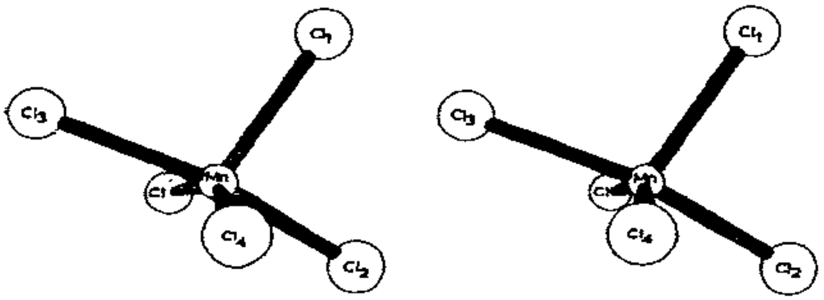

Fig. 5. Structure of $MnCl_5^{2-}$ in the salt $(BiPH_2)MnCl_5$. The bond lengths are as follows: Mn–Cl_1, 2.566 Å; Mn–Cl_2, 2.353 Å; Mn–Cl_3, 2.363 Å; Mn–Cl_4, 2.241 Å (two symmetrical bonds). This is a stereo-pair which can be examined with a handheld stereo viewer (Courtesy of Dr. I. Bernal).

Co^{III}-EDTA product in the reaction between Co^{II}-EDTA and Mn^{III}-EDTA complexes at pH's where the form $Mn(EDTA)OH_{aq}^{2-}$ is known to be present[13b]. This suggests that oxidation proceeds by an inner-sphere hydroxo-bridged mechanism. Five and six-co-ordinated Co^{II}-EDTA complexes apparently react with identical rates in outer-sphere oxidations[91]. One of the few low-spin complexes of Mn^{III} is the hexacyanomanganate(III) ion for which a magnetic moment of 3.18 B.M. was observed[92] in $K_3Mn(CN)_6$. Electron exchange between $Mn(CN)_{6aq}^{4-}$ and $Mn(CN)_{6aq}^{3-}$ in solution is rapid[93]. Studies of cyanide exchange in $Mn(CN)_{6aq}^{3-}$ have shown that the reaction proceeds by an aquation mechanism[94].

(ii) *Oxygen-bonded complexes*

Several chelating ligands in which binding through oxygen atoms occurs have been reported as suitable for application in analysis by colorimetric procedures[95]. As mentioned previously, the oxalato complexes are photochemically unstable[86,87], and this has been taken as partial evidence for a "charge-transfer" mechanism ($t_{1g} \rightarrow t_{2g}$, ligand → metal) as being responsible for the broad band which is often observed in the near infra-red (5000–15,000 cm^{-1}) for Mn^{III} complexes[86]. (See ref. 87 and later discussion).

The sulphato complexes are unstable, producing "MnO_2" on standing. Welsh[47a] has obtained an equilibrium constant $K_s = (1.8 \pm 0.2) \times 10^6 M^3$ for the reaction

$$2Mn^{III} + 2H_2O \rightleftharpoons MnO_2 + Mn^{II} + 4H^+ \qquad K_s \tag{38}$$

in the acid range 2.40–7.44M H_2SO_4 with $[Mn^{II}] = 0.138$–$0.364M$ at 15°. The equilibrium is slow from left to right and rapidly attained from right to left with "freshly produced MnO_2". The decomposition reaction is apparently fourth-order in $[Mn^{III}]$, and MnO_2 production proceeds on the surface of MnO_2 particles already formed[47a]. Piccardi and Guidelli[96] have concluded that the reaction

$$4\mathrm{Mn^{II}} + \mathrm{Mn^{VII}} \rightleftharpoons 5\mathrm{Mn^{III}}$$

is too slow for analytical application in acid sulphate solution and have calculated equilibrium constants for the reaction

$$2\mathrm{Mn^{III}} \rightleftharpoons \mathrm{Mn^{IV}} + \mathrm{Mn^{II}}$$

which decrease from 4.8×10^{-2} to 2.0×10^{-3} in going from 4.5 to 12M H_2SO_4 (*cf.* refs. 27, 28). The sulphato system merits further study in view of the complicated kinetics which have been observed, for example, in the $\mathrm{Mn^{III}}$–$\mathrm{Ce^{III}}$ system in sulphuric acid media[19,20]. Thus, the $\mathrm{Mn^{III}}$ species present in these solutions[86] must be considered largely unknown at the present time. Kinetic methods, such as those used by Taube might be useful for clarification of the equilibria involved.

The pyrophosphato complexes have probably been the most widely used $\mathrm{Mn^{III}}$ complexes for analytical purposes[4]. This system received careful study some years ago[12], and recent kinetic evidence[3] suggests that at least two pyrophosphatomanganese(III) complexes are involved in the reaction with various $\mathrm{Fe^{II}}$-phenanthroline complexes at pH 1.0. The pK of the reaction

$$\mathrm{Mn(H_2P_2O_7)_3}^{3-} \rightleftharpoons \mathrm{Mn(HP_2O_7)_2}^{3-} + \mathrm{H_4P_2O_7} \qquad (39)$$

has been found[97] to be 4.25 at 25°.

Many studies of the oxidation of organic substrates by sulphato- and pyrophosphato-$\mathrm{Mn^{III}}$ complexes have appeared in the literature and an excellent review of these reactions, in which emphasis is placed more on the nature of organic intermediates than on the nature of the oxidising ion, is available[10]. Evidence is sometimes obtained for discrete metal-substrate complex formation[10,62b]. An example of a more detailed study, in which the reactants are well-characterised, is the reaction between $\mathrm{Mn^{III}}$ and isopropanol in acid perchlorate solution[74].

Dingle[86], and Fackler *et al.*[87] have recently considered the assignment of the bands of the visible and near infra-red spectra of a large number of $\mathrm{Mn^{III}}$ complexes. The considerations are important from the point of view of understanding, for example, the nature of solvent co-ordination in the complexes in solution. In particular, the position of the low energy $^5B_{1g} \rightarrow {}^5A_{1g}$ band is noticeably sensitive to the choice of solvent environment[87]. Four assignments of this low energy band have been considered[86,87], *viz.*,

(1) static or dynamic splitting of the ^5E_g ground state,
(2) distortional splitting of the excited state,
(3) the possibility of a spin-forbidden transition, and,
(4) ligand → metal "charge transfer".

Available evidence is strongly in favour of possibility (1), with distortion towards a D_{4h}-type symmetry removing the degeneracy of the ^5E_g ground state. Small distortions with or without "pseudorotation"[87] could account for the broadness of the low-energy and visible bands (see *e.g.*, ref. 21, Fig. 2). Both the trisacetylacetonato[98] and trisoxalato-[99] Mn^{III} complexes have the magnetic moments expected of high spin complexes. However, all the Mn-O bond lengths in the trisacetylacetonate are found to be the same[87], in sharp contrast to the well-defined four short—two long arrangement in other Mn^{III} complexes (*e.g.* Mn_2O_3, ref. 100). A possible reason for the lack of the anticipated distortion is suggested by the observation that the C_2-H stretching frequency of the acetylacetonate complex at about 3090 cm^{-1} is similar to that found in benzene. This implies some aromaticity in the chelate rings by conjugation through the metal centre[101]. Such effects may also explain, at least in part, the similarity of the spectra of, *e.g.*, the tris-2,2-bipyridyl-1,1-dioxide-Mn^{III} complex in the single crystal and in dimethylsulphoxide[86].

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REFERENCES

1 A. H. Sully, *Manganese*, Academic Press, Inc., New York, N.Y., 1955.
2 D. R. Rosseinsky, *J. Chem. Soc.*, (1963) 1181.
3 H. Diebler and N. Sutin, *J. Phys. Chem.*, 68 (1964) 174.
4 R. Belcher and T. S. West, *Anal. Chim. Acta*, 6 (1952) 322; T. S. West, *Metallurgia*, 47 (1953) 46; A. Berká, J. Vulterin and J. Zýka, *Newer Redox Titrants*, Pergamon Press, Oxford, 1965, Chapter 2.
5 A. W. Adamson, *J. Phys. Chem.*, 55 (1951) 293.
6 C. F. Wells and G. Davies, *Nature*, 205 (1965) 692; *J. Chem. Soc.* (A), (1967) 1858.
7 M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, 6 (1967) 142.
8 G. Davies, L. J. Kirschenbaum and K. Kustin, *ibid.*, 7 (1968) 146.
9 C. F. Wells and D. Mays, *J. Chem. Soc.* (A), (1968) 665.
10 W. A. Waters and J. S. Littler in *Oxidation in Organic Chemistry*, Ed. K. B. Wiberg, Academic Press, Inc., New York, N.Y., 1965, pp. 185–241.
11 K. J. Vetter and G. Manecke, *Z. Physik. Chem.*, 195 (1950) 270.
12 J. I. Watters and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 70 (1948) 2455.
13 (a) R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, 6 (1967) 139; (b) Y. Yoshino, A. Ouchi, Y. Tsunoda and M. Kojima, *Can. J. Chem.*, 40 (1962) 775.
14 Y. K. Gupta and S. Ghosh, *Naturwiss.*, 45 (1958) 184.
15 D. N. Chakravarty and S. Ghosh, *Proc. National Acad. Sci. India*, Sect. A28, (5) (1959) 236.
16 C. P. Lloyd and W. F. Pickering, *Talanta*, 11 (1964) 1409.
17 E. Pungor and J. Trompler, *Acta. Chim. Acad. Sci.*, 13 (1958) 243.
18 A. E. Ogard and H. Taube, *J. Phys. Chem.*, 62 (1958) 357.
19 A. J. Aspray, D. R. Rosseinsky and G. B. Shaw, *Chem. Ind.*, *(London)*, (1963) 911.

20 G. A. Rechnitz, G. N. Rao and G. P. Rao, *Anal. Chem.*, 38 (1966) 1900.
21 J. P. Fackler Jr. and J. D. Chawla, *Inorg. Chem.*, 3 (1964) 1130 *cf.* ref. 86 and Section E of this Review.
22 A. R. J. P. Ubbelohde, *J. Chem. Soc.*, (1935) 1065.
23 E. J. Cuy, M. E. Rosenberg and W. C. Bray, *J. Amer. Chem. Soc.*, 46 (1924) 1796.
24 D. R. Rosseinsky and M. J. Nicol, *Trans. Faraday Soc.*, 61 (1965) 2718.
25 G. Davies and K. Kustin, unpublished results.
26 R. P. Buck, *Anal. Chem.*, 35 (1963) 692.
27 R. G. Selim and J. J. Lingane, *Anal. Chim. Acta*, 21 (1959) 536.
28 A. J. Fenton and N. H. Furman, *Anal. Chem.*, 32 (1960) 748.
29 S. Sazuki, *Kogyo Kagaku Zasshi*, 64 (1961) 2116.
30 S. L. Saval'skiĭ, *Sb. Nauch. Tr. Karzakhsk. Gorno–Met. Inst.*, No. 14 (1957) 224.
31 V. M. Tarayan, G. M. Ekimyan and A. T. Kochoryan, *Izvest. Akad. Nauk SSSR., Khim. Nauk*, 10 (1957) 105.
32 P. Brouillet, I. Epelboin and M. Froment, *Compt. Rend.*, 239 (1954) 1795; I. Epelboin, *Z. Elektrochem.*, 59 (1955) 689.
33 C. E. H. Bawn, T. P. Hobin and L. Raphael, *Proc. Roy. Soc.*, A237 (1956) 313.
34 K. E. Heusler, *J. Electrochem. Soc.*, 110 (1963) 703.
35 C. B. Gorbacher and B. A. Belyaeva, *Zhur. Fiz. Khim.*, 37 (1963) 197.
36 G. Davies, Ph. D. Thesis, Birmingham, England, 1966.
37 R. I. Agladze and N. I. Kharabadze, *Electrokhim. Marguntsa. Akad. Nauk Gruzin. SSSR*, 1 (1957) 297.
38 A. Ríus, E. J. Baltá and M. Beltrán, *Anales fis. y. quim*, 40 (1944) 14.
39 W. A. Andreae, *Arch. Biochem. and Biophys.*, 55 (1955) 584.
40 M. S. Venkatachalapathy, R. Ramaswamy and H. V. K. Udupa, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, 8 (1960) 361.
41 I. Tsubaki, *Bunseki Kagaku*, 8 (1959) 318.
42 P. Desideri, *J. Electroanalyt. Chem.*, 4 (1962) 359; *ibid.*, 6 (1963) 344.
43 H. Taube, personal communication of unpublished results, 1968.
44 O. Holmes and D. S. McClure, *J. Chem. Phys.*, 26 (1957) 1686; D. S. McClure, *Solid State Physics*, Vol. 9, F. Seitz and D. Turnbull, Ed., Academic Press, Inc., New York, N.Y., 1959.
45 A. D. Liehr, *Progr. Inorg. Chem.*, 3 (1962) 281.
46 C. K. Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Addison-Wesley, Reading, Mass., U.S.A., 1962.
47 C. F. Wells, *Nature*, 205 (1965) 693.
47a J. Y. Welsh, *Electrochem. Technol.*, 5 (1967) 504.
48 J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, 53 (1957) 800; M. Anbar and I. Pecht, *J. Amer. Chem. Soc.*, 89 (1967) 2553.
49 H. Wendt, *Z. Elektrochem.*, 66 (1962) 235.
50 R. A. Marcus, *J. Phys. Chem.*, 67 (1963) 853.
51 D. R. Rosseinsky and M. J. Nicol, *Trans. Faraday Soc.*, 64 (1968) 2410.
52 G. Dulz and N. Sutin, *Inorg. Chem.*, 2 (1963) 917.
53 M. H. Ford-Smith and N. Sutin, *J. Amer. Chem. Soc.*, 83 (1961) 1830.
54 S. Fukushima and W. L. Reynolds, *Talanta*, 11 (1964) 283; (*c.f.* ref. 56).
55 D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc.*, (A), (1968) 1022.
56 J. Silverman and R. W. Dodson, *J. Phys. Chem.*, 56 (1952) 846.
57 T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37 (1962) 307.
58 H. Taube, *J. Amer. Chem. Soc.*, 70 (1948) 1216, 3928.
59 J. A. Ibers and N. Davidson, *ibid.*, 72 (1950) 4744.
60 (a) C. F. Wells, D. Mays and C. Barnes, *J. Inorg. Nucl. Chem.*, 30 (1968) 1341; (b) C. F. Wells and C. Barnes, *J. Chem. Soc.* (A), (1968) 1626.
61 C. F. Wells and D. Mays, *J. Chem. Soc.* (A), (1968) 577.
62 A. J. Fudge and K. W. Sykes, *ibid.*, (1952) 119; K. W. Sykes, *ibid.*, (1952) 124.
63 E. L. King and M. L. Pandow, *J. Amer. Chem. Soc.*, 75 (1953) 3063.
64 C. F. Wells and D. Mays, *J. Chem. Soc. (A)*, (1968) 1622.

65 G. Davies, L. J. Kirschenbaum and K. Kustin, submitted to *Inorg. Chem.*

66 It is interesting that variations of [Co^{II}] have no effect on the rate of the Co^{III}-HN_3 reaction, (R. K. Murmann, J. C. Sullivan and R. C. Thompson, *Inorg. Chem.*, 7 (1968) 1876. This presumably indicates the absence of a back reaction and appreciable interference from Co^{II}-azide complexation for this reaction, as found for the analogous reaction with Mn^{III} at low azide concentrations.

67 N. Sutin, *Ann. Revs. Phys. Chem.*, 17 (1966) 119.

68 B. H. J. Bielski and A. O. Allen, *Proc. Second Tihany Symp. Radiation Chem., Akad. Kiado*, Budapest, 1967, p. 81; K. Sehested, O. L. Rasmussen and H. Fricke, *J. Phys. Chem.*, 72 (1968) 626; H. Taube, *J. Amer. Chem. Soc*, 64 (1942) 2468.

69 G. Czapski, B. H. J. Bielski and N. Sutin, *J. Phys. Chem.*, 67 (1963) 201.

70 G. Davies and K. Kustin, *Inorg. Chem.*, 8 (1969) in press.

71 G. Davies and K. Kustin, *J. Phys. Chem.*, 73 (1969) in press.

72 G. Davies and K. Kustin, *Trans. Faraday Soc.*, 65 (1969) in press.

73 W. T. Dixon, R. O. C. Norman and A. L. Buley, *J. Chem. Soc.*, (1964) 3625; W. T. Dixon and R. O. C. Norman, *ibid.*, (1964) 4850.

74 C. F. Wells and G. Davies, *Trans. Faraday Soc.*, 63 (1967) 2737.

75 C. F. Wells, *ibid.*, 61 (1965) 2194; 62 (1966) 2815.

76 N. Sutin, *Accts. Chem. Res.*, 1 (1968) 225.

77 R. Fuoss, *J. Amer. Chem. Soc.*, 80 (1958) 5059; M. Eigen, *Z. physik. Chem.*, 1 (1954) 176.

78 T. J. Connochiolli, G. H. Nancollas and N. Sutin, *Inorg. Chem.*, 5 (1966) 1.

79 (a) J. Hill and A. McAuley, *J. Chem. Soc. (A)*, (1968) 1169; (b) *idem.*, *ibid.*, (1968) 2405. Data at 7° and $\mu = 0.25$ M.

80 J. H. Baxendale, H. R. Hardy and L. H. Sutcliffe, *Trans. Faraday Soc.*, 47 (1951) 963; J. H. Baxendale and H. R. Hardy, *ibid.*, 50 (1954) 808.

81 E. E. Genser, Ph.D. Thesis, University of California, Berkeley, 1962.

82 G. Davies and K. Kustin, submitted to *Inorg. Chem.*

83 N. Tanaka, T. Shirakashi and H. Ogino, *Bull. Chem. Soc. Japan*, 38 (1965) 1515.

84 M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, 6 (1967) 2150.

85 C. H. Cartledge, *J. Amer. Chem. Soc.*, 73 (1951) 4416.

86 R. Dingle, *Acta Chem. Scand.*, 20 (1966) 13.

87 T. S. Davis, J. P. Fackler Jr. and M. J. Weeks, *Inorg. Chem.*, 7 (1968) 1994.

87a I. Bernal, N. Elliot and R. A. Lalancette, to be published; *Abstract G14, Proc. XIth Intern. Conf. Coord. Chem., Haifa, Israel, 1968*, M. Cais, Ed., Elsevier, Amsterdam, 1968. p. 518.

88 R. E. Hamm, personal communication, 1968.

89 L. Sacconi, P. Paoletti and M. Ciampolini, *J. Chem. Soc.*, (1964) 5046.

90 S. Richards, B. Pederson, J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, 3 (1964) 27.

91 R. G. Wilkins and R. Yellin, *J. Amer. Chem. Soc.*, 89 (1967) 5496.

92 B. N. Figgis and J. Lewis, in *Modern Coordination Chemistry*, J. Lewis and R. G. Wilkins, Eds., Interscience Publishers, London, 1960, p. 407.

93 A. W. Adamson, *J. Phys. Chem.*, 56 (1952) 858.

94 A. W. Adamson, J. P. Welker and W. B. Wright, *J. Amer. Chem. Soc.*, 73 (1951) 4786; *cf.* A. G. MacDiarmid and N. F. Hall, *ibid.*, 76 (1954) 4222.

95 *Spectrophotometric Data*, International Union of Pure and Applied Chemistry, Butterworths, London, 1963 p. 327 *ff.*

96 G. Piccardi and R. Guidelli, *Ric. Sci.* 38 (1968) 46, *cf.* ref. 28.

97 V. M. Tarayan and M. G. Ekimyan, *Isv. Akad. Nauk Arm. SSR Khim Nauki*, 11 (1958) 23.

98 L. C. Jackson, *Proc. Roy. Soc.*, A140 (1933) 695.

99 N. Goldenberg, *Trans. Faraday Soc.*, 36 (1940) 847.

100 R. Norrestam, *Acta Chem. Scand.*, 21 (1967) 2871.

101 F. A. Cotton, *The Infra-red Spectra of Transition Metal Complexes*, in ref. 92, p. 382.