Oxidation of Sulfur(IV) by Tris(acetylacetonato)manganese(III) and its Hydrolytic Derivatives: Possible Examples of Substitution-controlled Redox Processes†

Subrata Mukhopadhyay and Rupendranath Banerjee*
Department of Chemistry, Jadavpur University, Calcutta 700 032, India

The manganese(III) complex $[Mn(acac)_3]$ (Hacac = acetylacetone) hydrolyses partially to $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$ in aqueous perchlorate media containing excess acetylacetone and equilibriated between pH 4.0 and 8.6. Both $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$ oxidise S^{IV} to S^{VI} quantitatively. In the presence of excess S^{IV}, the observed kinetics between 20 and 40 °C are best explained by the reaction sequence (i)–(iii) where K_{i1} and K_{i2} are the formation constants for the

$$[Mn(acac)_2(H_2O)_2]^+ + HSO_3^- \underset{fast}{\overset{K_{i1}}{\rightleftharpoons}} [Int_1] \xrightarrow[slow]{k_1} Products \tag{i}$$

$$[Mn(acac)_2(H_2O)_2]^+ + SO_3^{2-} \underset{fast}{\overset{K_{i2}}{\rightleftharpoons}} [Int_2] \xrightarrow[slow]{k_2} Products \tag{ii}$$

$$[Mn(acac)_2(H_2O)(OH)] + SO_3^{2-} \xrightarrow[slow]{k_3} Products \tag{iii}$$

hydrogen-bonded ion-pair intermediates $[Int_1]$ and $[Int_2]$ respectively. At 30 °C and $I = 1.0$ mol dm^{-3} ($NaClO_4$), $K_{i1} = 30$ dm^3 mol^{-1}, $K_{i2} = 100$ dm^3 mol^{-1}, $k_1 = 7.0 \times 10^{-4}$ s^{-1}, $k_2 = 3.55 \times 10^{-4}$ s^{-1} and $k_3 = 0.41$ dm^3 mol^{-1} s^{-1}. The rate-determining steps appear to be the transformation of $[Int_1]$, $[Int_2]$ and $[Mn(acac)_2(H_2O)(OH)]$ to *bona-fide* inner-sphere adducts (not shown in the above sequence). Subsequent rapid redox processes *via* sulfur(V) intermediates led to the products. The complex $[Mn(acac)_3]$ was found to be kinetically inactive despite its abundance in the reaction media and only acts as a buffer for $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$.

The chemistry of Mn^{III} as oxidant has received much attention as $Mn^{3+}(aq)$[1,2] and in complex species.[3-12] Both inner- and outer-sphere mechanisms have been found to be operative in oxidation reactions involving Mn^{3+}, $[Mn(OH)]^{2+}$ and stable manganese(III) complexes. Despite the labile nature of Mn^{3+}-(aq), a substitution-controlled mechanism has been advanced for the reaction of $[Mn(OH)]^{2+}$ with some thioureas and benzene-1,2-diols.[13-16] However, reactions of $Mn^{3+}(aq)$ with the same reductants are redox-controlled on the basis of a comparison of rate constants and activation parameters.[13-16] An intermediate situation is observed in $[Mn(edta)]^- - N_3^-$ (H_4edta = ethylenediaminetetraacetic acid)[17] and $[Mn(bipy)_2]^{3+}(aq) - N_3^-$ (bipy = 2,2′-bipyridine)[7] reactions in which the precursor complex formation and the redox process occur simultaneously. The reaction of $[Mn(cdta)]^-$ (H_4cdta = *trans*-cyclohexane-1,2-diaminetetraacetic acid) with benzene-1,4-diols also belongs to the same intermediate category.[18]

Sutin[19] pointed out that the only obvious requirement for substitution control would seem to be a moderate-to-large driving force for electron transfer coupled with a moderate or slow rate of inner-sphere solvent exchange.[20] Unlike most other manganese(III) complexes, $[Mn(acac)_3]$ (Hacac = acetylacetone) has a moderately slow ligand exchange rate (1 s^{-1} at 25 °C in MeCN).[21] The complex $[Mn(acac)_3]$ and its hydrolytic derivatives, *viz.* $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$ have moderate oxidising strength.[9,22] Moreover, $[Mn(acac)_3]$ forms inner-sphere substitution products with a variety of potential reductants.[23-25] Substitution control in these complexes is therefore a distinct possibility which we have probed in the present study. Few data are available[8-12,26-28] on the kinetic behaviour of such species, though they are well characterised otherwise.

An additional interest is the role of higher valent manganese in the autooxidation of S^{IV}.[29-32]

Experimental

Materials.—All materials used except $Na_2S_2O_5$ were as described earlier.[8,9,33] Solid $Na_2S_2O_5$ (G.R., E. Merck) was the source of sulfite; this salt is very stable in the solid form but hydrates rapidly and completely when dissolved in water to yield sulfite.[34-37] Sulfite solutions were prepared daily and kept under nitrogen to prevent autooxidation, as trace-metal-catalysed autooxidaation of sulfite is well known.[29-32,38-41] Prepared thus, these solutions were iodometrically found to be stable for 48 h or more.[42] Acetylacetone (G.R., Loba) was purified as described earlier.[9,43]

Commercially available N_2 gas (Indian Oxygen Limited) for the deoxygenetion of solutions was cleansed of oxidising impurities by passing through solutions of chromium(II). The outcoming gas was first washed with water before entering the kinetic mixture and then saturated with blank solutions which were identical to those used for kinetic studies except that no Mn^{III} was added.

Physical Measurements and Kinetics.—Solution spectra and absorbances were obtained on a Shimadzu Graphicord (UV-

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† *Supplementary data available* (No. SUP 56928, 5 pp.): Values of k_{obs} kinetic data. See Intructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Oxidation of S^{IV} by Mn^{III}–acac complexes: stoichiometric results[a]

$[Mn^{III}]_T$/mmol dm^{-3}	pH	$[S^{IV}]_T$/ mmol dm^{-3}	$[Hacac]_T$/mol dm^{-3}	$[SO_4^{2-}]$ produced/mmol dm^{-3}	$\Delta[Mn^{III}]/\Delta[S^{VI}]$
4.0	4.5	20	0.5	2.20	1.82[b]
5.0	7.0	20	1.0	2.45	2.04[b]
5.0	8.0	60	0.1	2.55	1.96[b]
5.0	8.0	20	0.5	2.60	1.92[b]
4.0	8.6	30	0.1	1.90	2.10[b]
1.0	8.2	20	0.1	0.52	1.92[b]
5.0	4.1	15	0.1	5.80	0.86[c]
2.0	6.5	20	0.5	1.90	1.05[c]
4.0	6.0	30	1.0	5.30	0.75[c]
4.0	7.8	20	0.1	3.20	1.25[c]

[a] $T \approx 30$ °C, $I = 1.0$ mol dm^{-3}. [b] Reactions under anaerobic conditions, average consumption ratio 1.96 ± 0.14. [c] Reactions under aerobic conditions.

240) spectrophotometer with a 1 cm quartz cell. All rate measurements were made at an ionic strength of 1.0 mol dm^{-3} ($NaClO_4$) and over the acidity and temperature ranges indicated. The kinetics were studied in the presence of an excess of acetylacetone (0.1–1.0 mol dm^{-3}) and with $[S^{IV}]_T$ at least ten times in excess of $[Mn^{III}]_T$. Most of the experiments were performed at a wavelength setting of 560 nm, with some at 480 and 650 nm.

The pH values of the test solutions were adjusted with $HClO_4$ or NaOH by using a Systronics (model 335, India) pH meter having a combined glass–calomel microelectrode assembly containing gelled electrolyte (Gamma Instruments, India). Use of such electrodes reduce the diffusion of unwanted ions from the electrode. To minimise further such diffusion, the electrode was dipped into the test solutions for a minimum period of time. Although the measured pH is usually defined in terms of the activity of the hydrogen ion, we used the concentration of the hydrogen ion by calibrating the pH electrode with analytically prepared solutions. In kinetic measurements buffers were not used in the entire study in order to avoid any possible complexation with Mn^{III} and because no significant pH drift (within 0.05 unit) was observed during reactions.

Data Analyses.—Pseudo-first-order rate constants, k_{obs}, the individual rate constants and associated errors were measured as described earlier[8,9] and using a Lotus 123 spread sheet.[44]

Stoichiometric Measurements.—Both anaerobic and aerobic stoichiometries were determined only in the presence of excess S^{IV} owing to the slow nature of the reaction and background autodecomposition of the Mn^{III} complexes. Dinitrogen was used to deoxygenate the solutions. Sulfate in the product mixture (100 cm^3) was estimated gravimetrically as $BaSO_4$ after acidification with $HClO_4$ and removal of excess S^{IV} as SO_2 by bubbling with dinitrogen.

Free acetylacetone was determined colorimetrically at 510 nm using *o*-phenylenediamine as the colour forming reagent.[45] No extra acetylacetone was added to the reaction mixtures used for such determinations. It was verified that Mn^{II}, S^{IV} and S^{VI} do not interfere with the colour formation reaction.

Dithionate was tested with excess Cr^{VI} in 1.0 mol dm^{-3} H_2SO_4 after removal of S^{IV} by bubbling with N_2. Dithionate, if present, reduces Cr^{VI} quantitatively and may therefore be estimated from the decrease in absorbance of Cr^{VI} at 348 nm.[46] No extra acetylacetone was used in these experiments either. The method can detect dithionate concentration as low as 5×10^{-6} mol dm^{-3}.

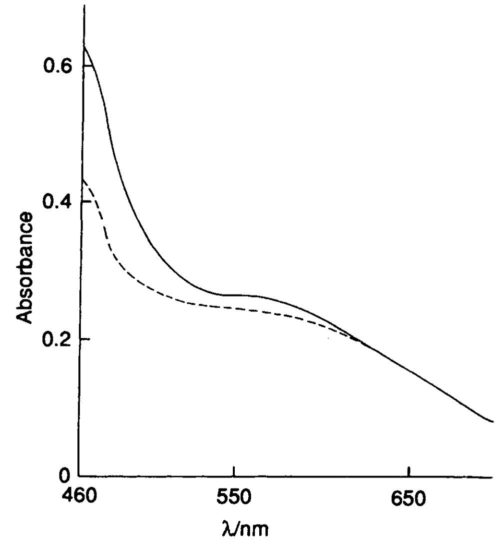


Fig. 1 Spectrum of 2.0 mmol dm^{-3} Mn^{III} complex (——); $[Hacac]_T$ = 0.5 mol dm^{-3}, pH = 4.5, $T \approx 25$ °C, $I = 1.0$ mol dm^{-3}. Spectrum upon addition of 0.06 mol dm^{-3} $[S^{IV}]_T$ immediately after mixing (– – –), other conditions being the same

Results and Discussion

Stoichiometry and Reaction Products.—Dithionate was not found in the product mixture under either aerobic or anaerobic conditions. The normal stoichiometric experiments under dinitrogen with S^{IV} in excess (Table 1) show that the reaction involves very nearly 2 moles of Mn^{III} for each mole of S^{IV} and further rules out the formation of dithionate, $S_2O_6^{2-}$, in more than trace amounts. The principal conversion may thus be represented by equation (1). However, the amount of

$$2Mn^{III} + S^{IV} \longrightarrow 2Mn^{II} + S^{VI} \qquad (1)$$

SO_4^{2-} produced shows significant positive deviation from the expected stoichiometry [equation (1)] for solutions not purged with dinitrogen (last four entries in Table 1).

No UV/VIS spectral change in the range 190–400 nm occurs when S^{IV} (0.01–0.06 mol dm^{-3}) is mixed with acetylacetone solutions in the range pH 4.0–8.6. Formation of a bisulfate addition product is thus excluded. Acetylacetone is not consumed by the oxidation reaction and can be recovered practically quantitatively after the reaction under both aerobic and anaerobic conditions.

Kinetics.—An immediate spectral change is observed when S^{IV} is added to an aqueous solution of the complex in excess of Hacac in the range pH 4.0–7.0 (Fig. 1). No such change occurs above pH 7.0. However, on leaving to stand, all solutions between pH 4.0 and 8.6 slowly lose the peak at 560 nm reducing the absorbance to less than 0.01. The pseudo-first-order rate constants, k_{obs}, defined by equation (2) were obtained from the slopes of log A_t (where A_t = absorbance after time t) *versus* t

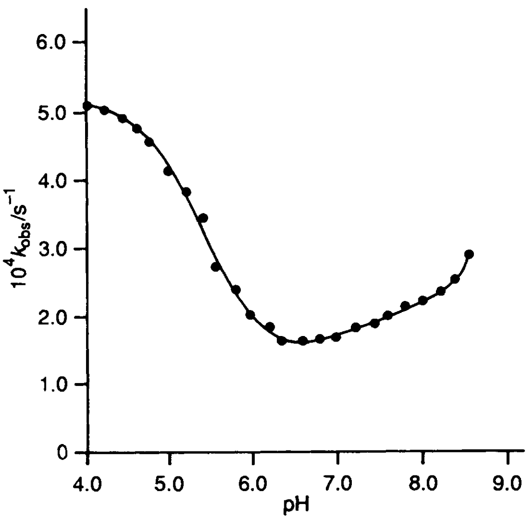


Fig. 2 Dependence of k_{obs} on pH; $[Mn^{III}]_T = 2.0$ mmol dm^{-3}, $[S^{IV}]_T = 0.02$ mol dm^{-3}, $[Hacac]_T = 0.5$ mol dm^{-3}, $T = 30$ °C, $I = 1.0$ mol dm^{-3}

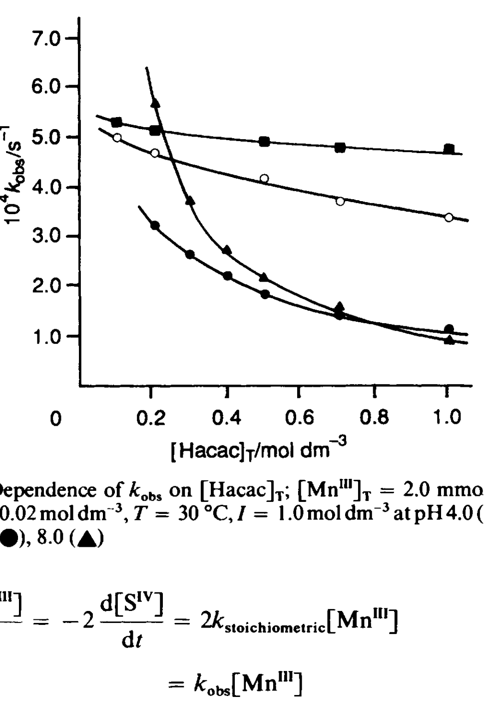


Fig. 3 Dependence of k_{obs} on $[Hacac]_T$; $[Mn^{III}]_T = 2.0$ mmol dm^{-3}, $[S^{IV}]_T = 0.02$ mol dm^{-3}, $T = 30$ °C, $I = 1.0$ mol dm^{-3} at pH 4.0 (■), 5.0 (○), 6.0 (●), 8.0 (▲)

$$-\frac{d[Mn^{III}]}{dt} = -2\frac{d[S^{IV}]}{dt} = 2k_{stoichiometric}[Mn^{III}] = k_{obs}[Mn^{III}] \quad (2)$$

plots. For non-deoxygenated reaction media these plots curve towards lower rate constants after 1–2 half-lives; consequently, rate constants under aerobic conditions were determined only from the initial linear portions (1–2 half-lives). In deoxygenated solutions the first-order plots proved to be linear for more than three half-lives. Moreover, k_{obs} obtained from such plots are the same (within 5%) as the values obtained from the first 1–2 half-lives of aerobic reactions. Duplicate runs reproduced individual k_{obs} values to within 2–5%. The background autodecomposition of the manganese(III) complexes is insignificant (< 5% of the overall reaction) under all experimental conditions.

Detailed kinetic data were obtained as a function of pH, total acetylacetone ($[Hacac]_T$) and total S^{IV} ($[S^{IV}]_T$) and some representative data at 30 °C are summarised in Tables 1–3 of SUP No. 56928 which reveal a complex dependence on pH and $[Hacac]_T$ (Figs. 2 and 3). At pH < 7.0, k_{obs} tends to saturate at higher $[S^{IV}]_T$ indicating association between Mn^{III} and S^{IV} (Fig. 4). Above pH 7.0 however, the reaction showed a clear first-order dependence on $[S^{IV}]_T$ and there is no evidence of a $[S^{IV}]_T$ independent term. The following changes in reaction conditions had, within experimental error, no influence on the values of k_{obs}: an increase in $[Mn^{III}]_T$ from 0.5×10^{-3} to 4.0×10^{-3} mol dm^{-3}, the presence of ambient light and Mn^{2+} (0.05 mol dm^{-3}), a change in wavelength at which the decay of Mn^{III} was followed (460–650 nm) or substitution of $NaHSO_3$ or Na_2SO_3 for $Na_2S_2O_5$ as the source of sulfite.

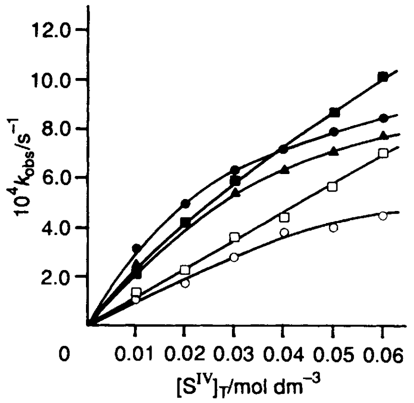


Fig. 4 Dependence of k_{obs} on $[S^{IV}]_T$; $[Mn^{III}]_T = 2.0$ mmol dm^{-3}, $T = 30$ °C, $I = 1.0$ mol dm^{-3} at pH 4.3 (●), $[Hacac]_T = 0.5$ mol dm^{-3}; pH 5.0 (▲), $[Hacac]_T = 0.5$ mol dm^{-3}; pH 6.0 (○), $[Hacac]_T = 0.5$ mol dm^{-3}; pH 7.0 (■), $[Hacac]_T = 0.2$ mol dm^{-3}; pH 8.0 (□), $[Hacac]_T = 0.5$ mol dm^{-3}

Table 2 Selected literature values of equilibrium constants

K_1[a]	1.22×10^5
K_2[b]/mol dm^{-3}	5.0×10^{-8}
K_3[c]/mol dm^{-3}	1.16×10^{-9}
K_4[d]/mol dm^{-3}	1.26×10^{-2}
K_5[d]/mol dm^{-3}	5.01×10^{-7}
K_D[d]/dm^3 mol^{-1}	7.0×10^{-2}

[a] $T = 20$ °C, $I = 1.0$ mol dm^{-3}. Values of K_1 at 30 and 40 °C were calculated to be 1.16×10^5 and 1.08×10^5 respectively from ref. 47. [b] At 25 °C. See refs. 43 and 47. Temperature depencence of K_2 is not known. [c] $T = 30$ °C, $I = 1.0$ mol dm^{-3}. Values of K_3 at 20 and 40 °C were calculated to be 8.77×10^{-10} and 1.54×10^{-9} mol dm^{-3} respectively using the expression given in ref. 48. [d] Ref. 36. K_5 is temperature independent.

Equilibria possible in solutions of Mn^{III} and S^{IV} under our experimental conditions are given in equations (3)–(8). Selected

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

$$[Mn(acac)_2(H_2O)_2]^+ \overset{K_2}{\rightleftharpoons} [Mn(acac)_2(H_2O)OH)] + H^+ \quad (4)$$

$$Hacac \overset{K_3}{\rightleftharpoons} H^+ + acac^- \quad (5)$$

$$SO_2(aq) \overset{K_4}{\rightleftharpoons} H^+ + HSO_3^- \quad (6)$$

$$HSO_3^- \overset{K_5}{\rightleftharpoons} H^+ + SO_3^{2-} \quad (7)$$

$$HSO_3^- + HSO_3^- \overset{K_D}{\rightleftharpoons} S_2O_5^{2-} + H_2O \quad (8)$$

values of the equilibrium constants are summarised in Table 2. According to the values of K_4 and K_5 the main sulfur(IV) species at pH > 4.0 will be HSO_3^- and SO_3^{2-}. The disulfite species $S_2O_5^{2-}$ is formed at higher concentrations of HSO_3^-, but the magnitude of K_D is such that solutions of $Na_2S_2O_5$ will exist as

>99% monomeric species, HSO_3^- and SO_3^{2-}, at $[S_2O_5^{2-}]_T < 0.05$ mol dm^{-3},[36,49] a condition always adopted in our experiments. Moreover, no second-order dependence of k_{obs} on $[S^{IV}]_T$ has been observed; $S_2O_5^{2-}$ is therefore considered kinetically insignificant. The complex $[Mn(acac)_3]$ is also found to be kinetically inactive as in redox reactions with glyoxylate[8] or $H_2PO_2^-$.[10] The sequence of reactions (9)–(12) therefore represents the simplest explanation for the observed spectral

$$[Mn(acac)_2(H_2O)_2]^+ + HSO_3^- \underset{\text{fast}}{\overset{K_{i1}}{\rightleftharpoons}} [Int_1] \xrightarrow[\text{slow}]{k_1} Mn^{II} + S^{V} \quad (9)$$

$$[Mn(acac)_2(H_2O)_2]^+ + SO_3^{2-} \underset{\text{fast}}{\overset{K_{i2}}{\rightleftharpoons}} [Int_2] \xrightarrow[\text{slow}]{k_2} Mn^{II} + S^{V} \quad (10)$$

$$[Mn(acac)_2(H_2O)(OH)] + SO_3^{2-} \xrightarrow[\text{slow}]{k_3} Mn^{II} + S^{V} \quad (11)$$

$$Mn^{III} + S^{V} \xrightarrow{\text{fast}} Mn^{II} + S^{VI} \quad (12)$$

and kinetic behaviour where Int represents intermediate association products. Postulation of the radical intermediate S^V is supported by copious polymerisation observed in the reaction medium when acrylonitrile (6% v/v) was present.

Intermediate adducts are formed only below pH 7.0 where $[Mn(acac)_2(H_2O)_2]^+$ is present in considerable amount but there is no kinetic or spectral evidence for the formation of any Mn^{III}–S^{IV} association products above pH 7.0 where $[Mn(acac)_3]$ dominates and $[Mn(acac)_2(H_2O)_2]^+$ is negligible. Failure of $[Mn(acac)_3]$ to form adducts with HSO_3^- and SO_3^{2-} signifies the outer-sphere nature of the association products $[Int_1]$ and $[Int_2]$.

Evaluation of K_{i1}.—The formation constant K_{i1} was evaluated spectrophotometrically at pH 4.5 assuming that K_{i1} represents the only $[Mn(acac)_2(H_2O)_2]^+$–S^{IV} equilibrium at this pH. Assuming further that $[HSO_3^-] \approx [S^{IV}]_T$ (pK_a of HSO_3^- is 6.4, see Table 2) this leads to equation (13) where ΔA

$$\frac{1}{\Delta A} = \frac{1}{\varepsilon_{Int_1} K_{i1}[Mn(acac)_2(H_2O)_2{}^+][S^{IV}]_T} + \frac{1}{\varepsilon_{Int_1}[Mn(acac)_2(H_2O)_2{}^+]} \quad (13)$$

represents the immediate change in absorbance observed at 460 nm when S^{IV} is added to Mn^{III} measured at pH 4.5 in the presence of excess $[S^{IV}]_T$ (0.01–0.06 mol dm^{-3}), $[Hacac]_T = 0.5$ mol dm^{-3} and $[Mn^{III}]_T = 2 \times 10^{-3}$–$5 \times 10^{-3}$ mol dm^{-3} at 30 °C and $I = 1.0$ mol dm^{-3}. At 460 nm ΔA is appreciable but free from other complications such as absorptions due to acetylacetone and S^{IV}. The value of K_{i1} was calculated from the intercept–slope ratio of the linear plot ($r > 0.98$) of ΔA^{-1} against $[S^{IV}]_T^{-1}$ and was found to be (30 ± 7) dm^3 mol^{-1}.

Evaluation of K_{i2}.—The total manganese(III) concentration in solution is distributed according to equation (14). Then, under

$$[Mn^{III}]_T = [Mn(acac)_2(H_2O)_2]^+ + [Mn(acac)_3] + [Mn(acac)_2(H_2O)(OH)] + [Int_1] + [Int_2] \quad (14)$$

the assumptions stated previously, the formation constant K_{i2} can be derived from equations (15) and (16) [obtained from equations (3)–(12)]. Now, for pH < 7.5, $(K_3 + [H^+]) \approx [H^+]$

$$k_{obs}P(K_5 + [H^+])/[S^{IV}]_T = 2k_1K_{i1}[H^+] + 2k_2K_{i2}K_5 + 2k_3K_2K_5/[H^+] \quad (15)$$

Table 3 Rate constants and activation parameters for Mn^{III}–S^{IV} reaction at $I = 1.0$ mol dm^{-3}

T/°C	$10^4\,k_1$/s^{-1}	$10^4\,k_2$/s^{-1}	k_3/dm^3 mol^{-1} s^{-1}
20	2.80 ± 0.20	1.40 ± 0.15	0.20 ± 0.01
30	7.00 ± 0.50	3.55 ± 0.40	0.41 ± 0.02
40	17.60 ± 1.50	8.70 ± 0.90	0.87 ± 0.05
$\Delta H^‡$/kJ mol^{-1}	70 ± 10	70 ± 20	50 ± 10
$\Delta S^‡$/J K^{-1} mol^{-1}	−80 ± 30	−90 ± 40	−75 ± 25

$$P = 1 + \frac{[Hacac]_T}{K_1(K_3 + [H^+])} + \frac{K_2}{[H^+]} + \frac{K_{i1}[S^{IV}]_T[H^+]}{(K_5 + [H^+])} + \frac{K_{i2}K_5[S^{IV}]_T}{(K_5 + [H^+])} \quad (16)$$

and equation (15) may be rearranged to equation (17), *i.e.* of the form $A[S^{IV}]_T/(B + C[S^{IV}]_T)$ where A, B and C are constants for

$$k_{obs} = \{(2k_1K_{i1}K_1[H^+]^2 + 2k_2K_{i2}K_5K_1[H^+] + 2k_3K_2K_5K_1)[S^{IV}]_T\}/\{(K_5 + [H^+])(K_1[H^+] + [Hacac]_T + K_1K_2) + (K_{i1}K_1[H^+]^2 + K_{i2}K_5K_1[H^+])[S^{IV}]_T\} \quad (17)$$

given pH and $[Hacac]_T$ and at a particular temperature. The plots of k_{obs}^{-1} against $[S^{IV}]_T^{-1}$ are good straight lines ($r > 0.98$) at each fixed $[H^+]$ and $[Hacac]_T$ studied with slope B/A and intercept C/A and hence the slope–intercept ratio gives B/C whence K_{i2} was evaluated to be (100 ± 30) dm^3 mol^{-1} in the experimental temperature range using known values of equilibrium constants in Table 2.

Formation constants K_{i1} and K_{i2} do not show a measureable trend with temperature in the range studied. We therefore chose constant values for K_{i1}(30 ± 10) dm^3 mol^{-1} and K_{i2}(100 ± 30) dm^3 mol^{-1}, which are the average of the values measured between 20 and 40 °C. These small values and the order $K_{i2} > K_{i1}$ further indicate an outer-sphere association although K_{i1} and K_{i2} are not as small as expected for a purely electrostricted ion pair. We believe that ion pairing occurs through double hydrogen bonding of the two *cis*-aqua ligands of $[Mn(acac)_2(H_2O)_2]^+$ with HSO_3^- or SO_3^{2-}. A species distribution curve constructed using these equilibrium constants is shown in Fig. 5.

Numerical values of P [equation (16)] can be evaluated since K_{i1} and K_{i2} both are now known. Equation (15) can therefore be rearranged to the form $y = ax_1 + bx_2 + cx_3$, and thus solved for a, b, c, with the help of a Lotus 123 spread-sheet and its ability to solve simultaneous equations and perform regression analysis.[44] The kinetic parameters listed in Table 3 were calculated from a, b, c, *i.e.* the coefficients of dependent variables x_1,x_2,x_3. They reproduce individual k_{obs} values to within 2–7%. The solid lines in Figs. 2–4 represent the calculated data on the basis of these kinetic constants and equation (15).

Reaction with N_3^-.—In order to know more about the mechanism of the reactions considered here we collected some kinetic data on reactions of N_3^- with the manganese(III) complexes. Preliminary investigations revealed an initial rise and subsequent slow decay in absorbance on mixing the reagents (Fig. 6). Similar observations were made previously in the reaction of $[Mn(edta)]^-$[17] and $[Mn(bipy)_2]^{3+}$ (aq)[7] with N_3^- for which the initial rise in absorbance was attributed to the formation of inner-sphere complexes, $[Mn(edta)(N_3)]^{2-}$ and $[Mn(bipy)_2(H_2O)(N_3)]^{2+}$ respectively. The initial slope in Fig. 6 may similarly be interpreted as due to the replacement of an aqua ligand in the manganese(III) complexes by N_3^-. The first-order rate constant of the initial anation reaction

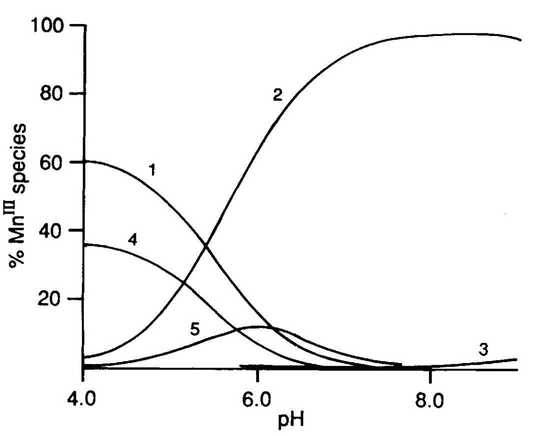


Fig. 5 Species distribution curves for 1, $[Mn(acac)_2(H_2O)_2]^+$, 2, $[Mn(acac)_3]$, 3, $[Mn(acac)_2(H_2O)(OH)]$, 4, $[Int_1]$, 5, $[Int_2]$. $[S^{IV}]_T$ = 0.02 mol dm^{-3}, $[Hacac]_T$ = 0.5 mol dm^{-3}, T = 30 °C

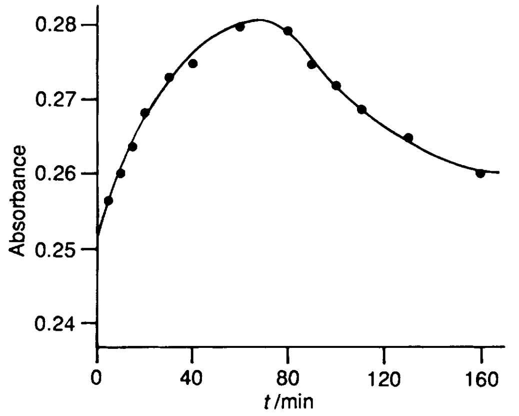


Fig. 6 Plot of absorbance at 560 nm *versus* time in the reaction of N_3^- with the Mn^{III} complex; $[Mn^{III}]_T$ = 2.0 mmol dm^{-3}, $[Hacac]_T$ = 0.5 mol dm^{-3}, $[N_3^-]$ = 0.04 mol dm^{-3}, pH 5.0, T = 30 °C, I = 1.0 mol dm^{-3}

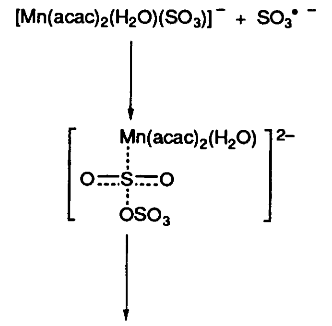
estimated from a Guggenheim plot[50,51] was 6.70 × 10^{-4} s^{-1} at pH 5.0, $[Hacac]_T$ = 0.5 mol dm^{-3}, $[N_3^-]$ = 0.04 mol dm^{-3}, $[Mn^{III}]_T$ = 0.002 mol dm^{-3} at 30 °C and at I = 1.0 mol dm^{-3}.

Mechanism.—It is seen from Table 3 that the rate constants decrease in the order $k_3 > k_1 > k_2$. This sequence, particularly the order $k_1 > k_2$ is unusual for the oxidation reactions of S^{IV}; generally SO_3^{2-} is at least twenty times more active than HSO_3^- towards a given oxidant.[52–54] Furthermore, the first-order rate constants for the reaction of S^{IV} and N_3^- with Mn^{III}–acac complexes are very similar; 6.33 × 10^{-4} s^{-1} for 0.04 mol dm^{-3} $[S^{IV}]_T$ and 6.70 × 10^{-4} s^{-1} for 0.04 mol dm^{-3} N_3^- at pH 5.0, $[Hacac]_T$ = 0.5 mol dm^{-3} at 30 °C. It is likely, therefore, that the reactions of Mn^{III}–acac complexes with S^{IV} are examples of substitution-controlled redox processes in which the rate determining steps are the conversion of $[Int_1]$, $[Int_2]$ and $[Mn(acac)_2(H_2O)(OH)]$ into *bona-fide* inner-sphere sulfito or bisulfito complexes which undergo fast intramolecular redox decomposition to produce Mn^{II} and S^{V}. The reported rate constants k_n (n = 1–3) then represent rate constants for ligand substitution not redox processes. The greater lability of $[Mn(acac)_2(H_2O)(OH)]$ relative to $[Mn(acac)_2(H_2O)_2]^+$ ($k_3 > k_1K_{i1}$ or k_2K_{i2}) may then be attributed to the uncharged nature of $[Mn(acac)_2(H_2O)(OH)]$ and hydroxide labilisation of its water molecule.

Reaction Course leading to SO_4^{2-}.—The radical ion $SO_3^{\bullet -}$ or $HSO_3^{\bullet}$ are the most probable forms of S^{V} proposed in reactions (9)–(11). Either of these can be visualised as undergoing a variety of subsequent reactions to produce SO_3^{2-}, SO_4^{2-} or $S_2O_6^{2-}$. However, our experiments rule out $S_2O_6^{2-}$ as an appreciable product and thus indicates that S^{V} is a good reducing agent,[55,56] oxidised very quickly by a second Mn^{III} to S^{VI} before it can dimerise with second-order kinetics.[55–57] Absence of $S_2O_6^{2-}$ also indicates for the Mn^{III}–S^{V} reaction an outer-sphere path in contrast to the inner-sphere paths proposed for the Mn^{III}–S^{IV} reactions. An inner-sphere reaction should be slow because of the slow ligand exchange rates for the manganese(III)–acac complexes[21] and cannot compete effectively with the dimerisation of S^{V} to $S_2O_6^{2-}$.

We cannot say why an inner-sphere mechanism should be favoured for the Mn^{III}–S^{IV} reactions but not for the Mn^{III}–S^{V} steps. We note, however, that the Mn^{III}–S^{V} reactions have a higher thermodynamic driving force than the Mn^{III}–S^{IV} reactions. Another example is known where SO_3^{2-} and $SO_3^{\bullet -}$ do not follow the same pathway for electron transfer. The reaction of HSO_3^- with bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) is outer-sphere, whereas an inner-sphere path is operative when the radical $SO_3^{\bullet -}$ is the reductant.[58] The self-reaction of $SO_3^{\bullet -}$ to produce SO_4^{2-} and SO_3^{2-} satisfies the stoichiometric requirements in our case and is a thermodynamically favourable process,[56] but we find this process unlikely because it it known that in most chemical reactions where $SO_3^{\bullet -}$ is generated by oxidation of S^{IV}, the radical will undergo further oxidation rather than self reactions. This is reasonable for a good reducing agent such as S^{V} (ref. 56).

Another conceivable mechanism for SO_4^{2-} production is the attack of $SO_3^{\bullet -}$ on the co-ordinated S^{IV} as shown below for $[Mn(acac)_2(H_2O)(SO_3)]^-$ [equation (18)]. This mechanism is analogous to that proposed for the $[Co(NH_3)_5(OH)]^{2+}$–S^{IV} reaction.[36] There is also some evidence in the literature for attack of $SO_3^{\bullet -}$ on a co-ordinated CN^- [59] or a co-ordinated aromatic ligand[55,56,60] leading to minor amounts of sulfonated products which on hydrolysis produce SO_4^{2-}. Such sulfonation reactions are analogous to the free-radical alkylation reactions reported by Rollick and Kochi.[61,62] Such a possibility cannot be ruled out in the present system which contains pseudo-aromatic chelate rings. But, if it occurs, it is not expected to have a significant influence on the interpretation of the rate law.



(18)

The sensitivity of stoichiometry and kinetics to O_2 is entirely consistent with other reports of reactions of S^{IV} with metal complexes and is attributed to the well known chain reactions of sulfite and oxygen. Mainly two types of chain mechanisms have been proposed. One of them is mediated by the $SO_5^{\bullet -}$ radical ion[63,64] while the other involves a C^{n+}–$C^{(n+1)+}$ catalytic cycle (C is a metal complex).[56,65–67] An analogous Mn^{II}–Mn^{III} catalytic cycle involving manganese complexes of acetylacetone seems unlikely in the present system since added Mn^{II} does not affect the kinetics. Such an innocent role of Mn^{II} mitigates any catalytic role of Mn^{II} and Mn^{III}–acac complexes in the autooxidation of S^{IV}. A more reasonable scheme for the involvement of oxygen is given in equations (19)–(22). The

$$Mn^{III} + SO_3^{2-} \longrightarrow Mn^{II} + SO_3^{\bullet -} \quad (19)$$

$$SO_3^{\bullet -} + O_2 \longrightarrow SO_5^{\bullet -} \quad (20)$$

$$SO_5^{\bullet -} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_4^{\bullet -} \quad (21)$$

$$SO_4^{\bullet -} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^{\bullet -} \quad (22)$$

$SO_3^{\bullet -}$ ion is almost wholly consumed by a second Mn^{III} and not by O_2 in the early stages of reaction but when $[Mn^{III}]$ is very low at the later part of the reactions, O_2 effectively competes for $SO_3^{\bullet -}$. There is no scope for any trace-metal-catalysed autooxidation of sulfite[29–32,38–41] in the present system as excess acetylacetone, used in the kinetic measurements, sequesters such metal ions including Mn^{2+} and inhibits the catalysis.

The Question of Pseudo-substitution.—Reactions of hydroxoaqua complexes with SO_2 enjoy a nearly absolute dominance in the SO_2-uptake reactions of different trivalent metal complexes. They proceed through O–H rather than M–O bond cleavage[36,68–70] *i.e.* by a pseudo-substitution[71] mechanism with rate constants generally much higher than those for the usual substitution reactions. Kinetic behaviour for the present system, however, cannot be explained if a similar pseudo-substitution [equation (23)] is assumed to dominate the system

$$[Mn(acac)_2(H_2O)(OH)] + SO_2(aq) \xrightarrow{k} \text{Products} \quad (23)$$

absolutely. With such a scheme the extracted rate contant k is not constant but increases substantially with pH from $\approx 7.0 \times 10^3$ (at pH 4.0) to $\approx 7.0 \times 10^8$ mol^{-1} dm^3 s^{-1} (at pH 8.6) at 30 °C. Moreover, a pseudo-substitution mechanism cannot be reconciled with the observation that the first-order rate constants for reactions of S^{IV} and N_3^- with Mn^{III}–acac complexes are so similar. van Eldik and co-workers[72] have noted that SO_2 uptake by *cis*-$[Co(phen)_2(OH_2)_2]^{3+}$ (phen = 1,10-phenanthroline) and its $(bipy)_2$ congener does not lead to an observable O-bonded species but goes directly to the S-bonded aquasulfito complex. The mechanism appears to be S_N1 (limiting) or D substitution, not pseudo-substitution. While SO_2 uptake for most other aquaamminecobalt(III) complexes follows a pseudo-substitution process,[36,68–70] the reason for a switch over in the mechanism for the $(phen)_2$ and $(bipy)_2$ complexes is not clear. However, it was suggested that the aromatic ligands might have some role. In our system the pseudo-aromatic Mn^{III}–acac ring system may behave similarly.

The activation parameters $\Delta H^‡$ and $\Delta S^‡$ are not very precise. Yet the trend of low $\Delta H^‡$ and moderately negative $\Delta S^‡$ is apparent. A similar situation was observed for the azide anation reaction of $[Mn(edta)]^-$ [17] and suggests similar mechanisms in all cases. Anation processes at $[Mn(edta)]^-$, a seven-co-ordinated species, is likely to be dissociative as observed recently for the anation of $[Fe^{III}(edta)(H_2O)]^-$ by S^{IV} (ref. 73). By analogy, a dissociative pathway is also anticipated for the Mn^{III}–acac complexes.

Conclusions

The stoichiometry and kinetics of the oxidation of S^{IV} to S^{VI} by the acetylacetonato complexes of manganese(III) have been determined in aqueous perchlorate media containing excess acetylacetone in the range pH 4.0–8.6. The complex $[Mn(acac)_3]$ is kinetically inactive but its hydrolytic derivatives $[Mn(acac)_2(H_2O)_2]^+$ and $[Mn(acac)_2(H_2O)(OH)]$ are active in different pH ranges. In the pH interval 4.0–5.0 only the reaction between $[Mn(acac)_2(H_2O)_2]^+$ and HSO_3^- (k_1 path) is kinetically significant; similarly only the reaction between $[Mn(acac)_2(H_2O)(OH)]$ and SO_3^{2-} is significant between pH 7.6 and 8.6. In the intermediate range $5.0 < pH < 7.6$, $[Mn(acac)_2(H_2O)_2]^+$ is reduced by SO_3^{2-} (k_2 path) in parallel with the k_1 and k_3 paths. $[Mn(acac)_2(H_2O)_2]^+$ forms hydrogen-bonded outer-sphere adducts with HSO_3^- and SO_3^{2-}. The paths k_1, k_2 and k_3 appear to be substitution-controlled from the unusual order of rate constants *viz.* $k_1 > k_2$, *i.e.* the superior kinetic activity of the hydroxoaqua complex over the diaqua complex, and similar first-order rate constants for S^{IV} oxidation and N_3^- anation at the Mn^{III}–acac complexes. Subsequent redox steps are rapid and proceed through intermediate generation of S^V radical species. The radical is further oxidised by a second Mn^{III} rather than undergoing dimerisation or self-reaction. Unlike the inner-sphere reaction between Mn^{III} and S^{IV}, the Mn^{III}–S^V reaction is outer-sphere. Added Mn^{2+} has no effect on the kinetics but the presence of O_2 affects both the kinetics and stoichiometry. It seems unlikely that the Mn^{III}–acac complexes could catalyse the autooxidation of S^{IV}, the effect of O_2 being instead due to the formation of $SO_5^{\bullet -}$ radicals which decay to SO_4^{2-}. Reactions studied here appear to be the first example of a moderately weak oxidising agent with a ground-state σ electron undergoing a substitution-controlled redox process. Previously known systems with firmly established substitution control are $[Co(OH)]^{2+}$ (aq)[74,75] and *cis*-$[Co(NH_3)_2(OH)]^{2+}$ (aq)[75] for oxidising metal centres and V^{2+} (aq)[19] and Ru^{2+} (aq)[76,77] for reducing metal centres, all of which are powerful redox agents with ground-state π-electronic configurations.

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