Thiosulphate-catalysed Reduction of Tris(acetylacetonato)-manganese(III) and its Hydrolytic Derivatives in Aqueous Perchlorate Media†

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The kinetics of reactions of $S_2O_3^{2-}$ with $[Mn(acac)_3]$ (Hacac = acetylacetone) and its derivatives $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$ have been investigated in aqueous perchlorate media containing different total quantities of acetylacetone (c_{acac}) over the range pH 4.2–8.5. The observed dependences of the reaction rates on pH and c_{acac} arise from hydrolytic equilibria of $[Mn(acac)_3]$. The reaction is first order in $[S_2O_3^{2-}]$ but consumes no $S_2O_3^{2-}$. Instead, 1 mol of acetylacetone is consumed per mol of Mn^{III} reduced. EPR and kinetic data suggest a $S_2O_3^{2-}/S_2O_3^{-}$ catalytic cycle which provides a low-energy path for the acac $\longrightarrow$ Mn^{III} electron transfer. Rate constants for reduction of $[Mn(acac)_3]$ (k_1), $[Mn(acac)_2(H_2O)_2]^+$ (k_2) and $[Mn(acac)_2(H_2O)(OH)]$ (k_3) follow the sequence $k_1 < k_2 \approx k_3$. An inner-sphere mechanism seems plausible for the k_2 and the k_3 paths; k_1 probably involves an outer-sphere process.

Manganese plays an essential role in photosynthetic water oxidation[1–5] and in the autooxidation of sulphur(IV)[6–10] in flue gas scrubber, atmospheric water droplets and biological systems. The mechanisms of these cyclic redox processes are unknown, but manganese(III) is believed to be an intermediate.[11–13]

The kinetics of oxidation of inorganic and organic substrates by Mn^{III} have therefore attracted attention, but so far they are largely limited to oxidations by Mn^{3+} (aq) and $[Mn(OH)]^{2+}$ (aq).[14–17] Both these species are metastable in solution and their reactions with reductants can be investigated only in the presence of high $[H^+]$ and $[Mn^{2+}]$. This, coupled with the lability of Mn^{3+} and Mn^{2+}, is a stumbling block in the elucidation of mechanisms. Such problems are likely to be less serious with manganese(III) complexes because complexation often decreases kinetic lability, improves selectivity and increases solution stability of oxidizing aquametal ions.

Various β-diketones effectively stabilize[18] manganese(III) through the formation of β-diketoenolate complexes. The extent of such stabilization increases with increase in the pK_a value of the ligand. Pentane-2,4-dione (acetylacetone Hacac) has a fairly high pK_a (8.9) and forms the well characterized[19–22] six-coordinate, mononuclear complex $[Mn(acac)_3]$. The corresponding bis complex $[Mn(acac)_2(H_2O)_2]^+$ has also been described[23] and is a relatively rare[24] example of a cationic complex of manganese(III).

As might be expected for a high-spin d^4 metal-ion system, the tris complex $[Mn(acac)_3]$ is distorted from a regular octahedral geometry[19,25] due to the Jahn–Teller effect. It has been utilized as a free-radical generator and as a one-equivalent oxidant in selective organic syntheses.[26,27] The redox thermodynamics for the couples Mn^{III}–Mn^{IV} and Mn^{III}–Mn^{II} for $[Mn(acac)_3]$ have been discussed[3] in relation to the water oxidation process of photosystem II and the kinetics of redox reactions involving $[Mn(acac)_3]$ have been reported,[28,29] but no data are available on the redox kinetics of its hydrolytic derivatives. For this reason, the present investigation, which covers a fairly wide pH range, was initiated.

Experimental

Materials.—Solid tris(acetylacetonato)manganese(III), $[Mn(acac)_3]$, was synthesised by the literature method[23,30,31] {Found: C, 51.1; H, 6.1. Calc. for $[Mn(acac)_3]$: C, 51.1; H, 6.00%}.

Acetylacetone (LOBA, G.R.) was purified by washing with 2 mol dm^{-3} NaOH, followed by water. After drying over anhydrous sodium sulphate it was distilled under reduced pressure.

Sodium thiosulphate pentahydrate (S.D. Fine Chemicals, A.R.) solutions were freshly prepared and standardized iodometrically before use. Sodium perchlorate solution, used to maintain ionic strength, was prepared by neutralization 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 standardized by ion exchange through Dowex 50W X8 cation exchanger in the H^+ form.

All other chemicals were of reagent grade and used as received. Twice distilled, freshly boiled water was employed throughout.

Instrumentation.—Absorbances were measured on a Shimadzu Graphichord (UV-240) spectrophotometer. EPR spectra were recorded with a Varian EPR 4 X-band spectrometer; spectra of reactant solutions containing 2 mmol dm^{-3} complex were run at varying stages of their reactions. Microanalytical data (C, H) were obtained with a Perkin-Elmer 240C elemental analyser. pH measurements were made with a Systronics (model 335) digital pH meter having a combined glass–calomel electrode assembly. All reported pH values were calibrated against standard aqueous buffers.

Product Analyses.—Analyses were carried out after Mn^{III} had reacted completely under kinetic conditions. Sulphate was tested for with a saturated solution of $BaCl_2$ followed by acidification with HCl. Free acetylacetone was determined colorimetrically at 510 nm using *o*-phenylenediamine as the colour-forming reagent.[32] We verified that neither Mn^{2+} nor $S_2O_3^{2-}$ interferes in this determination. Thiosulphate in the product solution was quantified iodimetrically under conditions where $[S_2O_3^{2-}] > 10^{-4}$ mol dm^{-3} is measurable and acetylacetone does not interfere.

Kinetic Measurements.—In aqueous media the UV–VIS

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

Table 1 Determination of the average acetylacetone consumption ratio at 30 °C, pH 4.5, 2.0 mmol dm^{-3} [Mn(acac)$_3$]

c_{acac}/ mmol dm^{-3}	[$S_2O_3^{2-}$]/ mol dm^{-3}	$A = \frac{\lvert\Delta(c_{acac})\rvert}{\lvert\Delta[\mathrm{Mn^{III}}]\rvert}$
6.0	0.01	0.975
6.0	0.02	1.15[a]
6.0	0.04	1.02[b]
9.0	0.06	1.25
8.0	0.1	1.00
7.0	0.02	1.14
		av. = 1.09 ± 0.1

[a] In absence of ambient light. [b] Reaction media purged with purified nitrogen.

Table 2 Determination of average thiosulphate consumption ratio at 30 °C, pH 4.5

[Mn(acac)$_3$]/ mmol dm^{-3}	c_{acac}/ mmol dm^{-3}	[$S_2O_3^{2-}$]/ mol dm^{-3}	$S = \frac{\lvert\Delta[S_2O_3^{2-}]\rvert}{\lvert\Delta[\mathrm{Mn^{III}}]\rvert}$
2.0	6.0	0.002	0.02[a]
2.0	6.0	0.01	0.00
3.0	9.0	0.01	0.08
4.0	12.0	0.01	0.04[b]
			av. = 0.035 ± 0.029

[a] Reaction media purged with purified nitrogen. [b] In absence of ambient light.

spectrum of [Mn(acac)$_3$] exhibits a shoulder at 560 nm. Disappearance of Mn^{III} in the presence of excess (30–150 fold) thiosulphate was generally followed at this wavelength using a sample quenching technique. The product solution at this wavelength is practically non-absorbing. The autodecomposition rate of the complex was measured in the absence of thiosulphate but under otherwise similar conditions.

Ionic strength was maintained by the addition of NaClO$_4$. No external buffer was used because the pH change during the reactions was less than 0.05 unit. Under these conditions the pseudo-first-order rate constants, k_0, were evaluated from the slopes of $\log_{10} A$ against time data using a built-in linear least-squares program of a Casio (*fx* 3600 P) calculator. Associated errors were estimated using standard formulas. The second-order rate constants (k_1, k_2, k_3, *etc.*, see later) and associated errors were calculated by solving the appropriate rate law [equation (13) for example] with the help of the Lotus 123 spread sheet and its ability to solve simultaneous equations and perform regression analysis. 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. ... The kinetic and thermodynamic constants were calculated from a, b, c ... *i.e.* the coefficients of dependent variables x_1, x_2, x_3. ...

Results and Discussion

Product and Stoichiometry.—Saturated BaCl$_2$ solution produces a milky white precipitate with the product solution, but this disappears on acidification, indicating the absence of SO_4^{2-} in the product. At 30 °C, pH 4.5, 1 mol of acetylacetone is consumed for each mol of manganese(III) complex disappeared during the autodecomposition reaction and the reaction of Mn^{III} with excess of $S_2O_3^{2-}$ (Table 1).

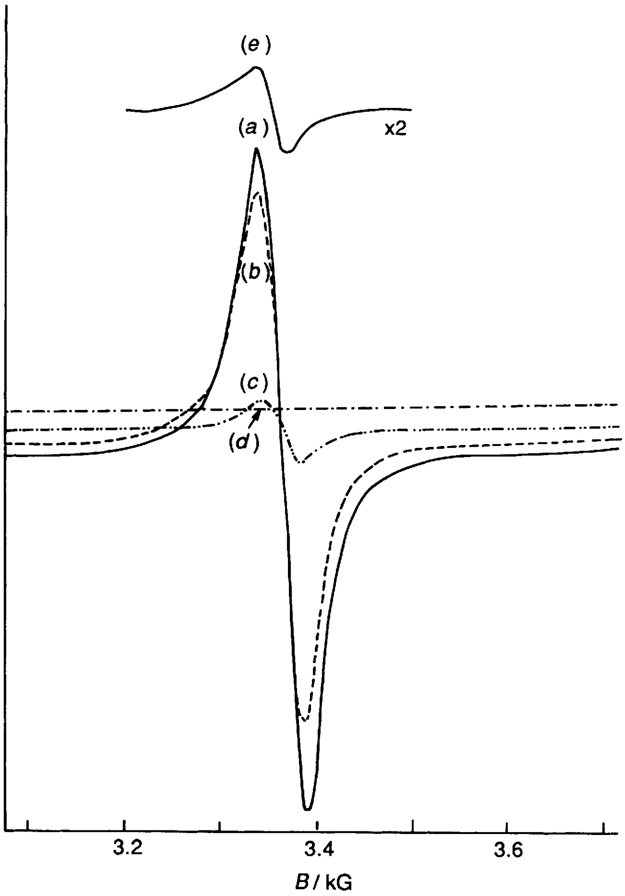

Fig. 1 X-Band EPR spectra of Mn^{III}–acac complexes in aqueous solution at different times [(*a*) 0, (*b*) 42, (*c*) 87 and (*d*) 167 min] after preparation: [complex] = 0.002 mol dm^{-3}, c_{acac} = 0.5 mol dm^{-3}, pH 7.5, [$S_2O_3^{2-}$] = 0.2 mol dm^{-3}, gain 1.6 × 10^3. When (*d*) was amplified (gain, 3.2 × 10^3) a weak spectral pattern typical of Mn^{II} (not shown) was obtained. Spectra similar to (*a*)–(*d*) are obtained when $S_2O_3^{2-}$ is replaced by glyoxylate. (*e*) [complex] = 0.002 mol dm^{-3}, c_{acac} = 0.5 mol dm^{-3}, pH 7.5, no added reductant; spectra recorded immediately after mixing; gain 3.2 × 10^3. No other resonance was observed in the extended scan range 0–10 kG

$$4S_4O_6^{2-} + 6OH^- \longrightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \quad (1)$$

Under similar reaction conditions little $S_2O_3^{2-}$ is consumed, in spite of the first-order dependence of the reaction on [$S_2O_3^{2-}$]. The near-zero value of the consumption ratio, *S*, for thiosulphate (see Table 2) does not result from disproportionation[33] [for example,[34] equation (1)] of an oxidation product of $S_2O_3^{2-}$ because such disproportionations are extremely slow[35] below pH 9. Furthermore, it was verified that the low c_{acac} (=[Hacac] + [acac$^-$]) used in these measurements did not interfere with the iodimetric determinations of unreacted $S_2O_3^{2-}$. The stoichiometric results, therefore, indicate that acetylacetone but not $S_2O_3^{2-}$ is oxidized by manganese(III). The overall reaction (2) then represents a $S_2O_3^{2-}$-catalysed

$$\mathrm{Mn^{III}} + \mathrm{Hacac} + S_2O_3^{2-} \longrightarrow \mathrm{Mn^{II}} + \text{oxidation product of Hacac} + S_2O_3^{2-} \quad (2)$$

oxidation reaction of acetylacetone by the manganese(III) complex.

Stoichiometric measurements could not be made at higher pH, where the complex dissolves in water only in the presence of a large excess of acetylacetone (>0.2 mol dm^{-3}).

EPR Measurements.—A weak resonance is observed at g = 2.006 during the autodecomposition of [Mn(acac)$_3$], the intensity of which increases almost 20 times when $S_2O_3^{2-}$ or glyoxylate is added (Fig. 1). No other resonance is observed over the range 0–10 kG. The resonance at g = 2.006 is not due to $S_2O_3^-$ for which $g \approx 2.1$,[36] neither is this due to

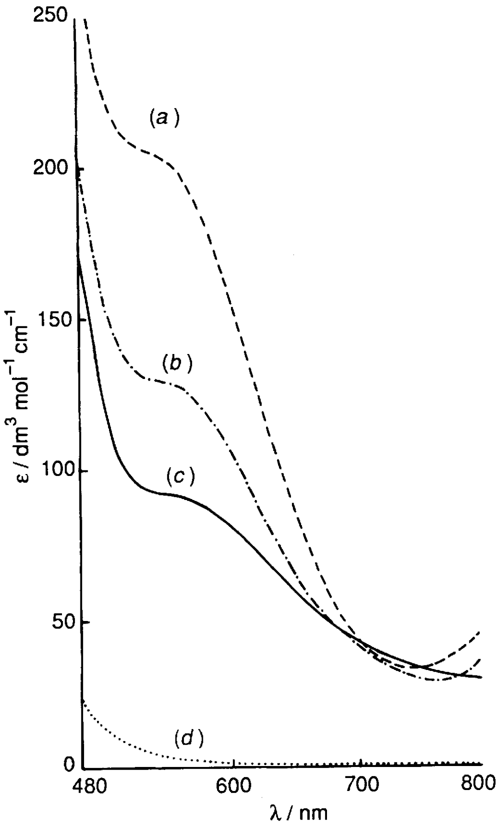

Fig. 2 Visible absorption spectra of Mn^{III}–acac complexes in aqueous media. Total [Mn^{III}(acac)$_3$] added = 2.0 mmol dm^{-3}, 30 ± 1 °C. (*a*) 0.5 mol dm^{-3} acetylacetone, pH 7.5; (*b*) c_{acac} = 0.5 mol dm^{-3}, pH 4.5; (*c*) c_{acac} = 0.1 mol dm^{-3}, pH 4.5; (*d*) c_{acac} = 0.5 mol dm^{-3}, pH 7.5 in presence of 0.2 mol dm^{-3} $S_2O_3^{2-}$ after complete reaction Spectrum (*d*) is very similar to that of a solution containing 2.0 mmol dm^{-3} Mn(ClO$_4$)$_2$ in 0.5 mol dm^{-3} acetylacetone at pH 7.5

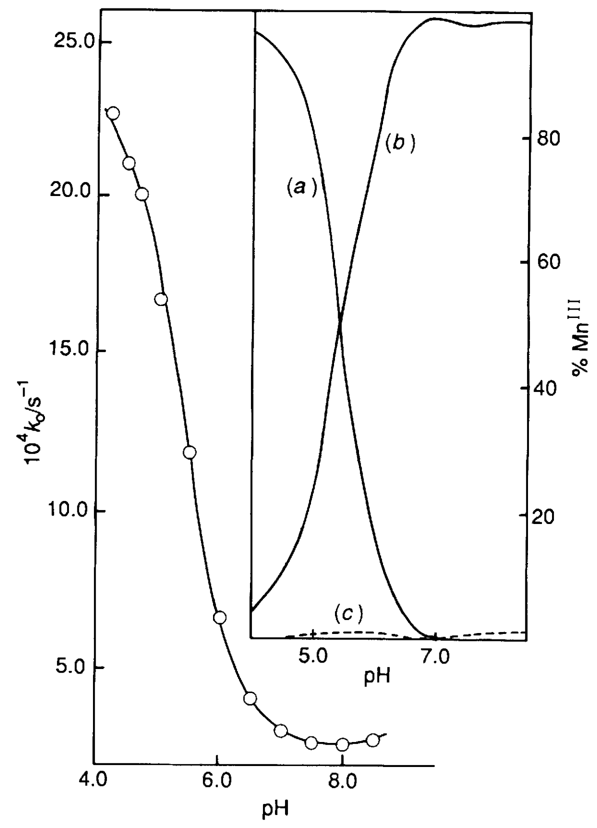

Fig. 3 Dependence of first-order-rate constant k_0 on pH at [complex] = 2 mmol dm^{-3}, c_{acac} = 0.5 mol dm^{-3}, [$S_2O_3^{2-}$] = 0.1 mol dm^{-3}, I = 1.0 mol dm^{-3} at 40 °C. The solid line is drawn for k_1 = 2.03 × 10^{-3}, k_2 = 2.36 × 10^{-2}, and k_3 = 4.7 × 10^{-2} dm^3 mol^{-1} s^{-1}. The change in the relative concentrations of manganese(III) complexes with pH is shown in the inset: (*a*) [Mn(acac)$_2$(H$_2$O)$_2$]$^+$, (*b*) [Mn(acac)$_3$] and (*c*) [Mn(acac)$_2$(H$_2$O)(OH)]

[Mn^{IV}(acac)$_3$]$^+$ [g = 4.0 (strong) and 2.0 (weak)][3] nor [Mn^{III}(acac)$_3$] (a d^4 system, EPR-silent). In all probability, therefore, the observed resonance is due to the radical of acetylacetone[37,38] formed concurrently through the slow autodecomposition reaction and the much faster oxidation of acetylacetone by $S_2O_3^-$ radical which is produced as an intermediate in the reactions of the manganese(III) complexes with $S_2O_3^{2-}$.

The resonance decays with time, finally leaving the pattern characteristic of a solution of manganese(II) ($I = \frac{5}{2}$) in aqueous acetylacetone (not shown in Fig. 1).

Kinetics.—At c_{acac} > 0.2 mol dm^{-3} and pH < 8.5, [Mn(acac)$_3$] is fairly soluble in water. Solution spectra at different pH and c_{acac} are shown in Figure 2(*a*)–(*c*). The shoulder at 560 nm (ε = 193 dm^3 mol^{-1} cm^{-1} at pH ⩾ 7.5, c_{acac} ⩾ 0.5 mol dm^{-3}) is attributed[19,20,39] to a $^5T_2 \longrightarrow {}^5E$ transition. These solutions are reasonably stable at ambient temperature but react with reducing agents like $S_2O_3^{2-}$, $S_2O_5^{2-}$, glyoxylate or $H_2PO_3^-$ and become faint greenish yellow [Figure 2(*d*)] in the course of time. However, addition of $S_2O_3^{2-}$ does not bring about any immediate spectral change.

The decrease in absorbance of the complex at 560 nm at [$S_2O_3^{2-}$] ≫ [Mn^{III}] follows first-order kinetics up to the maximum extent (90%) of the reaction studied. Values of the first-order rate constant, k_0, are collected in Table 3, which shows that k_0 is not affected by a five-fold variation (1–5 mmol dm^{-3}) in complex concentration, by the addition of excess of Mn(ClO$_4$)$_2$, by the presence or absence of dissolved oxygen or by ambient light. A ten-fold variation in [$S_2O_3^{2-}$] demonstrated a first-order dependence of rate on [$S_2O_3^{2-}$] at constant acidity, c_{acac}, temperature and ionic strength. As seen from Fig. 3, the rate *vs.* pH profile is closely similar to the species distribution[31] curves for [Mn(acac)$_3$] and its hydrolytic derivatives at different pH.

At fixed pH, the rate decreases with increasing concentration of acetylacetone.

Fig. 2 and equilibrium measurements by Cartledge[31] shows that under the experimental conditions the manganese(III) complex exists as an equilibrium mixture of [Mn(acac)$_3$], [Mn(acac)$_2$(H$_2$O)$_2$]$^+$ and [Mn(acac)$_2$(H$_2$O)(OH)]. The reductant exists[40] solely as $S_2O_3^{2-}$; its decomposition to S is not appreciable. Some redox potential data (estimated or experimentally evaluated) relevant to this system are cited in Table 4. These values are expected[43] to be more positive when measured in aqueous media. However the changes are likely to occur in the same direction for the couples considered and therefore the general conclusions drawn from the data in acetonitrile should be generally applicable to reactions in aqueous solutions. Considering this information and the observed kinetic, spectral and stoichiometric observations, the scheme in equations (3)–(11) is proposed. Here [Mn^{II}(acac)$_x$] represents various

$$[\mathrm{Mn(acac)_3}] + \mathrm{H^+} + 2\mathrm{H_2O} \overset{K_1}{\rightleftharpoons} [\mathrm{Mn(acac)_2(H_2O)_2}]^+ + \mathrm{Hacac} \qquad (3)$$

$$[\mathrm{Mn(acac)_2(H_2O)_2}]^+ \overset{K_h}{\rightleftharpoons} [\mathrm{Mn(acac)_2(H_2O)(OH)}] + \mathrm{H^+} \qquad (4)$$

$$\mathrm{H^+} + \mathrm{acac^-} \overset{K}{\rightleftharpoons} \mathrm{Hacac} \qquad (5)$$

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

			$10^4 k_0{}^b/s^{-1}$			
c_{acac}/mol dm^{-3}	pH	[$S_2O_3{}^{2-}$]/mol dm^{-3}	20.0	30.0	35.0	40.0 °C
0.5	7.5	0.1	0.193 (0.190)	0.68 (0.67)	1.45 (1.47)	2.67[c–f] (2.75)
	4.2		11.8 (11.6)	16.4 (16.2)	19.5 (19.0)	22.7 (22.3)
	4.5		11.1 (10.9)	15.5 (15.3)	18.3 (18.0)	20.5[d,e] (21.2)
	4.7		10.1 (10.3)	14.6 (14.3)	17.0 (17.0)	20.0 (20.2)
	5.0		8.58 (8.75)	12.3 (12.3)	14.5 (14.6)	16.7 (17.5)
	5.5		5.45 (5.39)	7.8 (7.7)	9.3 (9.5)	11.8 (11.7)
	6.0		2.52 (2.47)	3.7 (3.8)	5.2 (4.9)	6.6 (6.7)
	6.5					4.07 (4.08)
	7.0					3.08 (3.06)
	8.0					2.7 (2.69)
	8.5					2.8 (2.79)
0.6	5.2		6.8 (6.93)	10.4 (9.8)	12.0 (11.8)	14.6 (14.3)
0.4	5.5		5.92 (6.05)	9.0 (8.67)	10.5 (10.5)	13.1 (12.9)
0.6			4.95 (4.85)	7.08 (7.0)	8.67 (8.61)	10.5 (10.7)
0.7			4.36 (4.41)	6.34 (6.4)	7.67 (7.93)	9.67 (9.91)
0.8			4.08 (4.05)	5.83 (5.63)	7.16 (7.34)	8.83 (9.16)
0.1	7.5	0.4	2.25 (2.32)			
0.15			1.68 (1.70)			
0.2			1.3 (1.37)			
0.25			1.2 (1.17)			
0.5			0.74 (0.76)			
0.1		0.2		3.0 (2.92)	5.67 (5.65)	10.8 (10.8)
0.15				2.34 (2.28)	4.6 (4.55)	8.75 (8.72)
0.2				2.0 (1.95)	4.03 (3.98)	7.63 (7.6)
0.25				1.7 (1.75)	3.67 (3.62)	7.0 (6.9)
0.5				1.4 (1.34)	2.93 (2.9)	5.67 (5.5)
0.8				1.23 (1.16)	2.67 (2.62)	5.1 (5.34)
0.5		0.06		0.41 (0.40)	0.88 (0.88)	1.61 (1.65)
		0.08		0.55 (0.53)	1.18 (1.16)	2.22 (2.2)
		0.12		0.83 (0.8)	1.72 (1.77)	3.32 (3.32)
		0.15		1.04 (1.00)	2.15 (2.22)	4.15 (4.13)
		0.18		1.25 (1.20)	2.63 (2.65)	4.97 (4.97)
		0.22		1.53 (1.47)	3.22 (3.25)	6.16 (6.08)
		0.24		1.66 (1.6)	3.32 (3.55)	6.64 (6.63)
		0.26		1.79 (1.73)	3.82 (3.85)	7.32 (7.18)
		0.28		1.93 (1.87)	4.1 (4.13)	7.83 (7.82)
		0.3		2.07 (2.0)	4.4 (4.43)	8.3 (8.28)
0.5	4.5	0.06	6.45 (6.53)			
		0.08	8.56 (8.7)			
		0.12	12.86 (13.0)			
		0.15	16.5 (16.3)			
		0.18	19.4 (19.68)			
		0.2	21.9 (21.70)			

[a] Unless otherwise stated, [complex] = 2 mmol dm^{-3}, I = 1.0 mol dm^{-3}. [b] Calculated values in parentheses [c] $k_0 = (2.69 \pm 0.035) \times 10^{-4}$ s^{-1} for [complex] = 1–5 mmol dm^{-3}. [d] k_0 did not change appreciably (within ±5%) when the kinetics was measured after purging the reaction medium with purified nitrogen. [e] k_0 was invariant (within ±5%) when ambient light was totally excluded. [f] $k_0 = (2.67 \pm 0.02) \times 10^{-4}$ s^{-1} for [Mn^{2+}] = 0–0.01 mol dm^{-3}.

Table 4 Potentials (V *vs.* normal hydrogen electrode, NHE) for some reactions

Reaction	$E°$	Ref.
$[Mn^{III}(acac)_3] \longrightarrow [Mn^{II}(acac)_3]^-$	0.11[a,b]	3
$[Mn^{IV}(acac)_3]^+ \longrightarrow [Mn^{III}(acac)_3]$	1.21[b]	3
$[Mn^{IV}(acac)_3]^+ \longrightarrow$ Reduction products	1.16[b]	3
$[Mn^{II}(acac)_2(acac^{\bullet})] \longrightarrow [Mn^{II}(acac)_3]^-$	0.18[b]	41
$S_2O_3{}^- \longrightarrow S_2O_3{}^{2-}$	1.3[c]	42
$acac^{\bullet} \longrightarrow acac^-$	0.55[b]	41

[a] We measured $E° = 0.50$ V in aqueous solution, pH 7.5, $c_{acac} = 0.5$ mol dm^{-3} (scan rate 0.05 V s^{-1}). The value increases ($E° = 0.56$ V at pH 4.5) on lowering the pH. [b] Average of E_{pc} and E_{pa} in MeCN; scan rate 0.1 V s^{-1}. [c] Estimated value.

$$[Mn(acac)_3] \xrightarrow{k} [Mn^{II}(acac)_2(acac^{\bullet})] \quad (6)$$

$$[Mn(acac)_3] + S_2O_3{}^{2-} \xrightarrow{k_1} [Mn^{II}(acac)_3]^- + S_2O_3{}^- \quad (7)$$

$$[Mn(acac)_2(H_2O)_2]^+ + S_2O_3{}^{2-} \xrightarrow{k_2} [Mn^{II}(acac)_2(H_2O)_2] + S_2O_3{}^- \quad (8)$$

$$[Mn(acac)_2(H_2O)(OH)] + S_2O_3{}^{2-} \xrightarrow{k_3} [Mn^{II}(acac)_2(H_2O)(OH)] + S_2O_3{}^- \quad (9)$$

$$[Mn^{II}(acac)_x] + S_2O_3{}^- \xrightarrow{\text{fast}} [Mn^{II}(acac)_{x-1}] + acac^{\bullet} + S_2O_3{}^{2-} \quad (10)$$

$$acac^{\bullet} \xrightarrow{\text{fast}} \text{Products} \quad (11)$$

manganese(II) complexes of acetylacetone.

The scheme, when considered together with Table 4, reveals that $S_2O_3{}^{2-}$, *via* a $S_2O_3{}^{2-}/S_2O_3{}^-$ cycle, provides a low-energy path for the transfer of an electron from acac$^-$ to Mn^{III} and hence enables the catalysis. This is possible because acac$^-$, when bound to Mn^{II}, is oxidized in preference[41] to Mn^{II} and thus protects at its own cost, as it were, the manganese(II) centre. The same acac$^-$ ⟶ Mn^{III} electron transfer and consequent generation of acac may also be effected thermally [equation (6)] or

Table 5 Rate constants ($dm^3\ mol^{-1}\ s^{-1}$) and activation parameters for the reaction of $S_2O_3^{2-}$ with Mn^{III}–acac complexes

T/°C	10^4k_1	10^2k_2	10^2k_3
20.0	0.826 ± 0.04	1.23 ± 0.056	0.102 ± 0.01
30.0	4.5 ± 0.2	1.72 ± 0.07	0.75 ± 0.07
35.0	10.6 ± 0.5	2.02 ± 0.1	1.97 ± 0.24
40.0	20.3 ± 1.6	2.36 ± 0.02	4.7 ± 0.4
	20.1 ± 0.1 *	3.59 ± 0.07 *	4.46 ± 0.28 *
$\Delta H^‡$/kJ mol^{-1}	121 ± 7	22 ± 4	144 ± 11
$\Delta S^‡$/J K^{-1} mol^{-1}	90 ± 44	−206 ± 29	190 ± 75

* $I = 0.5$ mol dm^{-3}, all other k at $I = 1.0$ mol dm^{-3}.

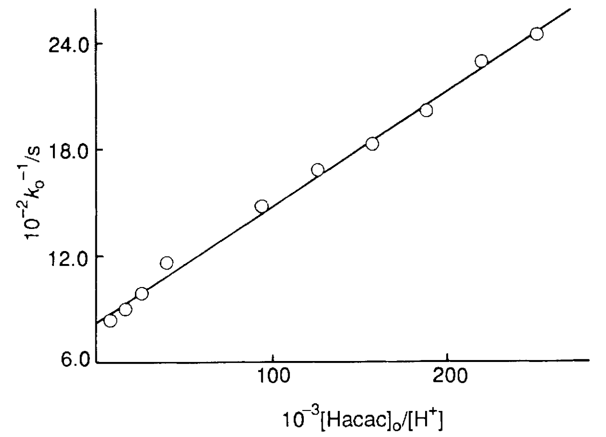

Fig. 4 Plot of $1/k_0$ *vs.* $c_{acac}/[H^+]$ at [complex] = 2 mmol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$) and 20.0 °C

by UV irradiation[44] of an alcoholic solution of $[Mn(acac)_3]$. The acac• produced may decompose to acetone and/or acetic acid[44,45] or forms[46] α,α,β,β-tetraacetylacetone.

The autodecomposition reaction (6) contributes little (< 7%) to the overall decay of the complex. Therefore the predicted rate law for the above scheme is (12). The values of k_1, k_2 and k_3 and

$$-d[\text{complex}]/dt = k_0[\text{complex}] \qquad (12)$$

$$k_0 = \left\{k_1 + \frac{k_2K_2(1 + K[H^+])}{c_{acac}} \cdot \frac{k_3K_hK_2(1 + K[H^+])}{c_{acac}[H^+]}\right\} \frac{[S_2O_3^{2-}]}{P} \qquad (13)$$

$$P = 1 + \frac{K_2(1 + K[H^+])}{c_{acac}} + \frac{K_hK_2(1 + K[H^+])}{c_{acac}[H^+]} \qquad (14)$$

$$K_2 = K_1/K = 1.39 \times 10^{-4} \qquad (15)$$

the associated errors (Table 5) were evaluated from equation (13) using known values[31] of $K_1 = 1.22 \times 10^5$, $K_h = 5 \times 10^{-8}$ mol dm^{-3} and $K = 8.6 \times 10^8$ dm^3 mol^{-1}, all at 25 °C, $I = 0.2$ mol dm^{-3}; ΔH and ΔS for K_1 are[31] −4.7 kJ mol^{-1} and 8.12 J K^{-1} mol^{-1}, while those for[31] K are −17.6 kJ mol^{-1} and 114 J K^{-1} mol^{-1}. No determination of K_h at different temperatures is available. However, from the trend of ΔH and ΔS of K_1 and K it might be anticipated that K_h would not be particularly sensitive to temperature. We utilized therefore the equilibrium constant values at 25 °C reported above for evaluation of rate constants at the experimental temperatures. We also verified that a 20% variation in K or K_1 induces only a 0.3% change in the calculated k_0 value. The k_1, k_2 and k_3 thus evaluated generally reproduced individual k_0 within ±7% (see Table 3). It transpires from these k_1, k_2 and k_3 values that for pH < 5.5 only $[Mn(acac)_2(H_2O)_2]^+$ is kinetically significant and equation (16) is valid, so that $K_1 = 1.1 \times 10^5$ at 25 °C could be

$$k_0 = \frac{K_1k_2[H^+][S_2O_3^{2-}]}{c_{acac} + K_1[H^+]} \qquad (16)$$

evaluated from the slope and intercept of the linear plots of $1/k_0$ against $c_{acac}/[H^+]$ (see Fig. 4) and this value agreed within 10% of its literature value (see above).

The activation parameters $\Delta H^‡$ and $\Delta S^‡$ (see Table 5) for k_1, k_2 and k_3 were evaluated using the built-in least-squares program of a Casio (fx-3600P) scientific calculator. Reported standard deviations include propagated errors.

Mechanism.—The complex $[Mn(acac)_3]$ appears to be co-ordinatively saturated but its ligand-exchange rate[47] (1 s^{-1} at 25 °C in MeCN) does not exclude an inner-sphere path since the electron-transfer rate k_1 is 10^{-3} s^{-1}. Thus, the ligand-exchange rate of $[Mn(acac)_3]$, though about 10^6 times slower[14,47] than that for Mn^{3+} and $[Mn(OH)]^{2+}$, is a stumbling block in a clear-cut distinction between inner- and outer-sphere mechanisms. Kinetic investigations of some faster redox reactions of $[Mn(acac)_3]$, as with HSO_3^-, may be useful to make the distinction. However, the pattern of reactivity established by Fe^{II}, V^{II}, Ag^{II} and Mn^{III} in their inner-sphere reactions is that the M–OH path makes a significant contribution to the overall rate.[48–53] By contrast, aqua complexes generally predominate for outer-sphere reactions with little or no contribution from the M–OH path. In the reaction of $S_2O_3^{2-}$ the $[Mn(acac)_2(H_2O)(OH)]$ (k_3) path contributes significantly to the overall rate ($k_2 \approx k_3$) and this may be indicative of an inner-sphere mechanism, at least for the k_2 and the k_3 paths.

Alternatively, an outer-sphere hydroxide-mediated pathway could also operate, as has been proposed for the reactions of $[Co(OH)]^{2+}$ with the square-planar nickel(II) macrocycles.[54] However, the small activation enthalpy for the k_2 path, coupled with its negative activation entropy, is in the range expected[16,55] for inner-sphere reactions of Mn^{III}.

Recently, Heyward and Wells[56] have studied the inner-sphere oxidation of hydrazoic acid by $[Mn(bipy)_2(H_2O)_2]^{3+}$ and $[Mn(bipy)_2(H_2O)(OH)]^{2+}$ (bipy = 2,2′-bipyridine); active inner-sphere intermediates, *viz.* $[Mn(bipy)_2(H_2O)(N_3)]^{2+}$ and $[Mn(bipy)_2(OH)(N_3)]^+$, were presumed. Analogous acetylacetonato complexes are known,[57] *e.g.* the octahedral $[Mn(acac)_2X(B)]$ complexes, where X = mononegative anion, B = neutral Lewis base, pyridine, methanol, *etc.* Similar complexes are likely to be formed as intermediates in the present case. Heyward and Wells[56] also observed that both $\Delta H^‡$ and $\Delta S^‡$ for the reaction of the hydroxo complex are much larger than those for the aqua complex. A similar trend has been observed by us for the present system. However, little information is available on the temperature dependence for the reaction of manganese(III) hydroxo species. So any attempt to interpret this observed trend could be at best speculative at this stage. Most probably the pseudo-aromatic[47] chelate rings in the stable (first dissociation constant = 1.39×10^{-4} mol dm^{-3}), co-ordinatively saturated, $[Mn(acac)_3]$ are not replaceable by the unidentate $S_2O_3^{2-}$ and it is presumed that $[Mn(acac)_3]$ reacts predominantly by an outer-sphere path. Replacement of the aqua ligand in $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$

$$[Mn(acac)_2(H_2O)_2]^+ + S_2O_3^{2-} \overset{K_5}{\rightleftharpoons} [Mn(acac)_2(S_2O_3)(H_2O)]^- + H_2O \qquad (17)$$

$$[Mn(acac)_2(H_2O)(OH)] + S_2O_3^{2-} \overset{K_6}{\rightleftharpoons} [Mn(acac)_2(S_2O_3)(OH)]^{2-} + H_2O \qquad (18)$$

should be thermodynamically much more facile and the k_2 and k_3 paths should follow an inner-sphere mechanism provided the intermediate thiosulphate complexes are not redox-inert 'dead-ends'.

As expected in terms of the proposed scheme, k_2 decreases with increase in ionic strength but k_1 and k_3 remain unchanged (Table 4).

Acknowledgements

Financial assistance and the award of a research fellowship (to R. D.) from the University Grants Commission (New Delhi) is thankfully acknowledged. The authors are grateful to Miss S. Sarkar and Mr. J. Roy for their kind assistance in computation.

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Received 7*th September* 1990; *Paper* 0/04113K