Kinetics of Reactions of Pentane-2,4-dionato Complexes of Manganese(III) with Glyoxylate Anion in Aqueous Perchlorate Media†

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Glyoxylate (gox) catalyses the reduction of $[Mn(pd)_3]$ to Mn^{II} in aqueous perchlorate media (pH 5.5—7.5) containing excess of pentane-2,4-dione (Hpd). In this process, 1 mol of Hpd, but no gox, is consumed per mol of Mn^{III} reduced. E.p.r. studies indicate the generation of a pd$^•$ radical in a cyclic redox process. The kinetically active manganese(III) species are $[Mn(pd)_2(gox)]$ and $[Mn(pd)_2(H_2O)(OH)]$; $[Mn(pd)_3]$ makes no appreciable contribution to the rate. The rate constants for the $[Mn(pd)_2(gox)]$ and $[Mn(pd)_2(H_2O)(OH)]$ paths are $(1.27 \pm 0.03) \times 10^{-4}$ s^{-1} and $(9.58 \pm 0.26) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} respectively while the formation constant for $[Mn(pd)_2(gox)]$ from $[Mn(pd)_2(H_2O)_2]^+$ and gox is 902 ± 42 dm^3 mol^{-1} at 30 °C, $I = 1.0$ mol dm^{-3}. Inner-sphere paths seem reasonable.

Involvement of manganese(III) in photosynthetic water oxidation[1–5] and in the auto-oxidation of S^{IV} (refs. 6—10) is now well established[11–13] but the mechanistic role of manganese in these cyclic redox processes is not known. In this context kinetic investigations on redox reactions involving $[Mn(pd)_3]$ (Hpd = pentane-2,4-dione) seem interesting. The complex is well characterised,[14–18] has been utilised in free-radical-mediated organic syntheses,[19–21] and its redox thermodynamics have been discussed by Yamaguchi and Sawyer[3] in relation to the photosynthetic water oxidation and oxygen-evolving processes (photosystem II). However, so far the complex has rarely been subjected to kinetic studies.[22–24] The present investigation was initiated therefore. Another reason is the importance of glyoxylic acid (Hgox) in metabolic processes such as glycine catabolism[25] and plant physiology[26] where manganese(III) complexes play an essential role.

Experimental

Materials.—Solid tris(pentane-2,4-dionato)manganese(III), $[Mn(pd)_3]$ was synthesised by the method[27,28] involving the oxidation of Mn^{2+} by $KMnO_4$ in the presence of pentane-2,4-dione (Found: C, 51.1; H, 6.1. Calc. for $C_{15}H_{21}MnO_6$: C, 51.1; H, 6.0%).

Pentane-2,4-dione (LOBA, G.R.) was purified further by washing with 2 mol dm^{-3} NaOH, followed by water. After drying over anhydrous sodium sulphate it was distilled under reduced pressure. Solutions of A.R. grade glyoxylic acid monohydrate (Koch-Light) were standardised against standard alkali using Weslow's indicator.

Sodium perchlorate solution, used to maintain ionic strength, were prepared by neutralisation of $HClO_4$ (70%; E. Merck, G.R.) with a solution of NaOH (LOBA G.R., chloride free) to a final pH of *ca.* 6—7. This was standardised by ion exchange through Dowex 50W X8 cation exchanger in the H^+ form. All other chemicals including acrylonitrile were of reagent grade and used as received. Twice distilled, freshly boiled water was employed throughout.

Instrumentation.—Optical densities were measured on a Shimadzu Graphicord (UV-240) spectrophotometer. E.p.r. spectra were recorded with a Varian EPR 4 *X*-band spectrometer; reactant solutions containing 2 mmol complex were measured at varying stages in their reactions. Microanalytical data (C, H) were obtained with use of a Perkin-Elmer 240C elemental analyser. pH Measurements were made with a Systronics digital pH meter (model 335) having a combined glass–calomel electrode assembly with gelled electrolyte (Gamma Instrument). Such electrodes did not interfere with pH measurements in perchlorate media.

Before each measurement the pH meter was calibrated against standard aqueous buffers. The $[H^+]$ values were obtained from a calibration curve formed by plotting meter reading against the $[H^+]$ of standard acid and alkali solutions.

Kinetics and Data Analyses.—The decay in solution absorbance with time was followed at 560 nm in the presence of large excess of the reducing agent and Hpd over the complex. Ionic strength was maintained at 1.0 mol dm^{-3} using $NaClO_4$. First-order rate constants, k_0, were evaluated from $\log_{10}A$ against time data using a built-in linear least-squares program of a Casio-3600 P calculator. Associated errors were estimated using standard formulas. The second-order rate constants (k'_c, k_h, *etc.* see later), the equilibrium constant K_c, and associated errors were calculated by solving the appropriate rate law [equation (12) for example] with the help of the Lotus 123 spread sheet and its ability to solve simultaneous equations and perform regression analysis.[29] The appropriate rate law was first rearranged to a form $y = ax_1 + bx_2 + cx_3 \ldots$ and thus solved for $a,b,c \ldots$ The kinetic and thermodynamic constants were calculated from $a,b,c \ldots$, the coefficients of dependent variables $x_1, x_2, x_3 \ldots$

Product Analyses.—Analyses were generally carried out after all Mn^{III} had reacted under the kinetic conditions. As suggested by a referee, some quenching experiments were carried out at different time intervals where approximately 40 and 70% Mn^{III} was consumed. Free pentane-2,4-dione was determined colorimetrically at 510 nm using *o*-phenylenediamine as the colour-forming reagent;[30] glyoxylate or Mn^{2+} does not interfere. Glyoxylate, on the other hand, was determined colorimetrically[31] at 520 nm under conditions where pentane-2,4-dione or Mn^{2+} does not interfere.

Results and Discussion

Product and Stoicheiometry.—At 30 °C and pH 4.5, 1 mol of

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† *Non-S.I. unit employed:* G = 10^{-4} T.

Table 1. Determination of the average pentane-2,4-dione consumption ratio at 30 °C, pH 4.5

$[Mn(pd)_3]$/ mmol dm^{-3}	$[Hpd]_0$/ mmol dm^{-3}	[glyoxylate]/ mol dm^{-3}	$P = \frac{\lvert\Delta[Hpd]_0\rvert}{\lvert\Delta[Mn^{III}]\rvert}$
2.0	6.0	0.02	1.0[a]
2.0	6.0	0.04	1.15
2.0	6.0	0.06	1.06
2.0	7.0	0.04	1.11[b]
2.0	8.0	0.06	1.02[c]
2.0	9.0	0.02	1.12
		av. =	1.07 ± 0.05

[a] Reaction media purged with purified dinitrogen. [b] In absence of ambient light. [c] $P = 1.09$ for consumption of 40% Mn^{III} (quenching experiment).

Table 2. Determination of the average glyoxylate consumption ratio at 30 °C, pH 4.5

$[Mn(pd)_3]$/ mmol dm^{-3}	$[Hpd]_0$/ mmol dm^{-3}	[glyoxylate]/ mol dm^{-3}	$G = \frac{\lvert\Delta[\text{glyoxylate}]\rvert}{\lvert\Delta[Mn^{III}]\rvert}$
1.0	3.0	0.01	0.03
2.0	6.0	0.02	0.04[a]
2.0	6.0	0.01	0.00[b]
3.0	9.0	0.01	0.01
4.0	12.0	0.01	0.02[c]
		av. =	0.02 ± 0.014

[a] Reaction media purged with purified dinitrogen. [b] In absence of ambient light. [c] $G = 0.01$ for consumption of 70% Mn^{III} (quenching experiment).

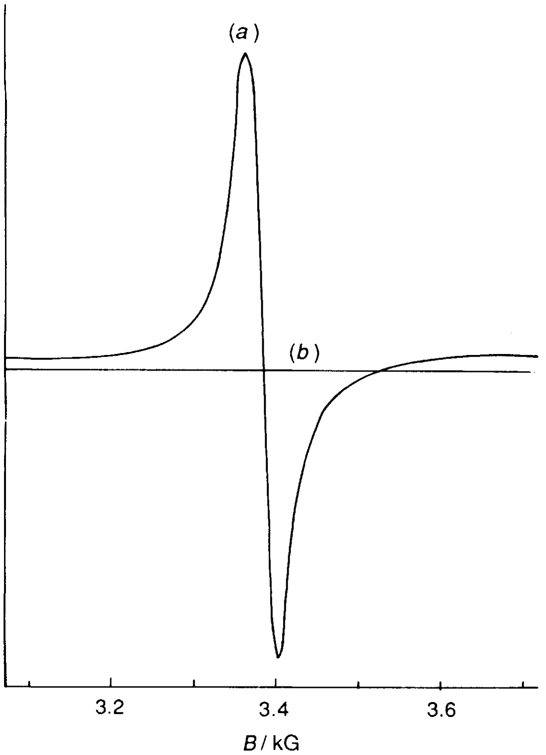

Figure 1. *X*-Band e.p.r. spectra of Mn^{III}–pd complexes in aqueous solution. [complex] = 2 mmol dm^{-3}, $[Hpd]_0$ = 0.5 mol dm^{-3}, pH 7.5, [glyoxylate] = 0.1 mol dm^{-3}, gain 1.6×10^3. (*a*) Within 5 min of mixing, (*b*) after completion of reaction; when amplified (gain 8×10^3) a spectral pattern typical for Mn^{II} in Hpd is obtained. No other resonance was observed in the extended scan range 0—10 kG

pentane-2,4-dione is consumed per mol of Mn^{III} reduced (Table 1), but within the limits of experimental error no glyoxylic acid is consumed during the reaction under the kinetic conditions (Table 2). The same results were obtained also in the quenching experiments which thus ensures completeness of all the reactions under the experimental conditions. The reaction rate, however, increases with increasing concentration of glyoxylate ion. Thus, in all probability the overall reaction (1) represents

$$Mn^{III} + Hpd + gox^- \longrightarrow Mn^{II} + \text{Oxidation product(s) of } Hpd + gox^- \quad (1)$$

a glyoxylate-catalysed oxidation of acetylacetone by the manganese(III) complexes. Here gox = glyoxylate anion, $CHOCO_2^-$, or its monohydrated form[32] $CH(OH)_2CO_2^-$. Stoicheiometric measurements were not possible at higher pH where the complex is soluble only in the presence of a large excess of Hpd (>0.2 mol dm^{-3}). At higher pH insoluble hydrolytic species are formed unless excess of Hpd is present to suppress hydrolytic decomposition reactions.

E.P.R. Measurements.—A single resonance without any hyperfine splitting at $g = 2.006$ is observed within 0—10 kG (receiver gain 1.6×10^3) (Figure 1). The same resonance is observed[33] also with thiosulphate as the reducing agent and even in the absence of a reducing agent. However, the e.p.r. intensity in the absence of reducing agent is about 20 times weaker (barely perceptible at receiver gain = 3.2×10^3) than that in its presence. It is likely, therefore, that the resonance does not arise from the reducing agents. Now it is known that $[Mn(pd)_3]$ (a d^4 system) is e.p.r. silent and that the e.p.r. spectrum of $[Mn^{IV}(pd)_3]^+$ is completely different[3] from that observed here. The observed resonance is, therefore, due to the radical of pentane-2,4-dione.[34,35,*] The signal decays with time and finally there appears the pattern (weak) of a solution of Mn^{II} ($I = \frac{5}{2}$) in aqueous pentane-2,4-dione (not shown in Figure 1).

Kinetics.—Dependence of the reducing agent. The decrease in absorbance at 560 nm at [glyoxylate] ≫ $[Mn^{III}]$ follows first-order kinetics up to the maximum extent (90%) of the reaction studied. Some representative first-order rate constants, k_0, are given in Table 3. A four-fold variation in the concentration of glyoxylate demonstrates a Michaelis–Menton type of relation (2) (see Figure 2) at constant acidity, $[Hpd]_0$ (= total pentane-2,4-dione added) and ionic strength, where $[gox]_0$ is the total

$$k_0 = \frac{A[gox]_0}{B + C[gox]_0} \quad (2)$$

glyoxylate and *A*, *B*, and *C* are constants at a given pH and $[Hpd]_0$. This suggests the formation of an intermediate adduct between the oxidant and glyoxylate. Formation of an adduct is indicated also by a modest but significant spectral change observed immediately after the addition of glyoxylate (see Figure 3). This is followed by a slow decay in absorbance.

Dependence on pH. Other conditions remaining the same, k_0 decreases with increasing pH. The change at 20 °C is, however, barely appreciable.

Dependence on $[Hpd]_0$. Rate constant k_0 decreases with increasing $[Hpd]_0$ under otherwise similar reaction conditions.

Dependence on other conditions. Rate constant k_0 does not change appreciably upon a five-fold variation in [complex]

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[*] A very similar e.p.r. spectrum was observed in the course of the thermal decomposition of $[Ru(pd)_3]$ in acid perchlorate media (B. Chakraborty, personal communication).

Table 3. Some representative first-order rate constants for the reaction of Mn^{III}–pd complexes under different conditions[a]

			$10^4\ k_0/s^{-1}$							
			20		30		35		40 °C	
$[Hpd]_0$/ mol dm^{-3}	pH	$[gox]_0$/ mol dm^{-3}	exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.
0.5	5.5	0.1	0.324	0.323	1.26[b]	1.25	2.48	2.41	4.66	4.64
0.5	6.0	0.1	0.32	0.323	1.26	1.25	2.38	2.40	4.53	4.60
0.5	6.5	0.1	0.323	0.323	1.25	1.25	2.33	2.39	4.48	4.53
0.5	7.0	0.1	0.328	0.321	1.20	1.22	2.32	2.32	4.33	4.30
0.5	7.5	0.1	0.334	0.321	1.22[c]	1.20	2.28	2.24	4.16	4.12
0.8	7.5	0.1	0.266	0.275	0.916	0.906	1.66	1.6	2.8	2.83
0.25	7.5	0.1	0.4	0.393	1.65	1.66	3.16	3.33	6.66	6.55
0.2	7.5	0.1	0.415	0.41	1.77	1.82	3.5	3.7	7.30	7.45
0.15	7.5	0.1	0.434	0.428	2.0	1.96	4.26	4.16	8.66	8.62
0.1	7.5	0.1	0.454	0.43	2.27	2.16	4.65	4.73	10.0	10.2
0.5	7.5	0.08	0.292	0.303	1.03	1.06	1.96	1.91	3.5	3.45
0.5	7.5	0.12	0.337	0.348	1.30	1.33	2.46	2.52	4.6	4.70
0.5	7.5	0.15	0.35	0.366	1.52	1.49	2.93	2.88	5.67	5.5
0.5	7.5	0.2	0.396	0.395	1.70	1.69	3.33	3.33	6.67	6.63
0.5	7.5	0.25	0.403	0.411	1.92	1.95	3.68	3.75	7.36	7.5
0.5	7.5	0.3	0.433	0.423	2.07	2.0	4.08	4.06	8.30	8.3

[a] Unless otherwise stated, [complex] = 2 mmol dm^{-3}, I = 1.0 mol dm^{-3}. [b] $k_0 = (1.26 \pm 0.02) \times 10^{-4}\ s^{-1}$ for [complex] = 1—5 mmol dm^{-3}; it does not change appreciably (within 6%) when ambient light was totally excluded. [c] k_0 was invariant (within 5%) when the kinetics were measured after purging the reaction medium with purified dinitrogen. $k_0 = (1.21 \pm 0.01) \times 10^{-4}\ s^{-1}$ for $[Mn^{2+}]$ = 0—0.01 mol dm^{-3}.

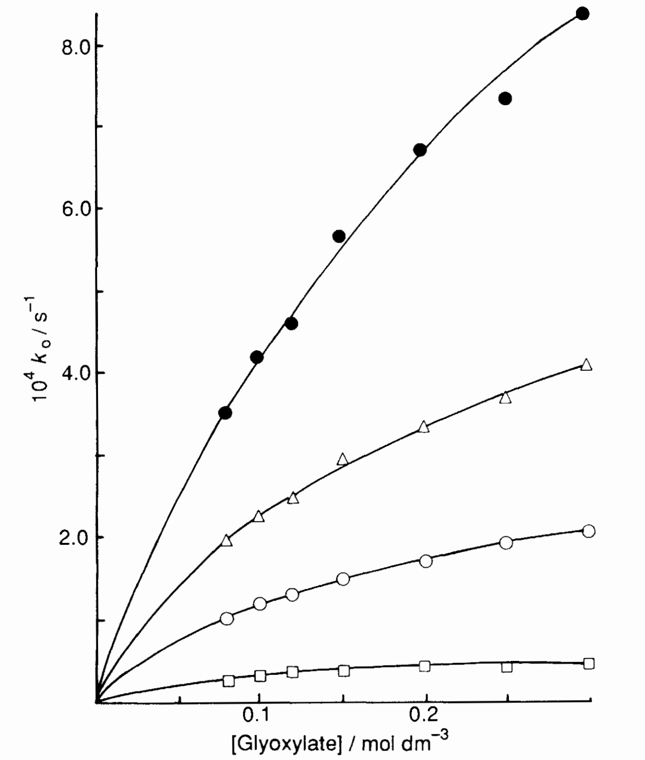

Figure 2. Dependence of k_0 on [glyoxylate] at [complex] = 2.0 mmol dm^{-3}, $[Hpd]_0$ = 0.5 mol dm^{-3}, pH 7.5, and I = 1.0 mol dm^{-3}. The solid lines were drawn using the fitted data. Temperature: 20 (□), 30 (○), 35 (△), and 40 °C (●)

(1—5 mol dm^{-3}), upon the addition of excess of $Mn(ClO_4)_2$ (up to 0.01 mol dm^{-3}), and in the presence of dissolved oxygen and ambient light.

Mechanism.—Known hydrolysis constants[36] of $[Mn(pd)_3]$ and u.v.–visible spectral studies of solutions of $[Mn(pd)_3]$ containing different amounts of $[Hpd]_0$ at different pH suggest that under the experimental conditions a solution at equilibrium contains $[Mn(pd)_3]$, $[Mn(pd)_2(H_2O)_2]^+$, and $[Mn(pd)_2(H_2O)(OH)]$. Equation (2) and Figure 3 suggest that an adduct, plausibly $[Mn(pd)_2(gox)]$ (see p. 4 and Figure 4) is also formed when excess of glyoxylate is added. No free Hgox (pK_a 3.2)[37] exists within the experimental pH interval. These known equilibria along with the kinetic results discussed earlier are consistent with the Scheme in equations (3)—(10). In this Scheme we have not considered the slow background autodecomposition reaction of the complex, because its rate is only 3—8% of the rate of reaction with glyoxylate. The predicted rate law for the Scheme is (11) where $K_2 = K^{H}_{1}/K$, $K' = K^{H}_{1}K_h$, and $k_c' = K_c k_c$. Values of k_c', k_h, and K_c and the

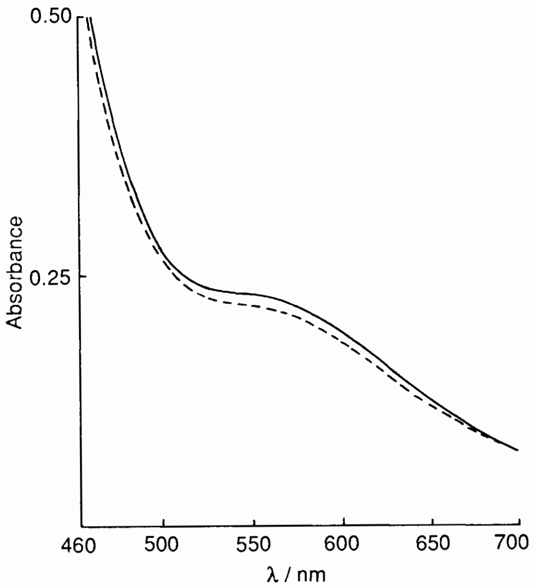

Figure 3. Spectral change observed immediately after addition of glyoxylate: (*a*) [complex] = 2 mmol dm^{-3}, $[Hpd]_0$ = 0.5 mol dm^{-3}, pH 5.5; (*b*) as in (*a*) but with 0.1 mol dm^{-3} glyoxylate

$$[\mathrm{Mn(pd)_3}] + \mathrm{H^+} + 2\mathrm{H_2O} \rightleftharpoons [\mathrm{Mn(pd)_2(H_2O)_2}] + \mathrm{Hpd};\quad K_1^{\mathrm{H}} = 1.22 \times 10^5 \qquad (3)$$

$$[\mathrm{Mn(pd)_2(H_2O)_2}]^+ \rightleftharpoons [\mathrm{Mn(pd)_2(H_2O)(OH)}] + \mathrm{H^+};\quad K_{\mathrm{h}} = 5 \times 10^{-8}\ \mathrm{mol\ dm^{-3}} \qquad (4)$$

$$\mathrm{pd^-} + \mathrm{H^+} \rightleftharpoons \mathrm{Hpd};\ K = 8.8 \times 10^8\ \mathrm{dm^3\ mol^{-1}} \qquad (5)$$

$$[\mathrm{Mn(pd)_2(H_2O)_2}]^+ + \mathrm{gox^-} \overset{K_c}{\rightleftharpoons} [\mathrm{Mn(pd)_2(gox)}] + 2\mathrm{H_2O} \qquad (6)$$

$$[\mathrm{Mn(pd)_2(gox)}] \xrightarrow{k_c} \mathrm{Mn^{II}} + \mathrm{gox^{\bullet}} \qquad (7)$$

$$[\mathrm{Mn(pd)_2(H_2O)(OH)}] + \mathrm{gox^-} \xrightarrow{k_h} \mathrm{Mn^{II}} + \mathrm{gox^{\bullet}} \qquad (8)$$

$$\mathrm{gox^{\bullet}} + \mathrm{pd^-} \xrightarrow{\text{fast}} \mathrm{gox^-} + \mathrm{pd^{\bullet}} \qquad (9)$$

$$\mathrm{pd^{\bullet}} \xrightarrow{\text{fast}} \text{Products} \qquad (10)$$

Scheme.

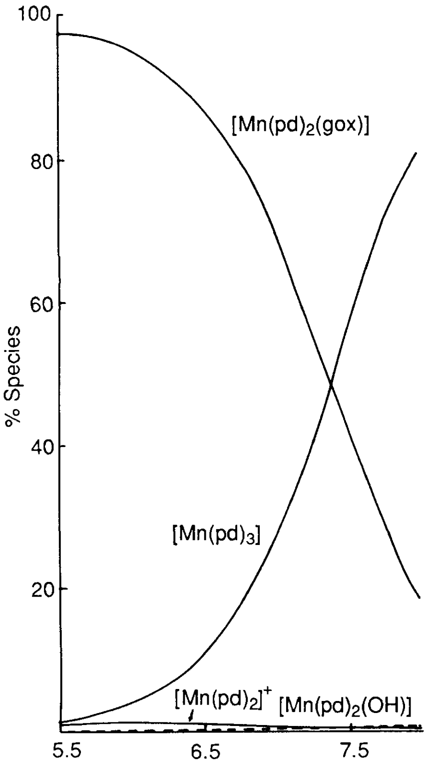

Figure 4. pH Dependence of the percentage of different manganese(III) species assuming the Scheme. $[\mathrm{Hpd}]_0$ = 0.5 mol dm^{-3}, [gox] = 0.1 mol dm^{-3}, I = 1.0 mol dm^{-3}, and 30 °C

associated errors (Table 4) were evaluated from equation (12)

$$-\,\mathrm{d}[\mathrm{Mn^{III}}]/\mathrm{d}t = k_0[\mathrm{Mn^{III}}] \qquad (11)$$

$$k_0 = \frac{(k'_cK_1^{\mathrm{H}}[\mathrm{H^+}] + k_hK')[\mathrm{gox}]}{P[\mathrm{Hpd}]_0 + K_cK_1^{\mathrm{H}}[\mathrm{H^+}][\mathrm{gox}]} \qquad (12)$$

$$\mathrm{P} = 1 + \frac{K_2(1 + K[\mathrm{H^+}])}{[\mathrm{Hpd}]_0} + \frac{K_hK_2(1 + K[\mathrm{H^+}])}{[\mathrm{Hpd}]_0[\mathrm{H^+}]} \qquad (13)$$

Table 4. Rate constants and activation parameters for the reaction of glyoxylate with Mn$^{\mathrm{III}}$–pd complexes^a

T/°C	10^4k_c/s^{-1}	10^2k_h/dm^3 mol^{-1} s^{-1}	$K_c{}^b$/dm^3 mol^{-1}
20	0.324 ± 0.004	2.63 ± 0.08	2 184 ± 108
30	1.27 ± 0.03	9.58 ± 0.26	902 ± 42
35	2.45 ± 0.08	17.8 ± 0.05	693 ± 37
40	4.76 ± 0.13	32.6 ± 0.5	426 ± 16
$\Delta H^‡$/ kJ mol^{-1}	100 ± 3	96 ± 3	
$\Delta S^‡$/ J K^{-1} mol^{-1}	9 ± 20	52 ± 21	

^{a} [complex] = 2 mmol dm^{-3}, I = 1.0 mol dm^{-3}. ^{b} ΔH = −63 ± 6 kJ mol^{-1}; ΔS = −152 ± 40 J K^{-1} mol^{-1}.

as stated earlier using known values of K_h, K_1^{H}, and K.[28,36] Values of k_c $(=k'_c/K_c)$ were then calculated. Activation parameters corresponding to k_c and k_h (see Table 4) were evaluated using the Eyring equation and a linear least-squares program as usual. These k_c, k_h, and K_c values reproduce individual k_0 values within 7% (see Table 3). A species distribution graph constructed using the equilibrium constants is shown in Figure 4.

The $E_{\frac{1}{2}}$ value for the pd$^-$–pd$^{\bullet}$ couple is 0.58 V (*vs.* n.h.e.)[3] and pd$^-$ can be oxidised to pd$^{\bullet}$ by various oxidants like NiO(OH), $\mathrm{KMnO_4}$, Cr$^{\mathrm{VI}}$,[38] and $[\mathrm{PtX_6}]^{2-}$.[39] Acid-catalysed thermal decomposition of $[\mathrm{Co(pd)_3}]$[40] and u.v. irradiation[41] of an alcoholic solution of $[\mathrm{Mn(pd)_3}]$ also produce pd$^{\bullet}$ which subsequently forms[38] α,α,β,β-tetra(pentane-2,4-dione) or decomposes to acetone and/or acetic acid.[40,41] The radical gox$^{\bullet}$ is likely to be an oxidant for pd$^-$ and reaction (9) seems fairly probable. It has been shown[42] that in an aqueous solution of Mn$^{\mathrm{II}}$ containing excess of Hpd the oxidation of Hpd is much more facile than that of Mn$^{\mathrm{II}}$. In the present system, therefore, it is likely that gox$^{\bullet}$ will preferentially oxidise pd$^-$ rather than Mn$^{\mathrm{II}}$.

We tested whether the experimental k_0 values could be fitted to schemes involving the same equilibrium steps (3)—(6), but with different combinations of other kinetic steps, *e.g.* (*i*) reaction (14) with the k_c and k_h paths, (*ii*) k_1 and k_c path only,

$$[\mathrm{Mn(pd)_3}] + \mathrm{gox^-} \xrightarrow{k_1} \mathrm{Mn^{II}} + \mathrm{gox^{\bullet}} \qquad (14)$$

(*iii*) k_1 and k_h path only, (*iv*) a reaction involving only the k_c path, and (*v*) a reaction involving only the k_h path. In these schemes K_c was allowed to vary. Combination (*i*) gave $k_1 \approx 0$; (*ii*) failed in the higher pH range, calculated k_0 values being too low. Condition (*iii*) signifies $[\mathrm{Mn(pd)_2(gox)}]$ to be a kinetic 'dead-end' and assumes decay of the complexes only through the k_1 and k_h paths; step (7) or any kinetic equivalent of it has been excluded. This combination thus denies kinetic significance for any interaction between $[\mathrm{Mn(pd)_2(H_2O)_2}]^+$ and gox$^-$. Hence this cannot reproduce k_0 data at low pH/low $[\mathrm{Hpd}]_0$. Scheme (*iv*) fails at high pH, while (*v*) fails at low pH.

The K_c values are about an order of magnitude larger than the third formation constants of glyoxylate complexes of tripositive rare-earth-metal cations.[37] Such high K_c values are improbable for an outer-sphere adduct and the postulation of the inner-sphere adduct $[\mathrm{Mn(pd)_2(gox)}]$ seems justified. As in the case of lanthanides, the speculated binding sites of glyoxylate with $[\mathrm{Mn(pd)_2(H_2O)_2}]^+$ are the hydroxo- and the carboxylato-groups in the monohydrated glyoxylate anion, $\mathrm{CH(OH)_2CO_2}^-$. Electron transfer within $[\mathrm{Mn(pd)_2(gox)}]$ as postulated in step (7) may then lead to the products.

Alternatively an outer-sphere mechanism where $[Mn(pd)_2(gox)]$ is a 'dead-end' but outer-sphere electron transfer occurs from gox^- to manganese(III) species could also operate. This signifies combination (*iii*), with the additional kinetic step (15). This mechanism, however, appears less attractive because manganese(III) carboxylato complexes like $[Mn(C_2O_4)]^+$, $[Mn(C_3H_2O_2)]^+$, $[Mn(MeCO_2)]^+$, and the glycolate complex are known to be redox active[43] and it is unlikely that $[Mn(pd)_2(gox)]$ would be a redox-inactive, kinetically inert species. The possibility of a mixed outer-sphere–inner-sphere path cannot be ruled out, however.

$$[Mn(pd)_2(H_2O)_2]^+ + gox^- \xrightarrow{k_2} Mn^{II} + gox^\bullet \quad (15)$$

The complex $[Mn(pd)_3]$ is kinetically labile (estimated ligand exchange rate 1 s^{-1} at 25 °C in MeCN)[44] and its direct ligand exchange with gox^- to form $[Mn(pd)_2(gox)]$ without intervention of the aqua species $[Mn(pd)_2(H_2O)_2]^+$ should be considered. However, the equilibrium constant for the reaction (16) is only 0.1. It is likely therefore that $[Mn(pd)_2(gox)]$ is formed almost exclusively through reaction (6) for which the equilibrium constant K_c is of the order of 10^2—10^3 dm^3 mol^{-1}.

$$[Mn(pd)_3] + gox^- \rightleftharpoons [Mn(pd)_2(gox)] + pd^- \quad (16)$$

Unambiguous assignment of the intimate mechanism for the k_h path is more difficult. However, it has been suggested earlier by Macartney and Sutin[45] that in oxidation reactions by Mn^{III} the aqua path should be much more important than the hydroxo path for a given outer-sphere reductant. Since this is not the case in this system, an inner sphere mechanism may be operative for the k_h path *via* the plausible intermediate $[Mn(pd)_2(gox')(OH)]^-$ where gox′ represents unidentate glyoxylate ion. Unidentate behaviour of glyoxylate anion has been suggested earlier.[37]

Acknowledgements

We are indebted to the University Grants Commission (New Delhi) for financial support.

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Received 14*th February* 1990; *Paper* 0/00699H