Coordination Chemistry Reviews, 135/136 (1994) 399–427

Oxidation reactions of mononuclear manganese(III) complexes

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(Received 12 April 1993; accepted 25 June 1993)

CONTENTS

ABSTRACT

This review encompasses the oxidation reactions of various manganese(III) coordinated molecules. The reactions have been categorized primarily with respect to the type of manganese(III) complexes. Emphasis has been given to the reactivity of the manganese(III) complexes derived from aminopolycarboxylic acids, acetylacetone, porphyrins, bipyridine and pyrophosphoric acid with various organic, inorganic and biochemical electron donors. Kinetic and mechanistic features associated with the interactions have been highlighted and analysed critically. The utility and scope of the catalytic oxidation of hydrocarbons and secondary amines by manganese(III) porphyrins are discussed at length.

1. INTRODUCTION

Manganese is considered to be an essential trace element, forming active sites of several metalloproteins such as pyruvate carboxylase, photosystem II, superoxide dismutase, diamine oxidase etc. [1]. In the photosynthetic process the

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0010-8545/94/$26.00

SSDI 0010-8545(93)00996-6

Mn^{II}–Mn^{III}–Mn^{IV} redox couple is believed to take part [2]. The superoxide dismutases are one of the best characterized manganese proteins [3–5], and contain only one Mn^{III} ion per subunit. Thus the application of manganese model systems is far reaching, and extensive studies of the coordination chemistry and reactivity of manganese(III) can provide useful insight into the functional role of this transition metal ion in biological systems. There have therefore been several reports in recent years on the kinetics of oxidation reactions involving mononuclear manganese(III) complexes. A review by Davies [6] appeared a long time ago, and this relates only to the reactivity of aquamanganese(III) species.

In view of the above observations, a review encompassing the redox reactivity of various manganese(III) coordinated molecules is timely. We attempt to categorize the reactions primarily with respect to the type of manganese(III) complex.

2. OXIDATION REACTIONS OF AMINOPOLYCARBOXYLATE COMPLEXES OF MANGANESE(III), [Mn^{III}(EDTA)]$^-$ AND [Mn^{III}(CDTA)]$^-$

A very large volume of work has appeared on the electron-transfer activity of the mononuclear aminopolycarboxylate complexes of manganese(III). The solid manganese(III) complex of ethylenediamine tetraacetic acid $[Mn^{III}(EDTA)]^-$ was synthesized and characterized by Yoshino et al. [7] in 1962. They found that this complex is unstable at room temperature and two forms of this complex exist in solution depending on the pH of the medium. An equilibrium was proposed to exist as

$$[Mn^{III}(EDTA)(H_2O)]^- \underset{}{\overset{K}{\rightleftharpoons}} [Mn^{III}(EDTA)(OH)]^{2-} + H^+ \qquad (1)$$

with a pK value of about 5.3.

The idea of seven-coordinate manganese is reasonable in the light of the crystallographic establishment [8] of the $[Mn^{II}(EDTA)(H_2O]^{2-}$ ion. The greater stability of the manganese(III) complex of *trans*-cyclohexane-1,2-diamine-$N,N,N'N'$-tetraacetic acid (CDTA) was explained by Day and Reilley [9] by the fact that the inflexibility of the cyclohexane ring makes it more difficult to move either of the acetate arms away from the metal ion. In 1967 Hamm and Suwyn [10] prepared this complex as $K[Mn^{III}(CDTA)]2.5H_2O$. An X-ray crystallographic study conducted by Rettig and Trotter [11] indicated a very distorted octahedron about Mn^{III} with two nitrogen and four oxygen atoms of the hexadentate ligand. The results of Karl–Fischer titrations indicate that one water molecule is bound sufficiently tightly to the manganese to remain coordinated even in solution.

The complex $[Mn^{III}(CDTA)]^-$ was stable at room temperature in the dark, and existed in two forms in aqueous solution [8]. The absorption spectrum of the complex in the pH range 2–7 showed a single broad peak at 510 nm ($\varepsilon = 345\ M^{-1}\ cm^{-1}$). In the pH range 7–10, the complex changes from pink to straw-yellow colour showing an absorption peak at 448 nm ($\varepsilon = 329\ M^{-1}\ cm^{-1}$). On addition of acid to the yellow species, it immediately reverts to the red species. The pK_m value between the red and yellow species was evaluated to be 8.10 ± 0.32 at 25°C, and represented by the equation

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

When the solution was raised to $pH > 11.0$, the complex decomposed into manganese(II) hydroxide and manganese(IV) oxide. In the pH range 3–6, the decomposition rate of the complex was found to be constant ($6.5 \times 10^{-6}\ s^{-1}$ at 25°C), and in the range pH 7–10 the specific rate of decomposition is $1.12 \times 10^{-4}\ s^{-1}$ at 30°C. The standard reduction potential of the couples $Mn(EDTA)^{2-}$–$Mn(EDTA)^-$ and $Mn(CDTA)^{2-}$–$Mn(CDTA)^-$ are reported to be 0.82 V and 0.81 V respectively and the couples are moderately strong oxidizing agents [8]. The following is an account of the large number of redox studies involving these complexes.

2.1. *Reactions with organic and non-metallic inorganic species*

Suwyn and Hamm reported the kinetics of oxidation of oxalate with $[Mn^{III}(CDTA)]^-$ [12] over the pH range 3.0–7.0 and the general rate law was fitted by the equation

$$-d[Mn^{III}(CDTA)^-]/dt = 2k_1[Mn^{III}(CDTA)^-][HC_2O_4^-] + 2k_2[Mn^{III}(CDTA)^-][C_2O_4^{2-}] \tag{3}$$

where k_1 and k_2 represent the reactivity of $HC_2O_4^-$ and $C_2O_4^{2-}$ respectively and the stoichiometry is given by the equation

$$2[Mn^{III}(CDTA)]^- + C_2O_4^{2-} \rightarrow 2[Mn^{II}(CDTA)]^{2-} + 2CO_2 \tag{4}$$

At 20°C the specific rate constants were determined to be $k_1 = 5.40 \times 10^{-3}\ M^{-1}\ s^{-1}$ and $k_2 = 7.08 \times 10^{-3}\ M^{-1}\ s^{-1}$ and experiments over a range of temperatures from 15 to 35°C gave $\Delta H_1^\ddagger = 87.4\ kJ\ M^{-1}$, $\Delta S_1^\ddagger = 14.6\ J\ K^{-1}\ M^{-1}$, $\Delta H_2^\ddagger = 66.9\ kJ\ M^{-1}$ and $\Delta S_2^\ddagger = -54.4\ J\ K^{-1}\ M^{-1}$. In this reaction the authors considered the slow step as the interaction of the two species, as no evidence for any relatively stable $[Mn^{III}(CDTA)(C_2O_4)]^{3-}$ species was gathered from spectroscopic studies and the involvement of any inner-sphere path was thereby ignored. This study does not throw any light on the reactivity of the $[Mn^{III}(CDTA)(OH)]^{2-}$ species formed at higher pH.

Poh and Stewart [13] have studied the composition and reactions of $[Mn^{III}(CDTA)]^-$ with methanol (2.5 vol.% water). They found a new form of the complex exists in methanol in the presence of excess acid, which has λ_{max} at 520 nm which is different from the value for the other two species $[Mn^{III}(CDTA)(H_2O)]^-$ ($\lambda_{max} = 510$ nm) and $[Mn^{III}(CDTA)(OH)]^{2-}$ ($\lambda_{max} = 448$ nm) in aqueous solution. This is believed to have the formula $HMn^{III}(CDTA)(H_2O)$, in which the protonation probably occurs at the unwrapped carboxylate arm of the CDTA ligand. In alkaline methanol the disappearance of complex with time is due to first-order decomposition of the complex by disproportionation and the following stoichiometric equation was valid:

$$2Mn^{III} + 4OH^- \rightarrow Mn^{II} + MnO_2 + 2H_2O \tag{5}$$

The first-order decomposition rate is $2.77 \times 10^{-4}\ s^{-1}$ at $[Mn^{III}]_0 = 5.4 \times 10^{-4}$ M, $[Me_4NOH] = 2.65 \times 10^{-2}$ M at 25°C. The corresponding activation parameters for the reaction are $\Delta H^{\ddagger} = 67 \pm 1\ kJ\ M^{-1}$ and $\Delta S^{\ddagger} = -63 \pm 6\ J\ K^{-1}\ M^{-1}$. When the same methanol solution is acidic, the disappearance of Mn^{III} is first order in both the complex and acid, but in this case methanol is oxidized to formaldehyde according to the equations

$$Mn^{III}p^- + H^+ \xrightleftharpoons{K_b} HMn^{III}p^0 \tag{6}$$

$$HMn^{III}p^0 + CH_3OH \xrightarrow{k} Mn^{II} + CH_3\dot{O} \tag{7}$$

$$Mn^{III} + CH_3\dot{O} \xrightarrow{fast} Mn^{II} + CH_2O \tag{8}$$

where $Mn^{III}p^- = [Mn^{III}(CDTA)(H_2O)]^-$ and $HMn^{III}p^0 = [HMn^{III}(CDTA)(H_2O)]$.

The small (1.25 or less) isotope effect observed in the oxidation of CH_3OD, CD_3OH and CD_3OD together with the acid dependence indicate that the oxidation proceeds by rate-controlling electron abstraction from methanol by the protonated form of the complex, possibly by an intermediate in which one of the coordinating ligands is replaced by methanol. $HMn^{III}(CDTA)(H_2O)$ is a more powerful oxidant than $[Mn^{III}(CDTA)(H_2O)]^-$. The pseudo-first-order rate constant for the slow disappearance of the latter in methanol is $2.24 \times 10^{-6}\ s^{-1}$ at 25°C, close to the reported decomposition rate of $[Mn^{III}(CDTA)(H_2O)]^-$ in water ($6.8 \times 10^{-6}\ s^{-1}$ at 25°C). This result still does not explain whether this slow disappearance in methanol is due to oxidation of methanol or simply the decomposition of the complex.

An extension of the above work was carried out by Stewart and Poh [14] on the oxidation of a series of hindered phenols, such as 4-substituted 2,6-di-*t*-butylphenols with $[Mn^{III}(CDTA)(H_2O)]^-$ in methanol containing 2.5 vol.% water. The rate of disappearance of $[Mn^{III}(CDTA)]^-$ was expressed as

$$-d[Mn^{III}(CDTA)^-]_{tot}/dt = k'[Mn^{III}(CDTA)^-]_{tot} \tag{9}$$

Addition of either acid or base causes a drastic increase in the reaction rate and the reactions in acidic methanol were represented as

$$Mn^{III}p^- + H^+ \xrightleftharpoons{K_b} HMn^{III}p^0 \tag{10}$$

$$HMn^{III}p^0 + CH_3OH \rightarrow CH_3\dot{O} + Mn^{II} \tag{11}$$

$$HMn^{III}p^0 + ArOH \rightarrow Ar\dot{O} + Mn^{II} \tag{12}$$

$$CH_3\dot{O} + Mn^{III} \xrightarrow{\text{fast}} CH_2O + Mn^{II} \tag{13}$$

$$CH_3\dot{O} + ArOH \xrightarrow{\text{fast}} CH_3OH + Ar\dot{O} \tag{14}$$

In the proposed mechanism, 2,4,6-tri-*t*-butyl-phenol and the Mn^{III} complex compete for the methoxy radical. When the concentration of the phenol is very small or near to zero, the methoxy radicals are essentially oxidized to formaldehyde (eqn. (13)), hence a second mole of Mn^{III} is reduced. A small amount of added phenol hinders the methoxy radical, giving methanol and inert aryloxy radicals (eqn. (14)) and thus reduction of Mn^{III} is slowed. When the concentration of added phenol is increased, the reaction rate rises as a function of phenol concentration as eqn. (12) becomes dominant. Hence a plot of k' *vs.* concentration of 2,4,6-tri-*t*-butyl-phenol showed a minimum at a certain concentration of the phenol. The acceleration of rate in base is due to production of both $[Mn^{III}(CDTA)(OH)]^{2-}$ and phenolate ions which are considered to be a more active oxidant and reductant respectively. In this solution $[Mn^{III}(CDTA)(OH)]^{2-}$ converts the hindered phenols to aryloxy radicals, some of which are stable and others undergo further reaction. The greater reactivity of $[Mn^{III}(CDTA)(OH)]^{2-}$ is rather surprising in view of later studies where its inactive nature towards electron transfer has been firmly established. The large substituent effect in basic solution probably originates from the greater degree of ionization of the different phenols.

Giraudi and Mentasti [15] carried out a kinetic and mechanistic investigation on the oxidation of 1,4-dihydroxybenzene (H_2Q), 2,5-dihydroxy-benzenesulphonic acid (H_2SQ) and 4,5-dihydroxy-1,3-benzenesulphonic acid (H_2T) to the corresponding *ortho*- and *para*-quinones by $[Mn^{III}(EDTA)(H_2O)]^-$ by stopped-flow spectrophotometry in the pH range 2.5–6.0 at 20°C. A general inner-sphere reaction scheme for the oxidation of dihydroxybenzenes (H_2L) by $[Mn^{III}(EDTA)]^-$ was given as in the equations

$$[Mn^{III}(EDTA)]^- \overset{K_a}{\rightleftharpoons} [Mn^{III}(EDTA)]^{2-} + H^+ \tag{15}$$

$$[Mn^{III}(EDTA)]^- + H_2L \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Mn^{III}(EDTA), H_2L]^- \tag{16}$$

$$[Mn^{III}(EDTA), H_2L]^- \xrightarrow{k_3} [Mn^{II}(EDTA)]^{2-} + H\dot{L} + H^+ \tag{17}$$

$$[\mathrm{Mn^{III}(EDTA)}]^- + \mathrm{H\dot{L}} \xrightarrow{\text{fast}} [\mathrm{Mn^{II}(EDTA)}]^{2-} + \text{quinones} + \mathrm{H^+} \tag{18}$$

In the oxidation of H_2Q, k_2 and k_3 are found to be comparable at $2.5 \leqslant \mathrm{pH} \leqslant 4.5$ and a complex kinetic behaviour results, while at $\mathrm{pH} \geqslant 5.0$ the $\mathrm{Mn^{III}}$ complex disappearance is separated into two successive stages (the first of which was nearly complete within the dead time of the stopped-flow apparatus). The rate expression corresponding to the reactions (15)–(18) with reaction (16) as the rate-determining step is

$$-\mathrm{d}[\mathrm{Mn^{III}(EDTA)^-}]/\mathrm{d}t = \frac{2k_1k_3k_2^{-1}[\mathrm{H_2Q}][\mathrm{Mn^{III}(EDTA)^-}]}{1+k_1k_2^{-1}[\mathrm{H_2Q}]+K_\mathrm{a}[\mathrm{H^+}]^{-1}} \tag{19}$$

In the oxidation of H_2SQ and H_2T, strict first-order dependence on both the oxidant and reductant concentrations was noted and the reaction scheme was given as the same as in H_2Q oxidation (eqns. (15)–(18)) with the exception that, in H_2T, the second-order rate constant k was found to be inversely dependent on $[\mathrm{H^+}]$ which accounts for the concomitant release of one proton through reaction (16) leading to the rate expression

$$k_\mathrm{obs} = \frac{2k_1k_3k_2^{-1}[\mathrm{H^+}]^{-1}[\mathrm{H_2T}][\mathrm{Mn^{III}(EDTA)^-}]}{1+k_1k_2^{-1}[\mathrm{H^+}]^{-1}[\mathrm{H_2T}]+K_\mathrm{a}[\mathrm{H^+}]^{-1}} \tag{20}$$

with $k = 2k_1k_3k_2^{-1}[\mathrm{H^+}]^{-1}$.

The occurrence of an inner-sphere mechanism for the oxidation of H_2Q, H_2SQ and H_2T by the labile oxidant $[\mathrm{Mn^{III}(EDTA)}]^-$ was suggested from the kinetic behaviour and non-applicability of the Marcus cross-relation in evaluating the electron-transfer rate. This showed a difference of about three orders of magnitude between the computer (lower) and experimental (higher) values of H_2T. This comparison for H_2Q is not impressive. A concomitant partial EDTA unwrapping on an $\mathrm{Mn^{III}}$ centre and a proton release for the bidentate H_2T, and a simple coordination with an intramolecular proton rearrangement for the other substrates (monodentate) was thought to be one of the causes for the occurrence of an inner-sphere mechanism. As can be seen below, these expectations could only be verified through a rapid-scan spectrum on mixing the reactants.

In a related study by the same group [16] on the reduction of $[\mathrm{Mn^{III}(CDTA)(H_2O)}]^-$ by a series of substituted benzene-1,2-diols, namely benzene-1,2-diol (H_2L^1), 4-methyl-benzene-1,2-diol (H_2L^2), 3,4-dihydroxybenzoic acid (H_2L^3) and 2,3-dihydroxy benzoic acid (H_2L^4), an inner-sphere mechanism through the intermediate association was proposed. A very different dependence of rate on the oxidation of diols on acidity was noted and it accounted for the increased acidity of the substituted derivatives $L^2 < L^1 < L^3 \approx L^4$ with pK_a 11.0, 10.0, 9.0 and 9.0 respectively. H_2L^2 showed that the second-order rate k was independent of acidity, whereas an inverse dependence on acidity was encountered for H_2L^3 and H_2L^4 and intermediate behaviour was observed for H_2L^1. A general inner-sphere mechanism was proposed as

$$[\mathrm{Mn^{III}(CDTA)(H_2O)}]^- + \mathrm{H_2L} \xrightleftharpoons{K_{\mathrm{ass}}} \text{intermediate} \qquad (21)$$

$$\text{intermediate} \xrightarrow{k_{\mathrm{et}}} [\mathrm{Mn^{II}(CDTA)}]^{2-} + \text{semiquinone} \qquad (22)$$

$$\text{semiquinone} + [\mathrm{Mn^{III}(CDTA)}]^- \xrightarrow{\text{fast}} [\mathrm{Mn^{II}(CDTA)}]^{2-} + \text{orthoquinone} \qquad (23)$$

The dependence of acidity involves the release of a proton in the association step. The fact that the second-order rate k was independent of acidity for the oxidation of H_2L^2 could be interpreted in terms of a purely outer-sphere mechanism. However, an inner-sphere mechanism for its oxidation was supported by testing the non-applicability of the Marcus cross-relation which showed a much higher experimental rate ($k_{\mathrm{et}} \geqslant 5.4 \times 10^3\ \mathrm{M^{-1}\,s^{-1}}$) than the computed value ($13\ \mathrm{s^{-1}}$). For the H_2L^4 oxidation, an inner-sphere mechanism is preferred over the outer-sphere one, on the grounds of a higher value of K_{ass} (6.2×10^2 M) and explained by the presence of acidic –COOH group ($\mathrm{p}K_\mathrm{a} = 3.0$–$3.50$) which would exert an electrostatic repulsion on the anionic oxidizing agent. For the parent compound (H_2L^1) limited data preclude any mechanistic delineation.

The kinetics of electron-transfer reactions of $[\mathrm{Mn^{III}(CDTA)}]^-$ with ascorbic acid have been studied in the acid range (1.00×10^{-5})–(3.16×10^{-3}) M at different temperatures and at a constant ionic strength by Gangopadhyay et al. [17]. Both the molecular (H_2A) and monoanionic (HA^-) forms of ascorbic acid were found to be reactive in the experimental range of acidity and to follow the rate law

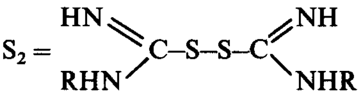
$$-\mathrm{d}[\mathrm{Mn^{III}}]/\mathrm{d}t = 2\,\frac{(k_1[\mathrm{H^+}] + k_2K_\mathrm{a})[\mathrm{A_T}][\mathrm{Mn^{III}}]}{K_\mathrm{a} + [\mathrm{H^+}]} \qquad (24)$$

The values of rate parameters evaluated are $k_1 = (1.37 \pm 0.10) \times 10^5\ \mathrm{M^{-1}\,s^{-1}}$ and $k_2 = (8.72 \pm 0.14) \times 10^5\ \mathrm{M^{-1}\,s^{-1}}$ at 28°C. Attempts were made to correlate the kinetic results in terms of the Marcus relationship for an outer-sphere electron-transfer reaction. The calculated $k_{\mathrm{OS(H_2A)}}$ ($6.15 \times 10^{-3}\ \mathrm{M^{-1}\,s^{-1}}$) and $k_{\mathrm{OS(HA^-)}}$ ($1.02 \times 10^2\ \mathrm{M^{-1}\,s^{-1}}$) at 20°C are significantly lower (10^7 times and four orders of magnitude respectively) than the experimental values and therefore the suggestion of an inner-sphere mechanism seems justified.

Kinetics of the reduction of $[\mathrm{Mn^{III}(CDTA)}]^-$ by some thiourea (TU) reductants (phenyl thiourea, methyl thiourea, TU and allyl thiourea) have been studied in the pH ranges 2.50–4.50 and 9.20–10.20 by Gangopadhyay et al. [18]. The reactions are first order in both oxidant and reductant. In the acid medium, a preliminary stopped-flow reaction trace showed an initial rise in absorbance followed by a steady decay with time, suggestive of the formation of a precursor complex prior to electron transfer and mechanistically interpreted as in the equations

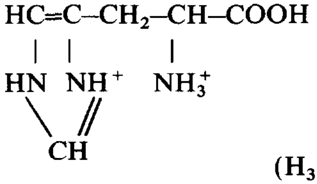
$$\mathrm{Mn^{III}} + \mathrm{S} \overset{K}{\rightleftharpoons} [\mathrm{Mn^{III}.S}] \xrightarrow[\text{slow}]{k'} \mathrm{Mn^{II}} + \dot{\mathrm{S}} \tag{25}$$

$$\dot{\mathrm{S}} + \dot{\mathrm{S}} \xrightarrow{\text{fast}} \mathrm{S_2} \tag{26}$$



where S_2 denotes the disulphide product. The interesting observations particularly featured in this study are that the reaction rates for *N*-allyl thiourea (ATU), *N*-methyl thiourea (MTU), TU and *N*-phenyl thiourea (PTU) are faster in alkaline medium than in acid medium in contrast to the previously reported results [19]. This has been explained by the higher reactivity of the hydroxo species of the complex than the aqua species, and reactivity of the former is consistent with the formation of a ligand-bridged activated species prior to electron transfer. In acid medium, the precursor complex formation takes place either by substitution of the aqua ligand or through the partial unwrapping of one carboxylate arm of CDTA. The reactivity order (PTU > TU > MTU > ATU) for the thiourea derivatives follows the order of their reported substituent effects (PTU > TU > MTU).

A series of kinetic investigations have been made by the same group of authors [20–22], involving the reduction of $[\mathrm{Mn^{III}(CDTA)}]^-$ with (a) simple carboxylates such as formate and malonate, (b) some amine-*N*-polycarboxylic acids such as iminodiacetic acid (H_2ida), nitrilotriacetic acid (H_3nta) and ethylenediaminetetraacetic acid (H_4EDTA), and (c) amino acid, histidine (H_3L^{2+})



(H_3L^{2+})

All the reactions are first order in both oxidant and reductant concentrations and follow the general rate law

$$-\mathrm{d}[\mathrm{Mn^{III}}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{Mn^{III}}] = \{k_\mathrm{d} + nk_\mathrm{s}[\mathrm{R}]\}[\mathrm{Mn^{III}}] \tag{27}$$

where k_d denotes the autodecomposition rate of the complex and k_s the electron transfer rate, R is the reductant irrespective of the nature and type of the reacting species and n is the stoichiometric factor. The complex $[\mathrm{Mn^{III}(CDTA)}]^-$ has been found to show an interesting behaviour in acidic and alkaline media.

In the oxidation of formate (pH 3.60–5.25) and malonate (pH 4.50–8.30) [20], a slight initial increase in absorbance was encountered for the formate reaction alone.

A plausible inner-sphere mechanism has been invoked for the formate oxidation whereas the corresponding malonate oxidation seems to follow an outer-sphere path, and is supported by the applicability of a Marcus-type cross-relation. The pH rate profile for malonate oxidation is a bell-shaped curve, the consistent analysis of which affords the reactivities of $Hmal^-$ and mal^{2-} towards $[Mn^{III}(CDTA)(H_2O)]^-$, where mal = malonate.

The oxidation of nitrilotriacetic acid, EDTA [21] and histidine [22] follows mechanistic features similar to those encountered in the malonate oxidation. In all these studies, a plot of k $(=(k_{obs}-k_d)/n[R])$ *vs.* pH showed an initial increase in rate, attained a maximum and then decreased, yielding the bell-shaped curves. This type of behaviour was explained by considering the hydroxo form of the complex $[Mn^{III}(CDTA)(OH)]^{2-}$ to be unreactive towards the reductants on the basis that on deprotonation the formal electrode potential of the complex decreases significantly. Taking $[Mn^{III}(CDTA)(H_2O)]^-$ as the sole reacting species of the complex, a representative reaction scheme for the oxidation of H_4EDTA could be framed by the following equations:

$$H_3EDTA^- \overset{K_2}{\rightleftharpoons} H_2EDTA^{2-} + H^+ \qquad K_2 = 2.14 \times 10^{-4}\ M \tag{28}$$

$$H_2EDTA^{2-} \overset{K_3}{\rightleftharpoons} HEDTA^{3-} + H^+ \qquad K_3 = 6.92 \times 10^{-7}\ M \tag{29}$$

$$HEDTA^{3-} \overset{K_4}{\rightleftharpoons} EDTA^{4-} + H^+ \qquad K_4 = 5.50 \times 10^{-11}\ M \tag{30}$$

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

$$K_m = 7.76 \times 10^{-9}\ M \tag{2}$$

$$[Mn^{III}(CDTA)(H_2O)]^- + H_3EDTA^- \xrightarrow{k_1} [Mn^{II}(CDTA)(H_2O)]^{2-} + \text{free radical} \tag{31}$$

$$[Mn^{III}(CDTA)(H_2O)]^- + H_2EDTA^{2-} \xrightarrow{k_2} [Mn^{II}(CDTA)(H_2O)]^{2-} + \text{free radical} \tag{32}$$

$$[Mn^{III}(CDTA)(H_2O)]^- + HEDTA^{3-} \xrightarrow{k_3} [Mn^{II}(CDTA)(H_2O)]^{2-} + \text{free radical} \tag{33}$$

$$[Mn^{III}(CDTA)(H_2O)]^- + EDTA^{4-} \xrightarrow{k_4} [Mn^{II}(CDTA)(H_2O)]^{2-} + \text{free radical} \tag{34}$$

$$[\mathrm{Mn^{III}(CDTA)(H_2O)}]^- + \text{free radical} \xrightarrow{\text{fast}} [\mathrm{Mn^{II}(CDTA)}]^{2-} + \text{products} \tag{34a}$$

and the corresponding rate equation was given as

$$k_{\mathrm{ox}} = \frac{k_{\mathrm{obs}} - k_{\mathrm{d}}}{2[\mathrm{EDTA}]_{\mathrm{t}}} = \frac{(k_1[\mathrm{H}^+]^3 + k_2K_2[\mathrm{H}^+]^2 + k_3K_2K_3[\mathrm{H}^+] + k_4K_2K_3K_4)}{([\mathrm{H}^+]^3 + K_2[\mathrm{H}^+]^2 + K_2K_3[\mathrm{H}^+] + K_2K_3K_4)} \frac{[\mathrm{H}^+]}{[\mathrm{H}^+] + K_{\mathrm{m}}} \tag{35}$$

The rate parameters were evaluated by choosing a suitable pH region where the particular type of reacting species are available. For example, in the pH region 3.30–4.0, the k_1 and k_2 paths are operative ($k_2 = 2.14 \times 10^{-4}\ \mathrm{M^{-1}\,s^{-1}}$) which leads to the rate law

$$k_{\mathrm{ox}} = \frac{k_1[\mathrm{H}^+] + k_2K_2}{K_2 + [\mathrm{H}^+]} \tag{36}$$

In the pH region 5.0–6.8, the k_2 and k_3 paths are operative and the rate becomes

$$k_{\mathrm{ox}} = \frac{k_2[\mathrm{H}^+] + k_3K_3}{K_3 + [\mathrm{H}^+]} \tag{37}$$

Both these reactions were solved by employing a suitable non-linear computer-fit least-squares program. However, in the range of pH 7.5–9.5, the k_3 and k_4 paths and the K_{m} equilibrium process are operative and this leads to the rate expression

$$k_{\mathrm{ox}} = \frac{(k_3[\mathrm{H}^+] + k_4K_4)}{([\mathrm{H}^+] + K_4)} \cdot \frac{[\mathrm{H}^+]}{(K_{\mathrm{m}} + [\mathrm{H}^+])} \tag{38}$$

taking $[\mathrm{Mn^{III}(CDTA)(OH)}]^{2-}$ as unreactive. Equation (38) was solved by employing a simplex optimization program where a best fit of the experimental data was obtained by varying K_3, K_4 and K_{m} and keeping the other parameters constant. In a similar fashion other reactions of $\mathrm{H_3L^{2+}}$ were solved. The feature of these studies is that the proton dissociation constants were evaluated directly from the kinetic data which showed an excellent matching with the reported values. Another striking feature of these studies is that the complex $[\mathrm{Mn^{III}(CDTA)}]^-$ showed an interesting behaviour in acidic and alkaline medium towards the iminodiacetic acid ($\mathrm{H_2IDA}$). Contrary to the other oxidations, here both the aqua and hydroxo forms of the complex are reactive, and explained by considering an inner-sphere mechanism. This inner-sphere mechanism has been duly supported by comparing the rate data with those obtained for the oxidation of iminodiacetate by an established other-sphere oxidant, dodecatungstocobaltate(III) ($[\mathrm{Co^{III}W_{12}O_{40}}]^{5-}$). In other reactions, the deprotonated species of the reductant have been found to be more reactive than the corresponding protonated species and a possible explanation was suggested that on deprotonation the reduction potential changes. In the oxidation of histidine the reactivity was found to follow the order $H_2L^+ < HL < L^-$ and was explained by considering the inductive effects of the protonated and deprotonated imidazole ring and $-NH_2$ group. In this study it has been suggested from the product analysis that the reactions proceed through C–H bond fission on the α-C atom leading to β-imidazolyl pyruvic acid as the reaction product. The formation of a radical intermediate has been established through electron paramagnetic resonance (EPR) measurements.

A kinetic and equilibrium study of the reaction between $[Mn^{III}(EDTA)(H_2O)]^-$ and azide was carried out by Suwyn and Hamm [23]. These species react to form $[Mn^{III}(EDTA)(N_3)]^{2-}$ with a formal equilibrium constant of 32.1 M^{-1} at 25°C ($I = 0.25$ M). The azide complex has been recovered as the potassium salt, and the manganese(III) complex is inferred to be seven coordinate on the basis of IR spectroscopic study. In solution this decomposes by an electron-transfer step yielding $[Mn^{II}(EDTA)(H_2O)]^{2-}$ and dinitrogen. The kinetic results are compatible with the following sequence of reactions:

$$[Mn^{III}(EDTA)(H_2O)]^- + N_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mn^{III}(EDTA)(N_3)]^{2-} + H_2O \tag{39}$$

$$[Mn^{III}(EDTA)(N_3)]^{2-} \xrightarrow{k_2} [Mn^{II}(EDTA)(H_2O)]^{2-} + \dot{N}_3 \tag{40}$$

$$2\dot{N}_3 \xrightarrow{k_r} 3N_2 \tag{41}$$

The proposed scheme seems justified since the k_1 and k_{-1} values calculated are in good agreement with the equilibrium constant determined by an independent method. The thermodynamic values for reaction (39) have also been calculated in two ways: (i) from the equilibrium constants of the reactions at various temperatures, and (ii) from the activation parameters of the forward and backward reactions. The agreement between the two sets of values is considered to fit the proposed mechanism.

The reduction of $[Mn^{III}(CDTA)(H_2O)]^-$ by hydrogen peroxide was studied [24] in the concentration ranges $[H_2O_2] = (5.6\text{–}80.0) \times 10^{-3}$ M, $[Mn^{II}(CDTA)(H_2O)^{2-}]^{2-} = (0\text{–}18.2) \times 10^{-3}$ M, $[H^+] = (1.6\text{–}120) \times 10^{-4}$ M. The reaction was found to follow the rate law

$$-\frac{d[Mn^{III}(CDTA)(H_2O)^-]}{dt} = \frac{2Kk_1k_2[Mn^{III}(CDTA)(H_2O)^-]^2[H_2O_2]}{k_{-1}[H^+][Mn^{II}(CDTA)^{2-}] + k_2[H^+][Mn^{III}(CDTA)^-]} \tag{42}$$

and an inner-sphere mechanism consistent with the above rate law was proposed as

$$[Mn^{III}(CDTA)(OH_2)]^- + H_2O_2 \overset{K}{\rightleftharpoons} [Mn^{III}(CDTA)(O_2H)]^{2-} + H_2O + H^+ \tag{43}$$

$$[\mathrm{Mn^{III}(CDTA)(O_2H)}]^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Mn^{II}(CDTA)}]^{2-} + \mathrm{H\dot{O}_2} \tag{44}$$

$$[\mathrm{Mn^{III}(CDTA)(OH_2)}]^{-} + \mathrm{H\dot{O}_2} \xrightarrow{k_2} [\mathrm{Mn^{II}(CDTA)(OH_2)}]^{2-} + \mathrm{O_2} + \mathrm{H^+} \tag{45}$$

with $2Kk_1k_2/k_{-1} = 2.71 \times 10^{-3}\ \mathrm{s^{-1}}$ and $k_2/k_{-1} = 2.63$. No direct evidence in favour of an inner-sphere association could be gathered, and an alternative outer-sphere route following the same rate law was attempted as

$$\mathrm{H_2O_2} \overset{K_a}{\rightleftharpoons} \mathrm{H^+} + \mathrm{O_2H^-} \qquad K_a = 5.4 \times 10^{-12}\ \mathrm{M} \tag{46}$$

$$[\mathrm{Mn^{III}(CDTA)(OH_2)}]^{-} + \mathrm{HO_2^-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Mn^{II}(CDTA)(OH_2)}]^{2-} + \mathrm{\dot{O}_2H} \tag{47}$$

$$[\mathrm{Mn^{III}(CDTA)(OH_2)}]^{-} + \mathrm{HO_2} \xrightarrow{k_4} [\mathrm{Mn^{II}(CDTA)(OH_2)}]^{2-} + \mathrm{O_2} + \mathrm{H^+} \tag{48}$$

with $k_3 \approx 1.0 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$ which does not exceed the diffusion rate ($4.4 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$). However, since the reported rate constants for the oxidation by $[\mathrm{Mn^{III}(CDTA)(H_2O)}]^-$ and $[\mathrm{Mn^{III}(EDTA)(H_2O)}]^-$ are much smaller than the rate constant for water exchange, the inner-sphere path is more justified.

A complex kinetic behaviour in the oxidation of nitrite by $[\mathrm{Mn^{III}(CDTA)}]^-$ was noted by Jones and Hamm [25] following the rate law

$$-\frac{\mathrm{d}[\mathrm{Mn^{III}(CDTA)^-}]}{\mathrm{d}t} = \frac{k_a[\mathrm{Mn^{III}(CDTA)^-}]^2[\mathrm{NO_2^-}]^2}{k_b[\mathrm{Mn^{II}(CDTA)^{2-}}]^2 + [\mathrm{Mn^{II}(CDTA)^{2-}}]} \tag{49}$$

in the ranges $[\mathrm{Mn^{III}(CDTA)^-}]_0 = (1.9\text{–}13) \times 10^{-4}\ \mathrm{M}$, $[\mathrm{NO_2^-}] = (5.0\text{–}51) \times 10^{-3}\ \mathrm{M}$, and $[\mathrm{Mn^{II}(CDTA)^{2-}}] = (5.0\text{–}24) \times 10^{-3}\ \mathrm{M}$. The stoichiometric equation is given by

$$2[\mathrm{Mn^{III}(CDTA)(H_2O)}]^- + \mathrm{NO_2^-} + \mathrm{H_2O} \rightarrow 2[\mathrm{Mn^{II}(CDTA)(H_2O)}]^{2-} + \mathrm{NO_3^-} + 2\mathrm{H^+}$$

The results reported in this study appear to be unique in that the reaction is second order in metal ion oxidant and independent of pH. A second-order dependence in nitrite or nitrous acid has been explained by a mechanism described by the following equations which involves $\mathrm{N_2O_4}$ as an intermediate with hydrophilic dismutation of this intermediate as the last slow step (this also explains the lack of hydrogen ion dependence in the rate law):

$$[\mathrm{Mn^{III}(CDTA)(H_2O)}]^- + \mathrm{NO_2^-} \overset{K_1}{\rightleftharpoons} [\mathrm{Mn^{III}(CDTA)(NO_2)}]^{2-} + \mathrm{H_2O} \tag{51}$$

$$2[\mathrm{Mn^{III}(CDTA)(NO_2)}]^{2-} + \mathrm{H_2O} \underset{}{\overset{K_2}{\rightleftharpoons}} [\mathrm{Mn^{II}(CDTA)(OH_2)}]^{2-} + [\mathrm{Mn^{III}(CDTA)(N_2O_4)}]^{2-} \quad (52)$$

$$[\mathrm{Mn^{III}(CDTA)(N_2O_4)}]^{2-} + \mathrm{H_2O} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Mn^{II}(CDTA)(OH_2)}]^{2-} + \mathrm{N_2O_4} \quad (53)$$

$$\mathrm{N_2O_4} + \mathrm{H_2O} \xrightarrow{k_3} \mathrm{NO_2^-} + \mathrm{NO_3^-} + 2\mathrm{H^+} \quad (54)$$

The rate law can be deduced assuming a steady state approximation for N_2O_4, and $k_a = K_1^2 K_2 k_1$ and $k_b = k_2/k_3$. An independent determination of k_3 reports it to be $1.0 \times 10^3\ \mathrm{s^{-1}}$, and k_2 is thereby estimated to be $2.7 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$ from the experimental value of k_b. The rate of water exchange k_{ex} for $[\mathrm{Mn^{III}(EDTA)(H_2O)}]^-$ is reported to be $4.4 \times 10^8\ \mathrm{s^{-1}}$ and the corresponding rate for $[\mathrm{Mn^{III}(CDTA)(H_2O)}]^-$ is found to be similar to this. Since the value of k_2 is about 10^3 times smaller than k_{ex}, it is more likely that the intermolecular electron transfer is rate determining for that step.

The general reaction scheme for the oxidation of dithionite by metal ion oxidants follows the sequence

$$\mathrm{S_2O_4^{2-}} \overset{K_1}{\rightleftharpoons} 2\mathrm{SO_2^-} \quad (55)$$

$$\text{oxidant} + \mathrm{S_2O_4^{2-}} \xrightarrow{k_2} \text{reduced species} + \mathrm{S^{IV}} \quad (56)$$

$$\text{oxidant} + \mathrm{SO_2^-} \xrightarrow{k_3} \text{reduced species} + \mathrm{S^{IV}} \quad (57)$$

and

$$k_{obs} = k_2[\mathrm{S_2O_4^{2-}}] + k_3 K_1^{1/2}[\mathrm{S_2O_4^{2-}}]^{1/2} \quad (58)$$

However, in the corresponding reaction with $[\mathrm{Mn^{III}(CDTA)}]^-$ [26], no contribution from SO_2^-(50) could be detected. A plot of $k_{obs}/[\mathrm{S_2O_4^{2-}}]^{1/2}$ *vs.* $[\mathrm{S_2O_4^{2-}}]^{1/2}$ is linear with zero intercept, indicating the sole contribution of the k_2 path. The rate constant k_{12} for the reaction between $[\mathrm{Co^{III}(EDTA)}]^-$ and SO_2^- was applied to the $[\mathrm{Mn^{III}(CDTA)}]^-$ reaction with SO_2^- for testing the validity of the Marcus relationship. This yields $k_{12} \approx 10^8\ \mathrm{M^{-1}\ s^{-1}}$ which is consistent with the lower limit of the experimentally determined value of the electron-transfer rate. Reduction by either SO_2^- or $S_2O_4^{2-}$ or both together in metal complexes can operate through a bridged mechanism, and no attempt has been made to examine the alternative pathway.

Studies on the reduction of $[\mathrm{Mn^{III}(CDTA)(H_2O)^-}]$ by hydrazine and hydroxylamine were investigated by Arselli and Mentasti [27]. Simple first-order dependence on $[\mathrm{Mn^{III}(CDTA)(H_2O)}]^-$ and reductant concentrations was observed for hydrazine.

which showed a dependence of the specific second-order rate constant k on acidity according to the equation

$$k = k_1 + k_2[H^+]^{-1} \tag{59}$$

Such a dependence has been explained by considering the inner-sphere association of $N_2H_5^+$ with the complex which may again undergo a proton-release equilibrium as

$$[Mn^{III}(CDTA)(H_2O)]^- + N_2H_5^+ \overset{K_1}{\rightleftharpoons} [Mn^{III}(CDTA)(N_2H_5)] + H_2O \tag{60}$$

$$[Mn^{III}(CDTA)(N_2H_5)] \overset{K_2}{\rightleftharpoons} [Mn^{III}(CDTA)(N_2H_4)]^- + H^+ \tag{61}$$

Both these associated species undergo electron transfer with rate constants k_1 and k_2 respectively. For hydroxylamine, complex kinetic dependences on reductant and hydrogen ion concentration suggest a composite inner-sphere mechanism where addition of NH_3OH^+ into the labile and non-saturated coordination sphere of $[Mn^{III}(CDTA)(H_2O)]^-$ involves the proton release responsible for the inverse acidity dependence. The authors justified the above observations from the low values of enthalpies of activation computed for the above pathways. It may be argued that the carboxylate "arms" of the ligand may be rapidly unwrapped so that precursor mixed complexes may play important roles in redox reactions of this oxidant.

The mechanism of the reduction of $[Mn^{III}(CDTA)]^-$ by sulphite in the pH range 2.7–5.2 and temperature range 10–30°C [28] has been claimed to follow a 2:1 stoichiometry with respect to the complex, with sulphate as the reaction product. A composite behaviour involving a series of competitive paths was suggested leading to an empirical rate law

$$\text{rate} = (k + k'[H^+]^{-1}[S^{IV}])[S^{IV}][Mn^{III}(CDTA)^-] \tag{62}$$

An inner-sphere mechanism consistent with the first-order dependence on $[S^{IV}]$ was assumed as

$$[Mn^{III}(CDTA)(H_2O)]^- + S^{IV} \rightleftharpoons [Mn^{III}(CDTA)S^{IV}] + H_2O \tag{63}$$

$$[Mn^{III}(CDTA)S^{IV}] \xrightarrow{k_1} [Mn^{II}(CDTA)]^{2-} + S^V \tag{64}$$

and the second-order path as

$$[Mn^{III}(CDTA)S^{IV}] + S(IV) \xrightarrow{k_2} [Mn^{II}(CDTA)]^{2-} + S^V + S^{IV} \tag{65}$$

S^{IV} may be HSO_3^- or SO_3^{2-} related by

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ \tag{66}$$

and S^V represents the free radicals such as HSO_3 or SO_3^- which react with another molecule of $[Mn^{III}(CDTA)]^-$ in a fast step to give the sulphate product. The second-order dependence on S^{IV} can also be conceived by considering the dimerization reaction

$$2HSO_3^- \xrightarrow{K_d} S_2O_5^{2-} + H_2O \tag{67}$$

$(K_d \ll 1)$

$$[Mn^{III}(CDTA)]^- + S_2O_5^{2-} \xrightarrow{k_3} [Mn^{II}(CDTA)]^{2-} + S_2O_5^- \tag{68}$$

where $S_2O_5^-$ reacts with another molecule of $[Mn^{III}(CDTA)]^-$ in a fast step. The available data do not permit the distinction between the two mechanisms. The redox reactions of sulphite particularly with labile complexes often show varying stoichiometric ratios and yield a mixture of S^{VI} products. The present work does not focus on that aspect.

2.2. *Reactions with metal complexes*

Wilkins and Yelin [29] have studied the electron-transfer reactions of $[Mn^{III}(CDTA)]^-$ with $[Mn^{II}(EDTA)]^{2-}$, $[Fe^{II}(EDTA)]^{2-}$ and $[Co^{II}(EDTA)]^{2-}$ in the pH range 4.5–6.5 where one type of species predominates for the bivalent and tervalent metal complexes. The bulky nature of the ligands and the inertness of one of the reactant partners prompted the authors to assume that these redox reactions operate through an outer-sphere path, and are thereby amenable to theoretical treatment. The small value of $\Delta G_i^\ddagger = 72.7$ kJ M^{-1} which is the free energy required to reorganize the inner coordination shells of the reactants for $[Mn^{III}(CDTA)]^- - [Mn^{II}(EDTA)]^{2-}$ reaction probably reflects only small changes in the structure of the reactant, transition state and product. Application of the usual Marcus relationship to the other two cross-reactions leads to agreement between the results calculated and experimentally determined for the rate constants supporting the outer-sphere proposition. The reactivities of the monoprotonated forms of the reactants in more acidic regions or that of the hydroxo species in alkaline regions have not been explored.

Boone et al. carried out electron-transfer studies between oxovanadium(IV) with $[Mn^{III}(CDTA)(H_2O)]^-$ and $[Mn^{III}(EDTA)(H_2O)]^-$ [30]. The rate law for both of the complexes reacting with vanadium(IV) is first order with respect to each reactant. Both these reactions operate through parallel paths, one with inverse hydrogen ion dependence and the other with positive acid dependence. The presence of hydrolysed and unhydrolysed vanadium(IV) species in the pH range 1.5–3.0 readily accounts for the increase in apparent rate constant with decreasing $[H^+]$ and appears reasonable in view of the reported hydrolysis constant of $[VO(H_2O)]^{2+}$ ($K_h = 3.6 \times 10^{-6}$ M at 25°C). Keeping in view the large discrimination between hydroxide ion and water for the reaction studied, the proposition of an inner-sphere mechanism is reasonable. However, no evidence from other physical measurements was presented to establish the existence of any precursor complex.

A re-evaluation of the $[Mn^{III}(EDTA)(H_2O)]^-$ oxidation of $[VO(H_2O)_5]^{2+}$ along with $[VO(HEDTA)]^-$, $[VO(EDTA)]^{2-}$ and $[VO(NTA)(H_2O)]^-$ (where NTA denotes nitrilotriacetate) has been made by Nelson and Shepherd [31]. The complexes which possess an equatorial water molecule, i.e. $[VO(H_2O)_5]^{2+}$ and $[VO(NTA)(H_2O)]^-$, exhibit a rate law having an acid-independent (k_0) path and an inverse acid-dependent (k_1) path given by

$$-\frac{d[Mn^{III}(EDTA)(H_2O)^-]}{dt}=\left(k_0+\frac{k_1}{[H_3O^+]}\right)[Mn^{III}(EDTA)(H_2O)^-][VO^{2+}] \tag{69}$$

and this is equivalent to the rate expression proposed earlier by Boone et al. [30]. Chelation by $HEDTA^{3-}$ or $EDTA^{4-}$ which excludes water from the equatorial positions of VO^{2+} causes a change in mechanisms for the manganese(III)–vanadium(IV)aminocarboxylate redox reactions. Thus the rate dependence for the $[Mn^{III}(EDTA)(H_2O)]^-/[VO(HEDTA)]^-$ system conforms to the rate law

$$-\frac{d[Mn^{III}(EDTA)(H_2O)^-]}{dt}=k_2[H_3O^+][Mn^{III}(EDTA)(H_2O)^-][VO(HEDTA)^-] \tag{70}$$

The first-order behaviour in $[H_3O^+]$ is supportive of hydrolysis-independent kinetics, and can be anticipated if all the coordination positions on the vanadium(IV) centre are occupied by the chelating ligand. Since substitution and water exchange on $[Mn^{III}(EDTA)(H_2O)]^-$ and $[Mn^{III}(CDTA)(H_2O)]^-$ appear to be rapid compared with these redox events, it remains undetermined whether ligand rearrangement occurs prior to bringing the reactants together as in the equation

$$VOZ^- + H_3O^+ \overset{K}{\rightleftharpoons} VOZ'H(H_2O) \tag{71}$$

or after assembly of the manganese(III)–vanadium(IV) reactant partners as in

$$VOZ^- + [Mn^{III}(Y)(H_2O)]^- \overset{K'}{\rightleftharpoons} [Mn^{II}(Y)VOZ]^{2-} + H_2O \tag{72}$$

(where Y or Z denotes an aminocarboxylate of the EDTA family).

A binuclear intermediate has been detected on combination of manganese(III) acetate and $VO_2(DTPA)^{3-}$ by ESR. However, no long-lived intermediates which might be attributed to a hydroxy or oxobridged manganese(III)–vanadium(IV) complex on the same $DTPA^{5-}$ ligand could be observed from the visible spectrum. The results thus hint to an outer-sphere mechanism for the manganese(III)–vanadium(IV) systems in aminocarboxylate environments, since the proximity effect should favour a higher concentration of bridged species. The arguments are supported more strongly by experimental evidence than the earlier study [30].

A study on the kinetics of electron-transfer reactions involving the manganese(II) and (III) complexes of $EDTA^{4-}$ and *trans*-cyclohexane-1,2-diaminetetraacetate ($CDTA^{4-}$) has appeared recently [19]. The cross-reactants employed are osmium(III) and cobalt(III) tris(polypyridine) complexes, $IrCl_6^{2-}$ and several nickel(II) polyaza complexes. The reduction of $[Mn^{III}(EDTA)]^-$ and $[Mn^{III}(CDTA)]^-$ by $[Ni(H_2DIOX)]^{2+}$ (where H_2DIOX denotes 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) studied over the pH ranges 3.0–7.0 and 4.0–9.0 respectively shows several interesting aspects as follows.

(i) At $pH < 5.0$, the kinetic traces are monophasic first-order curves but above pH 5.0 these turn to biphasic. The absorption changes in the two steps are nearly equivalent, suggesting a nickel(III) intermediate. Below pH 5.0 the oxidation of the nickel(II) complex is expected to be the rate-determining step with a subsequent rapid oxidation of the nickel(III) intermediate to a stable nickel(IV) product. Above pH 5.0 biphasic behaviour is observed owing to the large separation of the E^0 values for the corresponding Ni(III)–(II) and Ni(IV)–(III) couples.

(ii) The pH rate profiles for the oxidation of the nickel(II) species are bell-shaped curves having peaks in the pH region 5.0–6.0. A reaction sequence involving the reaction of $[Ni(HDIOX)]^+$ and $[Ni(DIOX)]$ with $[Mn^{III}(CDTA)(H_2O)]^-$ was considered. The inertness of $[Mn^{III}(CDTA)OH]^{2-}$ towards electron transfer gets support from other studies [20–22]. A derived self-exchange rate constant of $0.74 \pm 0.4\ M^{-1}\ s^{-1}$ at 25°C for $[Mn^{II}(EDTA)(H_2O)]^{2-}-[Mn^{III}(EDTA)(H_2O)]^-$ and $[Mn^{II}(CDTA)(H_2O)]^{2-}-[Mn^{III}(CDTA)(H_2O)]^-$ is a useful parameter for further studies. However, deviations from the Marcus correlation are observed in the case of metal tris(polypyridine) complexes. This behaviour can be attributed to certain factors, e.g. an incompatibility of the self-exchange pathways, and hydrophobic–hydrophilic repulsions causing unfavourable precursor formation. The $[Mn(EDTA)(OH_2)]^{2-}-[Mn(EDTA)(OH_2)]^-$ and $[Mn(CDTA)(OH_2)]^{2-}-[Mn(CDTA)(OH_2)]^{2-}$ couples represent systems requiring much more complicated assessments in terms of their geometry, and thereby the usual calculation for an inner-sphere reorganization energy barrier may not be valid.

A recent report has been made on the kinetics of oxidation of bis(2,4,6-tripyrid yl-1,3,5-triazine)iron(II) by $[Mn^{III}(CDTA)]^-$ in acetate buffer [32]. Analysis of the kinetic data indicates a precomplexation between the oxidant and the substrate but no spectroscopic evidence was gathered for such association. Characterization of products using the radiotracers ^{54}Mn and ^{59}Fe indicated that $[Mn^{II}(CDTA)]^{2-}$ and $[Fe(TPTZ)_2]^{3+}$ (where TPTZ denotes 2,4,6-tripyridyl-1,3,5-triazine) are the final products.

2.3. Reactions with biomolecules

Adzamli et al. reported the kinetic reactivity of chromatium vinosum [33], a high potential ion–sulphur protein (HIPIP) of a single cubane-like Fe_4S_4 cluster, with several inorganic complexes as redox partners, one such being $[Mn^{III}(CDTA)(H_2O)]^-$. The oxidation of HIPIP(r) to HIPIP(o) with $[Mn^{III}(CDTA)(H_2O)]^-$ gives second-order rate constants $k = 1.26 \times 10^3\ M^{-1}\ s^{-1}$ at 25°C, $\Delta H^\ddagger = 15.0\ kJ\ M^{-1}$ and $\Delta S^\ddagger = -118\ J\ K^{-1}\ M^{-1}$. The slow rate constant for the manganese(III) oxidation of HIPIP(r) (though it has a very favourable driving force of 410 mV) is ascertained to be the result of a slow $[Mn(CDTA)(H_2O)]^-$ — $[Mn(CDTA)(H_2O)]^{2-}$ self-exchange. The authors rationalize it in terms of the geometry change (if seven coordinate) or distortion of the d^4 coordination sphere of manganese(III) (if six coordinate), and reorganization attendant on electron transfer. The pH rate profile is explained in terms of the acid dissociation constant of the coordinated H_2O of $[Mn^{III}(CDTA)(H_2O)]^-$, and the pK_m obtained from the data gives a value of 7.74 comparable with the independently measurable value of 8.11. The rate profile also indicates that the conjugate base $[Mn^{III}(CDTA)(OH)]^{2-}$ present at higher pH is much less redox active. The oxidations with $[Mn^{III}(CDTA)(H_2O)]^-$ and $[Fe(CN)_6]^{3-}$ both proceed unaffected by the presence of $Co(4,7\text{-}DPSphen)_3^{3-}$ (where 4,7-DPSphen denotes 4,7-bis(phenyl-4-sulphonate)-1,10-phenanthroline), which for the concentrations used does not contribute to the oxidation but binds to more than 50% of the protein.

The redox interaction of the blue copper protein, rusticyanin (from thiobacillus ferroxidans) and $[Mn^{III}(CDTA)(H_2O)]^-$ has been studied by McGinnis et al. [34]. The effect of pH on rate constants has been carried out in order to get certain information on active-site chemistry and binding sites on the protein surface. In the pH range 1.24–5.80, the rate profile corresponds to a flat S-shaped curve showing an initial decrease and then an increase in rate with increasing pH. This corresponds to the sequence of reactions

$$PH^+ \overset{K_a}{\rightleftharpoons} P + H^+ \tag{73}$$

$$C + PH^+ \xrightarrow{k_H} \text{products} \tag{74}$$

$$P + C \xrightarrow{k_0} \text{products} \tag{75}$$

(where PH^+ denotes the protonated form of the protein, and C denotes $[Mn^{III}(CDTA)(H_2O)]^-$).

The rate expression turns into the equation

$$k = (k_0 K_a + k_H[H^+])/(K_a + [H^+]) \tag{76}$$

From a computer fit of the kinetic data at pH > 2, we obtain $k_H = 104 \pm 7\ M^{-1}\ s^{-1}$, and $pK_a = 4.17 \pm 0.03$. Owing to rapid decomposition of $[Mn^{III}(CDTA)(H_2O)]^-$, data at pH < 1.5 are subject to some uncertainties, and therefore not further explored.

It is noteworthy that this pK_a (4.17) reflects the involvement of a carboxylate group as the most probable site for protonation in the protein molecule.

Oxidation of reduced cytochrome C551 and cytochrome oxidase by $[Mn^{III}(CDTA)(H_2O)]^-$ have been carried out by Tordi et al. [35]. The electron transfer from cytochrome C551 to the manganese(III) complex is a simple process described as

$$C551^{2+} + Ox \rightarrow C551^{3+} + red \tag{77}$$

with a rate constant $k = 2.31 \times 10^4\ M^{-1}\ s^{-1}$ at 20°C in 0.1 M phosphate buffer. The reaction of the c-heme of the oxidase with $[Mn^{III}(CDTA)(H_2O)]^-$ is somewhat complex, and implies kinetic heterogeneity of the c-heme sites belonging to two subunits. A pseudo-first-order rate constant for the whole oxidation has been calculated from the half-life of the overall reaction with a characteristic second-order rate constant $k = 4.30 \times 10^4\ M^{-1}\ s^{-1}$. We note that this is a familiar situation in a haemoglobin kinetics, and the separation of biphasic plots into their components by computer analysis should have been attempted. Under carbon monoxide (which binds the d_1-heme), the rate constant does not change significantly. The oxidation of the d_1-heme of the oxidase by $[Mn^{III}(CDTA)(H_2O)]^-$ occurs via a direct bimolecular electron transfer between the d_1-heme and the complex, competing (even at low concentrations) with the intramolecular oxidation via the oxidized c-heme. In the oxidation of reduced cytochrome C551, electrostatic phenomena play an important role since the negative charges on the manganese(III) complex and cytochrome C551 at pH 7.0 are likely to inhibit the formation of a competent transition species. A discussion in terms of Marcus theory would have been useful.

3. OXIDATION REACTIONS OF THE ACETYLACETONATE COMPLEX OF MANGANESE(III), $[Mn^{III}(AcAc)_3]$

The potential use of $[Mn^{III}(AcAc)_3]$ as in initiator for polymerization reactions has been highlighted in a study by Nikolaev et al. [36]. The reduction of $[Mn^{III}(AcAc)_3]$ in aqueous medium in the presence of mono- and dicarboxylic acids has been followed and a mechanism for the formation of primary radicals from $[Mn^{III}(AcAc)_3]$ is proposed. In the initial stage, the bis(acetylacetonato)-diaquamanganate(III) ion is formed by

$$[Mn^{III}(AcAc)_3] + 2H_2O + H^+ \rightleftharpoons [Mn^{III}(AcAc)_2(H_2O)_2]^+ + AcAcH \tag{78}$$

Binding of the carboxylate anion in either outer-sphere or inner-sphere mode is facilitated by

$$[Mn^{III}(AcAc)_2(H_2O)_2]^+ + RCOO^- \begin{array}{l} \rightleftharpoons Mn^{III}(AcAc)_2,\ RCOO + 2H_2O \\ \rightleftharpoons [Mn^{III}(AcAc)_2(H_2O)_2^+ . RCOO^-] \end{array} \tag{79}$$

The possibility of the formation of carboxylic radicals may occur by (i) a direct transfer of an electron from the carboxylate to the metal centre, or (ii) an electron transfer from the acid anions to the acetylacetonate ligand. From the polymerization and ESR spectroscopic data, it is concluded that some of the radicals formed are in the coordination sphere of the manganese(II) compound which increases the lifetime of these radicals.

The electron transfer from $Fe(DMF)_6^{2+}$ (where DMF denotes dimethylformamide) to $[Mn^{III}(AcAc)_3]$ in 1,2-propanediol cyclic carbonate [37] takes place intramolecularly within a binuclear intermediate $[(AcAc)_2Mn(AcAc)Fe(DMF)_5]^{2+}$, the formation of which is catalysed by $[Mn^{II}(AcAc)_2]$ (one of the primary reaction products). However, the autocatalytic effect imparted by $[Mn^{II}(AcAc)_2]$ decreases in the presence of excess $[Mn^{III}(AcAc)_3]$. The transfer of acetylacetonate ions from $[Mn^{II}(AcAc)_2]$ to $(Fe(AcAc)]^{2+}$ is faster than the rate of dissociation of the primary intermediate. In the second stage the involvement of another intermediate, $[Mn(AcAc)Fe(AcAc)_2]^{2+}$, leading to the final products Mn^{2+} and $[Fe^{III}(AcAc)_3]$ is suggested. This reaction is believed to be catalysed by DMF originated from the dissociation of $Fe(DMF)_6^{2+}$ [38]. Though the existence of an intermediate has been explained from the observation of saturation kinetics with iron(II) in excess, it needs to be verified by a rapid-scan spectrum.

An analogous reaction [39] reported from the same laboratory on the reduction of $[Mn(AcAc)_3]$ by $[Fe(DMF)_6^{2+}]$ in acetonitrile shows that the electron-transfer step is preceded by the one-ended dissociation of an acetylacetonate ligand and the formation of a bridged intermediate. The electron transfer occurs through the bridged ligand. The acceleration of the reaction by addition of donor (DMF) molecules and inhibition by admixing iron(III) are in keeping with the interpretation of the formation of a monodentate acetylacetonate species as the active agent, but here too no spectroscopic evidence for the bridged species has been furnished.

Results of two recent studies of the reaction of $[Mn^{III}(AcAc)_3]$ with glyoxylate and thiosulphate lead to interesting conclusions [40,41]. Glyoxylate catalyses the reduction of $[Mn^{III}(AcAc)_3]$ to Mn^{II} in aqueous perchlorate media (pH 5.50–7.50) containing excess of acetylacetone. The reaction stoichiometry is compatible with the consumption of 1 mole of acetylacetone per mole of Mn^{III} reduced with no consumption of glyoxylate. The kinetically active manganese(III) species are $[Mn(AcAc)_2(GOx)]$ (where GOx denotes glyoxylate) and $[Mn(AcAc)_2(H_2O)(OH)]$; $[Mn(AcAc)_3]$ does not make any appreciable contribution to the rate. Inner-sphere paths seem reasonable from kinetic observations. We note that the glyoxylate ligand is probably less bidentate in character than the glycolate or lactate ligands [42], and therefore a bis species, e.g. $[Mn(AcAc)_2(GOx)_2]^-$, can have a real existence especially at high ligand concentrations and relatively low pH (about 5.50). In the analogous thiosulphate-catalysed reactions (pH 4.20–8.50), contributions of $[Mn^{III}(AcAc)_3]$, $[Mn(AcAc)_2(H_2O)_2]^+$ and $[Mn(AcAc)_2(H_2O)(OH)]$ in the electron-transfer process have been considered. EPR and kinetic data suggest an $S_2O_3^{2-}$–$S_2O_3^-$ catalytic cycle which is able to provide a low energy path for the AcAc → Mn^{III} electron transfer.

Inner-sphere substitution of unidentate thiosulphate in $[Mn(AcAc)(H_2O)_2]^+$ and $[Mn(AcAc)(OH)(H_2O)]$ would be thermodynamically facile en route to electron transfer; the $[Mn(AcAc)_3]$ being coordinately saturated is likely to follow an outer-sphere path.

In the oxidation of hypophosphite ion [43] by $[Mn(AcAc)_2(H_2O)_2]^+$ in the pH range 4.0–5.50, the rate-determining step is considered to be the tautomerization of "normal" to "active" forms of hypophosphite bound to $[Mn(AcAc)_2(H_2O)_2]^+$. The activity of $[Mn(AcAc)_2(H_2O)(OH)]$ has been ignored. However, the autodecomposition of the manganese(III) species would be significant at relatively high pH, and it may well compete with the oxidation of hypophosphite. No kinetic data have been gathered on this aspect. The corresponding oxidations of HSO_3^- and SO_3^{2-} are believed to take place through hydrogen-bonded ion pair intermediates with $[Mn(AcAc)_2(H_2O)_2]^+$ [44].

4. OXIDATION REACTIONS OF PORPHYRIN COMPLEXES OF MANGANESE(III)

The reaction of manganese(III) porphyrins ($Mn^{III}P$) arises concurrently with the general interest in studying the interaction of reducing species with water-soluble metalloporphyrins. These undergo well-defined one-electron electrochemical reduction to the corresponding manganese(II) derivative for which the overall reversibility is very high [45]. The potentials for $Mn^{III} \rightarrow Mn^{II}$ reductions reported by Boucher [46] show that (i) the redox potential order for the various porphyrins corresponds to the pK_a order, and (ii) the Mn^{III} is stabilized by strong in-plane σ donation from the porphyrin. Rates of reduction of manganese(III) tetrapyridylporphyrin (TpyP) with chromium(II), vanadium(II) and $Cr(BPy)_3^{2+}$ (where BPy denotes 2,2′-bipyridine) have been measured [47] and conform to

$$\text{rate} = k_1 + k_2[X][Mn^{III}\text{-TpyP}][\text{reductant}] \qquad (80)$$

where X is a halide ion (Cl^-, Br^-, I^-) or NCS^-. The product study with chromous ion as a reducing agent indicates an inner-sphere bridging by chloride. The chloride-independent path is likely to follow an outer-sphere path. Owing to the lability of water molecules in the axial position of porphyrin, some uncertainty in drawing mechanistic conclusions in aqueous medium is due to occur. Hambright and Chock [48] followed the kinetics of reduction of a series of manganese(III) porphyrins by dithionite in aqueous pyridine medium. The basic equilibria considered are

$$Mn^{III}P + Py \xrightleftharpoons{K_1} Py - Mn^{III}P \qquad (81)$$

$$Py - Mn^{III}P + Py \xrightleftharpoons{K_2} (Py)_2 - Mn^{III}P \qquad (82)$$

$$S_2O_4^{2-} \underset{}{\overset{K_D}{\rightleftharpoons}} 2SO_2^- \tag{83}$$

$$SO_2 + H_2O \xrightarrow{\text{fast}} 2H^+ + SO_3^{2-} \tag{84}$$

(where Py denotes pyridine).

The rate-determining step for an outer-sphere path would be

$$(Py)_2 - Mn^{III}P + SO_2^- \xrightarrow{k_{os}} (Py)_2 - Mn^{II}P + SO_2 \tag{85}$$

with rate law

$$k_0 = \frac{k_{os}K_D^{1/2}[S_2O_4^{2-}]^{1/2}K_1K_2[Py]^2}{1 + K_1[Py] + K_1K_2[Py]^2} \tag{86}$$

For an inner-sphere pathway

$$Py - Mn^{III}P + SO_2^- \xrightarrow{k_{in}} Py - Mn^{III}P + SO_2 \tag{87}$$

the rate constant would be

$$k_0 = \frac{k_{in}K_D^{1/2}[S_2O_4^{2-}]^{1/2}K_1[Py]}{1 + K_1[Py] + K_1K_2[Py]^2} \tag{88}$$

The authors prefer the outer-sphere electron-transfer pathway. This is again not a strong proposition since the equilibrium constants on which the argument depends are not well known, and owing to solubility considerations the reactions had to be studied over a narrow range of ligand concentrations. For example, if $K_1[Py] \gg 1 + K_1K_2[Py]^2$ rather than $K_1K_2[Py]^2 \gg 1 + K_1[Py]$, the conclusions regarding electron-transfer path would be the opposite of those suggested. Quantitative reduction of $Mn^{III}TPP^+$ (TPP = tetraphenyl-porphyrin) by superoxide (O_2^-) in dimethyl sulphoxide (DMSO) [49] is noted to give the product $Mn^{II}TPP$. This provides information pertaining to the oxidation of $Mn^{II}TPP$ by molecular oxygen in the same solvent, a reaction that is seemingly difficult to follow owing to secondary reactions.

The overall mechanism for the interaction [50] of several manganese(III) metalloporphyrins with $Ru(NH_3)_6^{2+}$ involves a reductive demetallization process. The manganese(III) porphyrins undergo electron-transfer-induced solvolysis in acidic media as in

$$Mn^{III}P + [Ru(NH_3)_6]^{2+} \rightarrow Mn^{II}P + [Ru(NH_3)_6]^{3+} \tag{89}$$

$$Mn^{II}P \xrightarrow{H^+} Mn^{2+} + H_4P \tag{90}$$

Under conditions of low pH, electron transfer is rate limiting, and the redox constants allow the evaluation of $Mn^{III}TPPS–Mn^{II}TPPS$ (where TPPS denotes tetra-(*p*-sulphonatophenyl)porphyrin) and $Mn^{III}TPP–Mn^{II}TPP$ self-exchange rates of $3.2 \times 10^3\ M^{-1}\ s^{-1}$ and $2.6 \times 10^3\ M^{-1}\ s^{-1}$ respectively. These values are substantially higher than the corresponding value for the aqua complex ($k_{ex} \approx 3.0 \times 10^{-4}\ M^{-1}\ s^{-1}$).

The kinetics of reduction of manganese(III)-substituted myoglobin (Mn^{III}–Mb) by dithionite into its Mn^{II}–Mb form has been studied [51]. The suggested mechanism for the reaction is

$$S_2O_4^{2-} \xrightarrow{K_D} 2SO_2^- \tag{91}$$

$$Mn^{III} - Mb - H^+ \overset{K_A}{\rightleftharpoons} Mn^{III} - Mb + H^+ \tag{92}$$

$$Mn^{III} - Mb - H^+ + SO_2 \xrightarrow{k_1} Mn^{II} - Mb + \text{products} \tag{93}$$

$$Mn^{III} - Mb + SO_2 \xrightarrow{k_2} Mn^{II} - Mb + \text{products} \tag{94}$$

which considers the reactivity of both the protonated and deprotonated forms of Mn^{III}–Mb. The rate law derived is

$$k_{obs} = \frac{(k_1 K_D^{1/2}[H^+] + k_2 K_A K_D^{1/2})[S_2O_4^{2-}]^{1/2}}{[H^+] + K_A} \tag{95}$$

Taking $K_D = 1.4 \times 10^{-9}$ M and $K_A = 2.5 \times 10^{-5}$ M, values of k_1 and k_2 have been computed. With the help of Marcus theory and with the same self-exchange rate constants k_{11} assumed for the metalloproteins and metalloporphyrins, the reactivity ratio (Fe^{III}–Mb)/(Mn^{III}–Mb) for SO_2^- reductions is calculated to be in the range 10^2–10^3 (assuming a difference in potential ΔE of 0.1 and 0.2 V). The observed ratio of 385 obtained in the present result is close to this value and therefore an outer-sphere electron-transfer path is postulated. It may be commented that, while this agreement may reflect mere coincidence, the self-exchange rate parameters for the iron and manganese porphyrin may be lowered to the same relative extent in their metalloglobin forms. Studies of the redox reactions which accompany the reaction of OH^- with 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porhinatomanganese(III) ([$(TMP)Mn^{III}Cl$]) in coordinating solvents (CH_3CN, DMSO, Py) results in the formation of $(TMP)Mn^{II}$ (about $10^6\ M^{-1}\ s^{-1}$) which reacts slowly to give a product whose structure is suggested to be that of a porphyrinmanganese(III) peroxodimer, (TMP)Cl Mn^{III}–O–O–Mn^{II}(Cl)(TMP). This study [52] establishes that one-electron oxidation of water by a manganese(III) porphyrin occurs if the coordinated water molecule is first dissociated to OH^-. The formation of manganese(II) porphyrin by this process is only observed when OH^- can occupy one axial coordination site, the other being occupied by a coordinating solvent molecule. The oxidation of OH^- and proposed coupling of oxygen atoms to generate the peroxide species are believed to be relevant to the chemistry of photosystem II.

A recent report [53] on the reaction of $(TTP)Mn^{III}Cl$ (where TTP denotes 5,10,15,20-tetra(*p*-tolyl)porphyrin) in toluene with $(OEP)Mn^{V}{\equiv}N$ where OEP denotes 2,3,7,8,12,13,17,18-octal(ethyl)porphyrin results in a double exchange of axial ligand and a net two-electron transfer as in

$$(TTP)Mn^{III}Cl + (OEP)Mn^{V}{\equiv}N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (TTP)Mn^{V}{\equiv}N + (OEP)Mn^{III}Cl \qquad (96)$$

measured through both UV–visible and nuclear magnetic resonance spectroscopy. The reversibility of eqn. (96) was established by conducting the reaction identically in the opposite direction and the forward reaction (k_1) was found to be more favourable. Evidence for an inner-sphere bridging through a μ-nitrido binuclear intermediate has been put forward — the most convincing evidence being the demonstration of the reversibility of

$$(CAP)Mn^{III}Cl + (OEP)Mn^{V}{\equiv}N \overset{K}{\rightleftharpoons} (CAP)Mn^{V}{\equiv}N + (OEP)Mn^{III}Cl \qquad (97)$$

whereby the TTP ligand has been replaced by Baldwin's C_2-capped porphyrin (CAP) having an aryl ring blocking one face of the macrocycle. An analogous study [54] between $(OEP)Mn^{V}Cl$ and $(TPP)Cr^{III}Cl$, however, does not consider the μ-nitrido route. Further work is needed to elucidate the mechanism of the atom-transfer process.

Recent studies throw much emphasis on the catalytic oxidation by manganese(III) porphyrins rather than their role as stoichiometric participant. These metalloporphyrins resemble in structure those of the cytochromes P-450, nature's catalyst for oxidation of foreign organic compounds *in vivo* bodies. Although the cytochromes P-450 use dioxygen and an electron-transfer reducing agent, most of the synthetic metalloporphyrin catalysts are used with oxidizing agents such as iodosylbenzene, alkyl hydroperoxides, amine *N*-oxides, peroxy carboxylic acids, hydrogen peroxide, aqueous peroxodisulphate and aqueous hypochlorite that do not require a reducing agent [55].

The catalysed oxidation of hydrocarbons by manganese(III) porphyrins has been studied [56,57]. The tetrasodium salt of 5,10,15,20-tetrakis(2,6-dichloro-3-sulphonatophenyl)-porphinatomanganese(III) chloride is a more active catalyst [58] for epoxidation of styrene with hypochlorite bound to colloidal anion-exchange particles than in aqueous solution because of the higher concentration of styrene in the particles than in water. Aliphatic alkenes do not react under conditions that give 71%–81% conversion of styrene to styrene oxide, probably because the aliphatic alkenes are less soluble in the particles. An unidentified Mn(V)=O species with a 441 nm absorbance maximum has been claimed to be the active epoxidizing agent.

The oxidation of secondary amines to the corresponding imine by $Mn^{III}(TTPh)Cl$ (where TTPh denotes 5,10,15,20-tetra(*p*-phenyl)porphyrin) catalysis reaction [59] with iodosobenzene as the terminal oxidant has been reported. The first step in the reaction between the oxygen donor and the $Mn^{III}(TTPh)Cl$ is proposed to be the formation of an oxometal species which is the reactive intermediate. The reaction probably proceeds by a one-electron transfer from the amine to the putative oxomanganese(V) intermediate species with formation of an amine cation radical and an oxomanganese(IV) species. Further oxidation of the amine cation radical to the imine terminates the reaction. The mechanism is consistent with the earlier generalization [55(d),60].

Stereoselective deoxygenolyses of *N*-acetyl-L(+)- and D(−)-tryptophan methyl esters have been carried out [61] with $Mn^{III}ClTPCP$ (where TPCP denotes $\alpha,\beta,\gamma,\delta$-tetra(*p*-carboxyphenyl)porphin) and $Mn^{III}ClTTPh$ bound to a carrier protein, bovine serum albumin (BSA) in tetrahydrofuran–water medium under oxygen atmosphere. The maximum stereoselectivity evaluation rate ratio k_L/k_D is 1.63. Modification of the BSA hybrid catalyst by polyethyleneglycol retains the catalyst activity as well as the stereoselectivity.

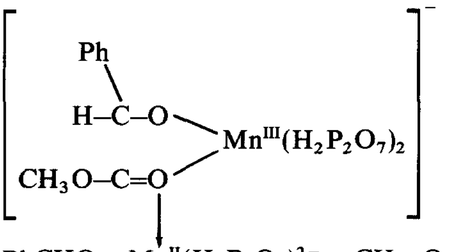
5. OXIDATION REACTIONS OF MISCELLANEOUS MANGANESE(III) COMPLEXES

The complex of BPy with manganese(III) has only two bipyridine ligands attached to each manganese(III), and is formulated by Cooper and Calvin [62] as $[Mn^{III}(BPy)_2(H_2O)(OH)]^{2+}_{aq}$. Heyward and Wells carried out several studies with this oxidant. In the oxidation of hydrazoic acid by $[Mn(BPy)_2(OH)(H_2O)]^{2+}$ [63] the conclusions drawn from the kinetic and equilibrium studies are that two 1:1 complexes are formed between the N_3^- and the manganese(III) oxidant. There is an initial rise in absorbance on mixing the reactants which is supportive of the complex association. The kinetics of the subsequent decay in absorbance show that both these complexes, $[Mn^{III}(BPy)_2(N_3)]^{2+}$ and $[Mn^{III}(BPy)_2(OH)(N_3)]^+$, are involved in the intramolecular electron-transfer process generating free radicals $N_3^{\cdot}$. The kinetics of oxidation of hydrogen peroxide with the same manganese(III) oxidant [64] are found to vary with the initial ratio $[H_2O_2]/[Mn(BPy)_2]^{3+}_{aq}$: (i) if k_0 is the observed pseudo-first-order rate constant, linear plots are found for k_0^{-1} against $[H_2O_2]^{-1}$ at low $[H_2O_2]$; (ii) linear plots of k_0 against $[H_2O_2]$ with an intercept on the k_0 axis are found at high $[H_2O_2]$. The detailed kinetic analysis of rate data led to the postulation of three complexes, $[Mn(BPy)_2HO_2]^{2+}_{aq}$, $[Mn(BPy)_2(H_2O_2)_2]^{3+}_{aq}$ and $[Mn(BPy)_2(H_2O_2)(HO_2)]^{2+}_{aq}$ contributing to the redox step. No spectroscopic evidence supports such inner-sphere species. Also there is uncertainty from the kinetics about which equilibria participate in the production of the species involved in the rate-determining steps. A similar study of the oxidation of bromide ions [65] shows kinetically that the decomposition of $[Mn(BPy)_2Br]^{2+}$ is involved as a rate-controlling step though a protonated species $[Mn(BPy)(BPyH^+)Br]^{3+}_{aq}$ may impart an identical role. Analysis of the kinetic data leads to a value of 2.88 M^{-1} for the formation constant of the protonated species, but there is too much scatter in the data and no discussion has been presented on the magnitude of the equilibrium parameter for the $[Mn(BPy)_2Br]^{2+}_{aq}$ species. Likewise the intermediate complexes $[Mn(BPy)_2HQ]^{2+}_{aq}$ and $[Mn(BPy)_2(OH)HQ]^{+}_{aq}$ are claimed to be [66] involved in rate-controlling steps for the oxidation of quinol. The composite parameters reported give very little idea about the real existence of such species with regard to their stability or electron-transfer property. The ascorbate oxidation of $[Mn(BPy)_2(H_2O)(OH)]^{2+}$ by Gangopadhyay et al. [17] reports an acid dependence as

$$k_{ox} = a + b[H^+]^{-1}$$

in the region $[H^+] = (0.1\text{–}1.0)$ M where reactivities of both H_2Asc and $HAsc^-$ have been considered. $HAsc^-$ reacts about 3–4 times faster than H_2Asc. An inner-sphere route through the substitution of labile aqua ligand by ascorbate may be the preferred route but no detailed discussion in the light of a Marcus cross-relationship is possible owing to non-availability of self-exchange rate parameters.

A few reports [67–70] have appeared on the oxidation chemistry of manganese(III) pyrophosphate ($Mn^{III}(H_2P_2O_7)_3^{3-}$). In the oxidation of methyl mandelate [67], removal of a pyrophosphate ligand in an equilibrium step is suggested. The formation of methanol occurs as in the scheme



$$PhCHO + Mn^{II}(H_2P_2O_7)_2^{2-} + CH_3\text{–}O\text{–}\dot{C}{=}O \tag{98}$$

$$CH_3\text{–}O\text{–}\dot{C}{=}O + Mn^{III}(H_2P_2O_7)_2^{-} \xrightarrow{\text{fast}} CH_3\text{–}O\text{–}\overset{+}{C}{=}O + Mn^{II}(H_2P_2O_7)_2^{2-} \tag{99}$$

$$CH_3\text{–}O\text{–}\overset{+}{C}{=}O \xrightarrow{\text{fast}} CO_2 + \overset{+}{C}H_3 \xrightarrow{H_2O} CH_3OH \tag{100}$$

The interaction of manganese(III) pyrophosphate with CDTA [68] involves two processes: slow substitution by CDTA results in an inner-sphere process while a more rapid outer-sphere oxidation of the ligand by $Mn^{III}(H_2P_2O_7)_3^{3-}$ also takes place. Observation of the substitution step seems justified in view of the vacant site available upon dissociation of a coordinated $H_2P_2O_7^{2-}$ from the parent oxidant.

Inhibition by the pyrophosphate ion suggests an inner-sphere mechanism in the $[Mn(H_2P_2O_7)_3]^{3-}$ oxidation of isopropyl mandelate (L) [69]. The rate is first-order in the [oxidant] and [L] but showed a squared acidity dependence consistent with the mechanism

$$L + [Mn^{III}(H_2P_2O_7)_3]^{3-} + 2H^+ \rightleftharpoons H_4P_2O_7 + [LMn(H_2P_2O_7)_2]^- \quad (101)$$

$$[LMn(H_2P_2O_7)_2]^- \rightarrow \dot{L} + [Mn(H_2P_2O_7)_2]^{2-} + H^+ \quad (102)$$

Carbon–carbon bond scission takes place in the rate-determining step, and comparison with data for the corresponding oxidation of mandelic acid and 1-phenyl ethanol shows that the differences in the overall rates of oxidation are determined by the extent of complex formation. The interpretation for C–C bond fission lacks kinetic isotope effect studies in the rates of oxidation.

The report by Diebler and Sutin [70] on the oxidation of ferroin and related complexes by manganese(III) pyrophosphate in pyrophosphoric acid–sulphuric acid medium at pH 1 is the only study on the oxidation of an inorganic molecule by this oxidant. These workers evaluated only the overall equilibrium constant rather than that for the actual electron-transfer rate. The reactions were designated to follow an outer-sphere route. The slopes of the plots of rate constant against the formal oxidation potential of the reductants were about 30% lower than the theoretical value. This discrepancy may arise either due to the complexation between the substrate and oxidant or due to systematic changes in the redox potentials because of the high pyrophosphate concentration.

6. CONCLUDING REMARKS

In this review we have discussed work that clearly demonstrates the oxidative role of mononuclear manganese(III) complexes in their reactions with various organic, inorganic (both metallic complexes and non-metallic reagents) and biochemical species. Significant mechanistic conclusions can be deduced from the results but attention must be paid in the interpretation of results, particularly in the absence of reliable cross-reaction kinetic data. Although this review focusses on stoichiometric oxidation, information on the catalytic reactions of many manganese(III) porphyrin complexes has also been discussed at length. Manganese(III) porphyrins are currently being considered as potential contrast-enhancement agents for magnetic resonance imaging [71] and herein may lay another impetus for studying these complexes.

7. NOTE ADDED IN PROOF

The kinetics and mechanisms of the oxidation of hydroxylamine and L-ascorbic acid by $[Mn^{III}(AcAc)_2(H_2O)_2]^+$ in aqueous solution at 25°C have been reported [72]. The kinetic data have been interpreted through inner-sphere mechanisms. In the case of hydroxylamine two competing pathways, one of which is first-order in reductant and another which is second-order in reductant, are encountered. An outer-sphere path cannot be completely ruled out for the first-order path. The oxidations of thioglycolic acid and glutathione by $[Mn^{III}(CDTA)]^-$ have been investigated [73] by stopped-flow spectrophotometry at 30°C in aqueous media in the pH range 2.0–10.33. Both the reactions have been assumed to proceed via an inner-sphere mechanism with support for this coming from the observation of a rapid initial increase in absorption followed by a slower decay. Additional support for this mechanism is gathered from a comparison of the water-exchange rate of $[Mn^{III}(CDTA)(H_2O)]^-$ with the higher limit of the electron-transfer rates. The pH–rate profiles are bell-shaped curves and were successfully modelled by fitting the experimental data to a computer fitted programme, thereby evaluating multiple kinetic parameters.

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