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Kinetics and mechanism of reduction of tris(acetylacetonato)manganese(III) by $HONH(SO_3)^-$ and $HON(SO_3)_2{}^{2-}$ in aqueous solution †

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The kinetics and mechanism of reduction of tris(acetylacetonato)manganese(III) $[Mn^{III}(acac)_3]$ by $HONH(SO_3)^-$ and $HON(SO_3)_2{}^{2-}$ in aqueous solution was studied as a function of pH, [SN oxide], [acac], temperature and pressure. The oxidation of $[Mn^{II}(acac)_2]$ by one of the oxidation products of $HON(SO_3)_2{}^{2-}$, *viz.* $ON(SO_3)_2{}^{2-}$, was studied as a function of pH, $[ON(SO_3)_2{}^{2-}]$, $[Mn^{II}]$, $[Mn^{III}]$ and pressure. The activation parameters for the reduction by $HONH(SO_3)^-$ at pH 5.2, *viz* $\Delta H^‡ = 63 \pm 2$ kJ mol^{-1}, $\Delta S^‡ = 8 \pm 6$ J K^{-1} mol^{-1} and $\Delta V^‡ = -5.8 \pm 0.5$ cm^3 mol^{-1}, and for the oxidation by $ON(SO_3)_2{}^{2-}$, *viz.* $\Delta V^‡ = -13.4 \pm 0.7$ cm^3 mol^{-1}, are discussed in terms of the nature of the electron-transfer mechanism. The kinetic data confirm the inner-sphere nature of the reactions when SN oxides react with manganese(III) complexes in general. Both the reduction and oxidation reactions are substitution-controlled redox processes. Oxidation products are generated during the reduction of the trivalent metal-ion species, which participate in the reoxidation of the metal to its trivalent state. The results are discussed with reference to data available for related reactions.

We have a long-standing interest in the oxidation of sulfur(IV), nitrogen and sulfur–nitrogen (SN) oxides by transition-metal ions and complexes in aqueous solution.[1] Such processes result in acid-rain formation under atmospheric conditions. Relatively little is known about the interaction of mixed SN oxides with metal ions and complexes, and in recent years we have studied a number of iron and manganese systems.[2] These are not only of atmospheric relevance, but also important in terms of autoxidation processes in flue-gas desulfurization plants.[2a] The kinetics of reactions of transition-metal ions with sulfur(IV), nitrogen and sulfur–nitrogen oxides is so complex that, unless its analysis is done within the framework of simpler metal complexes, the kinetic data are easily misinterpreted. Furthermore, Mn^{III} is unstable in its trivalent state in aqueous solution and by complexing with a suitable ligand it can be stabilized in solution. In spite of this instability it is anticipated that upon oxidation of Mn^{II} by strong oxidizing agents such as peroxomonosulfate, $ON(SO_3)_2{}^{2-}$ and $^-NONO(SO_3)^-$, Mn^{III} is formed in solution which participates in the oxidation of sulfur(IV), nitrogen and sulfur–nitrogen oxides. In this context we recently investigated the redox behaviour of Mn^{III}(cydta) complexes (H_4cydta = *trans*-cyclohexane-1,2-diyldinitrilotetraacetic acid) with $HONH(SO_3)^-$ and $HON(SO_3)_2{}^{2-}$.[2d] The interpretation of the kinetic results was complicated by various protonation equilibria that controlled the reactivity of the Mn^{III}(cydta) species in solution. In an effort to continue our work in this area and to select a better defined manganese(III) system, we have now investigated the redox behaviour of the Mn^{III}(acac) system (acac = acetylacetonate) in the presence of $HONH(SO_3)^-$ and $HON(SO_3)_2{}^{2-}$.

The Mn^{III}(acac) complexes are for a number of reasons particularly suitable and interesting to study. First, at high [acac] very stable positively charged or neutral complex entities are formed in aqueous solution[3] which should favour complex formation and subsequent redox reactions with the anionic SN oxides. Secondly, the oxidation of Mn^{II}(acac) complexes should be considerably more favourable compared to many other manganese(II) complexes, since a value of 0.11 V has been reported for the $[Mn(acac)_3]^{0/1-}$ couple.[4] We previously[2d] referred to the slow reoxidation of Mn^{II}(cydta) to Mn^{III}(cydta) by $ON(SO_3)_2{}^{2-}$ that is formed during the reaction of Mn^{III} with $HON(SO_3)^{2-}$, but could not investigate this reaction in detail due to the relative instability of the Mn^{III}(cydta) complex [$E_0 = 0.76$ V for the $Mn(cydta)^{1-/2-}$ couple[5]]. The present system, however, offers a more favourable possibility to study the oxidation of Mn^{II} to Mn^{III} by $ON(SO_3)_2{}^{2-}$. Finally, $[Mn^{III}(acac)_3]$ has a moderately slow ligand-exchange rate[6] which will favour a substitution-controlled electron-transfer process. A changeover in mechanism is expected when SN oxides are oxidized by Mn^{III}(acac) complexes in going from low to high pH. At low pH the pseudo-aromatic rings in $[Mn^{III}(acac)_3]$ are not expected to be displaced by SN oxides. The displacement of the aqua ligand in $[Mn^{III}(acac)_2(H_2O)_2]^+$ and $[Mn^{III}(acac)_2(H_2O)(OH)]$ should be thermodynamically more favourable such that their reduction can proceed according to an inner-sphere process.

In the present study we report on the kinetics and mechanism of the redox reactions between the SN oxides $HONH(SO_3)^-$ and $HON(SO_3)_2{}^{2-}$ and Mn^{III}(acac) complexes, and on the oxidation of Mn^{II}(acac) by $ON(SO_3)_2{}^{2-}$.

Experimental

The tris(acetylacetonato)manganese(III) and bis(acetylacetonato)manganese(II) complexes were prepared *in situ* by dissolving $Mn^{III}(O_2CMe)_3 \cdot 2H_2O$ and $Mn^{II}(ClO_4)_2 \cdot 6H_2O$ in water–acetylacetone mixtures ([acac] > 0.2 mol dm^{-3}). The UV/VIS spectra of complexes prepared in this manner did not differ from those prepared in the crystalline state according to published procedures.[6,7] Only the complexes prepared *in situ* were used in the kinetic studies. Acetylacetone was distilled under reduced pressure before use. The ions $HONH(SO_3)^-$, $HON(SO_3)_2{}^{2-}$ and $ON(SO_3)_2{}^{2-}$ were synthesized according to standard literature procedures[8] and the purity was checked by ion chromatographic analysis. In an alternative procedure,

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† *Supplementary data available* (No. SUP 57239, 9 pp.): pseudo-first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

$ON(SO_3)_2^{2-}$ was prepared by the electrochemical oxidation of a basic solution of $HON(SO_3)_2^{2-}$ at a large-surface-area platinum anode. The pH of the test solutions was adjusted to a constant value with NaOH or $HClO_4$ and measured before and after the reactions. The reference electrode of the pH meter was filled with NaCl instead of KCl to prevent the precipitation of $KClO_4$, since $NaClO_4$ was used to adjust the ionic strength of the test solutions. No buffers were used in order to avoid possible complexation with Mn^{III} and because no significant drift in pH was observed during the reactions. Eluents for the ion-chromatographic analyses were prepared from sodium carbonate, sodium hydrogencarbonate, tetrabutylammonium hydroxide and acetonitrile. Ion-chromatographic analyses were performed on a Waters chromatograph equipped with an HPLC pump and a conductivity detector. Details on the ion-chromatographic procedures are given elsewhere.[9] The UV/VIS spectra were recorded on a Philips PU 8745 spectrophotometer and a Bio Sequential SX-17MV stopped-flow spectrofluorimeter. The generation of time-dependent spectra from individual absorbance *vs.* time measurements at different wavelengths is described elsewhere.[10] Kinetic measurements at ambient pressure were performed on a Bio Sequential SX-17MV stopped-flow spectrofluorimeter which was run on-line with an Applied Photophysics Kinetic Spectrometer Workstation (RISC OS 3 operating system) on which data acquisition and processing was done. Data fitting was performed with the SX-17MV kinetic package. Experiments at elevated pressure were carried out on a laboratory-made high-pressure stopped-flow unit[11] which was run on-line with an IBM compatible personal computer. In this case data fitting was performed with the OLIS KINFIT[12] set of programs. All kinetic measurements were performed under pseudo-first-order conditions, *i.e.* an excess of ligand was employed. In spite of the good reproducibility of the kinetic traces, the reported pseudo-first-order rate constants are the averages from at least 10 kinetic runs as a result of the ease of data accumulation with the instrument used.

Results and Discussion

Preliminary observations

Aqueous solutions of $[Mn^{III}(acac)_3]$ are unstable[13] and it was necessary to stabilize the metal complex in the trivalent state in order to investigate the redox behaviour of Mn^{III}. This was done by studying the reactions in an excess of acac ($[acac] \geqslant 0.25$ mol dm^{-3}). Under such conditions and at pH > 3, negligible decomposition of $[Mn^{III}(acac)_3]$ was observed spectrophotometrically over 24 h. Manganese(III) is effectively stabilized by various β-diketones through the formation of a β-diketoenolate complex. As was mentioned in the Introduction, the stabilization increases with an increase in the pK_a of the ligand.[13] Acetylacetone has a relatively high pK_a value (8.9[13]) and forms the well characterized six-co-ordinate, mononuclear complex $[Mn^{III}(acac)_3]$.[14,15]

The acetylacetonato complexes of Mn^{III} exist as an equilibrium mixture of $[Mn^{III}(acac)_3]$, $[Mn^{III}(acac)_2(H_2O)_2]^+$ and $[Mn^{III}(acac)_2(H_2O)(OH)]$ according to Scheme 1.[13] Based on our kinetic observations reported in this paper, we postulate the formation of a protonated dechelated complex at pH ⩽ 5, $[Mn^{III}(acac)(Hacac)(H_2O)_3]^{2+}$, which can be a π-bonded metal complex as found for acac complexes of Pt^{II}[16] and carbonyl and arene complexes of Mn,[17,18] respectively. According to available literature data[13] $K_2 = 8.2 \times 10^{-6}$, $K_3 = 5 \times 10^{-8}$ mol dm^{-3} and $K_4 = 1.16 \times 10^{-9}$ mol dm^{-3}.

$$[Mn^{III}(acac)(Hacac)(H_2O)_3]^{2+} \overset{K_1}{\rightleftharpoons} [Mn^{III}(acac)_2(H_2O)_2]^+ + H_3O^+$$

$$[Mn^{III}(acac)_2(H_2O)_2]^+ + Hacac \overset{K_2}{\rightleftharpoons} [Mn^{III}(acac)_3] + H_3O^+ + H_2O$$

$$[Mn^{III}(acac)_2(H_2O)_2]^+ \overset{K_3}{\rightleftharpoons} [Mn^{III}(acac)_2(H_2O)(OH)] + H^+$$

$$Hacac \overset{K_4}{\rightleftharpoons} H^+ + acac^-$$

Scheme 1

Ion-chromatographic analyses of the redox products are in agreement with our earlier findings on the reaction of $HONH(SO_3)^-$ and $HON(SO_3)_2^{2-}$ with $[Mn^{III}(N_3)]^{2+}$[2a] and $[Mn^{III}(cydta)]^-$,[2d] *i.e.* when $HON(SO_3)_2^{2-}$ reacts with $[Mn^{III}(acac)_3]$, $ON(SO_3)_2^{2-}$, $^-NONO(SO_3)^-$ and NO_2^- are formed. The ion $ON(SO_3)_2^{2-}$ decomposes to sulfate, nitrite, $HON(SO_3)_2^{2-}$ and $ON(SO_3)_3^{3-}$. Except for the latter, the decomposition products of $ON(SO_3)_2^{2-}$ were also found in this study. No $ON(SO_3)_3^{3-}$ could be detected under different conditions $\{2 \times 10^{-4} < [HON(SO_3)_2^{2-}] < 1 \times 10^{-2}$ mol dm^{-3}; $1 \times 10^{-4} < [Mn^{III}] < 1 \times 10^{-3}$ mol dm$^{-3}\}$. The ion $^-NONO(SO_3)^-$ is formed *via* the reaction of nitrite with $HONH(SO_3)^-$ which accounts for the low concentration of the latter and NO_2^- found during the redox reaction. The complex $[Mn^{III}(acac)_3]$ catalyses the hydrolysis of SN oxides in a very similar way to the acid-catalysed hydrolysis of these species and it also oxidizes $HONH(SO_3)^-$ to N_2O and $HON(SO_3)_2^{2-}$ to $ON(SO_3)_2^{2-}$, respectively. The possible reactions and reaction stoichiometry that occur during the oxidation of SN oxides by Mn^{III} and Fe^{III} were reported in detail before[2a,b] and are in agreement with the results obtained in this study. A generalization of these reactions is given in ref. 2(*d*).

Kinetic results

Reduction of $Mn^{III}(acac)$ by $HONH(SO_3)^-$ and $HON(SO_3)_2^{2-}$. Possible reactions of $Mn^{III}(acac)$ complexes with the SN oxides $HON(SO_3)_2^{2-}$, $HONH(SO_3)^-$, $ON(SO_3)_3^{3-}$, $N(SO_3)_3^{3-}$, $HN(SO_3)_2^{2-}$ and $^-NONO(SO_3)^-$ were studied by monitoring the UV/VIS absorption spectra of the manganese(III) species and by identifying the redox products by ion chromatography. As in the case of $Mn^{III}(cydta)$, only $HON(SO_3)_2^{2-}$ and $HONH(SO_3)^-$ react with the $Mn^{III}(acac)$ complexes, which can be attributed to the higher stability of $[Mn^{III}(acac)_3]$ compared to that of $[Mn^{III}(N_3)]^{2+}$. The latter complex reacts with all the mentioned SN oxides. The reactions of $Mn^{III}(acac)$ with $HONH(SO_3)^-$ and $HON(SO_3)_2^{2-}$ were studied as a function of pH, [SN oxide], $[Mn^{III}]$, temperature and pressure under pseudo-first-order conditions, *i.e.* at least a ten-fold excess of $HONH(SO_3)^-$ and $HON(SO_3)_2^{2-}$.

Only one reaction step was observed from the absorbance *vs.* time traces recorded between 340 and 400 nm for the acidity range 3 < pH < 8 when $HON(SO_3)_2^{2-}$ and $HONH(SO_3)^-$ react with $Mn^{III}(acac)$. In order to verify our measurements in the selected wavelength range some measurements were also performed at 560 nm, where the absorbance changes are much smaller. Nevertheless, at this wavelength identical rate constants to those measured between 340 and 400 nm were obtained. Under the selected conditions the acid-catalysed hydrolysis of $HONH(SO_3)^-$ and $HON(SO_3)_2^{2-}$ is insignificant[19] and only the redox reaction plays an important role.

The pH dependence for the reduction of the various $Mn^{III}(acac)$ species outlined in Scheme 1 by $HONH(SO_3)^-$ is reported in Fig. 1. This dependence can be accounted for in terms of the equilibria outlined in Scheme 1 and the reactions given in Scheme 2, for which the rate law under pseudo-first-order conditions is given by equation (1). Using the cited literature values

$$[Mn^{III}(acac)(Hacac)(H_2O)_3]^{2+} + HONH(SO_3)^- \xrightarrow{k_a} \text{products}$$

$$[Mn^{III}(acac)_2(H_2O)_2]^+ + HONH(SO_3)^- \xrightarrow{k_b} \text{products}$$

$$[Mn^{III}(acac)_3] + HONH(SO_3)^- \xrightarrow{k_c} \text{products}$$

$$[Mn^{III}(acac)_2(H_2O)(OH)] + HONH(SO_3)^- \xrightarrow{k_d} \text{products}$$

Scheme 2 Products = Mn^{II}, NH_2OH, N_2O and SO_4^{2-}

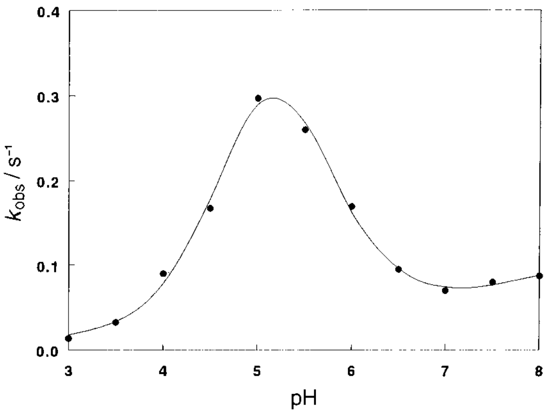


Fig. 1 pH Dependence of k_{obs} for the reaction of $HONH(SO_3)^-$ with $[Mn^{III}(acac)_3]$. Experimental conditions: $[Mn^{III}] = 1 \times 10^{-4}$, $[HONH(SO_3)^-] = 3 \times 10^{-3}$, $[acac] = 0.25$ mol dm^{-3}, $T = 25$ °C, $I = 0.25$ mol dm^{-3}

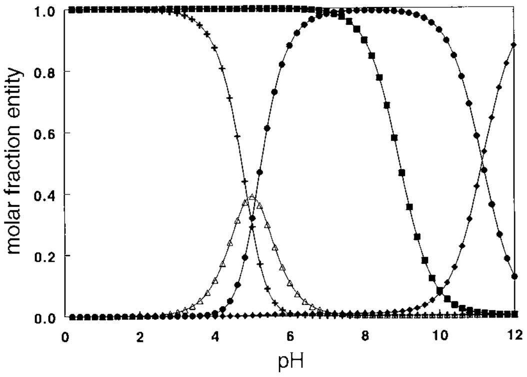


Fig. 2 Distribution curves of various Mn^{III}(acac) species: +, $[Mn^{III}(acac)(Hacac)(H_2O)_3]^{2+}$; △, $[Mn^{III}(acac)_2(H_2O)_2]^+$; ●, $[Mn^{III}(acac)_3]$; ■, Hacac; ◆, $[Mn^{III}(acac)_2(H_2O)(OH)]$

$$k_{obs} = (k_a[H^+]^2 + k_bK_1[H^+] + k_cK_1K_2[Hacac] + k_dK_1K_3)[HONH(SO_3)^-]/a \quad (1)$$

$$a = [H^+]^2 + K_1[H^+] + K_1K_2[Hacac] + K_1K_3$$

$$[Hacac] = [H^+][acac]_T/([H^+] + K_4)$$

for K_2 to K_4, a non-linear least-squares fit of the data in Fig. 1 resulted in $k_a = 2.0 \pm 1.6$ dm^3 mol^{-1} s^{-1}, $k_b = 161 \pm 4$, $k_c \approx 0$, $k_d = (6.5 \pm 1.0) \times 10^3$ dm^3 mol^{-1} s^{-1}, and $K_1 = (1.8 \pm 0.2) \times 10^{-5}$ mol dm^{-3}. The solid line in Fig. 1 represents the mathematical fit of the rate law derived from the proposed mechanism. Furthermore, it corresponds very well with the speciation curve for $[Mn^{III}(acac)_2(H_2O)_2]^+$ given in Fig. 2, which was calculated on the basis of the values of K_1 and K_4. It follows that $[Mn^{III}(acac)_2(H_2O)_2]^+$ reaches a maximum concentration at pH ≈ 5 and represents the main reactive species in the investigated pH range. The very high value found for the k_d path, *i.e.* reduction of the aquahydroxo complex, may be a good indication for the operation of an inner-sphere electron-transfer mechanism. Hydroxide ligands in general can labilize the aqua complex and increase the rate of the substitution process in order to favour the inner-sphere reaction path.[2d,3] Thus at pH > 7 the $[Mn^{III}(acac)_2(H_2O)(OH)]$ path will be the dominating rate-controlling species.

It should be noted that the pH profile in Fig. 1 cannot be explained without inclusion of the first equilibrium in Scheme 1. A similar trend was observed for the reduction by $HON(SO_3)_2^{2-}$. A pK_a value of 12 was reported for $HON(SO_3)_2^{2-}$,[20] such that the inflection point at pH < 5.2 can be attributed to an inner-sphere mechanism in which the pK_a of the coordinated group is lowered. However, no deprotonation exists for $HONH(SO_3)^-$ at pH > 1 [$HONH(SO_3)^-$ undergoes base hydrolysis at high pH[21]] and in this case a mechanism in which the protonation of $HONH(SO_3)^-$ between pH 3 and 5.2 could play a role can be ruled out. Based on earlier arguments, the formation of a protonated dechelated complex at lower pH is not unrealistic, and we prefer to explain the pH profile in Fig. 1 accordingly.

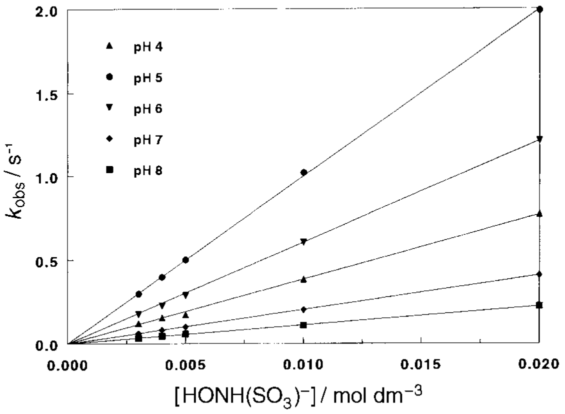


Fig. 3 Plots of k_{obs} *versus* $[HONH(SO_3)^-]$ at different pH for the reduction of $[Mn^{III}(acac)_2(H_2O)_2]^+$. Experimental conditions: $[Mn^{III}] = 1 \times 10^{-4}$ mol dm^{-3}, $I = 0.75$ mol dm^{-3}, $[acac] = 0.25$ mol dm^{-3}, $T = 25$ °C

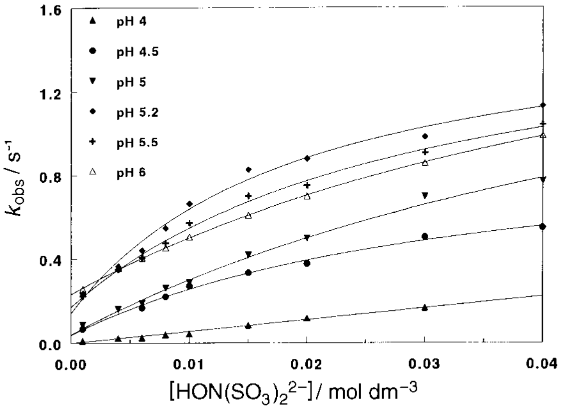


Fig. 4 Plots of k_{obs} *versus* $[HON(SO_3)_2^{2-}]$ at different pH for the reduction of $[Mn^{III}(acac)_2(H_2O)_2]^+$. Experimental conditions as in Fig. 3

Kinetic studies were performed as a function of pH at constant [acac] or at constant pH, *i.e.* where the pH profile reaches a maximum (pH 5.2), as a function of [acac], temperature and pressure. The k_{obs} values were not affected by the $[Mn^{III}]$ or by the light intensity used to monitor the reaction. The values of the pseudo-first-order rate constants, k_{obs}, are summarized in SUP 57239. A variation of $[HONH(SO_3)^-]$ between 3×10^{-3} and 2×10^{-2} mol dm^{-3} demonstrated a first-order dependence of k_{obs} on $[HONH(SO_3)^-]$ at constant pH, [acac] and temperature (see Fig. 3). In all the cases intercepts statistically equal to zero were found.

For the reaction with $HON(SO_3)_2^{2-}$ a variation of $[HON(SO_3)_2^{2-}]$ between 3×10^{-3} and 4×10^{-2} mol dm^{-3} resulted in a non-linear dependence of k_{obs} on $[HON(SO_3)_2^{2-}]$ and a significant intercept for all data at pH ⩾ 4.5 (see Fig. 4) at a fixed pH, [acac] and temperature. At pH 4 a linear dependence with an intercept statistically equal to zero was obtained. The observed curvature at pH ⩾ 4.5 is ascribed to a mechanism that involves a preassociation step that results in the saturation of the k_{obs} value at high $[HON(SO_3)_2^{2-}]$. The intercepts cannot be due to spontaneous decomposition of the complex, since the complex is stable at the acac concentrations used in this investigation. Furthermore, the intercepts in Fig. 4 increase with increasing pH (Table 1), which points to the role of the reverse reaction, *i.e.* the reoxidation of Mn^{II} to Mn^{III} that becomes more favourable at higher pH. The possibility that the Mn^{II}(acac) com-

Table 1 Rate constants and thermodynamic parameters for the reaction of $HONH(SO_3)^-$ and $HON(SO_3)_2^{2-}$ with Mn^{III}(acac) complexes[a]

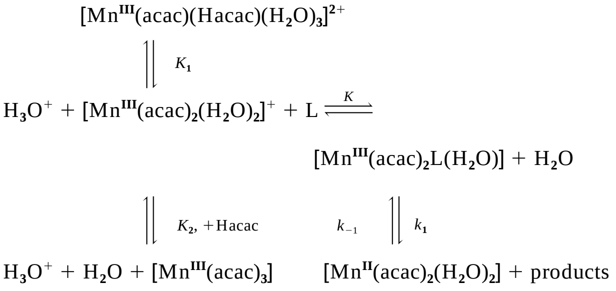
Oxide	pH	T/ °C	[acac]/mol dm^{-3}	k_1K/dm^3 mol^{-1} s^{-1}
$HONH(SO_3)^-$	4	25	0.25	256 ± 4
	5.2	5		24.2 ± 0.2
		10		44.3 ± 0.3
		15		72.7 ± 0.6
		20		111 ± 2
		25		168 ± 1
		30		257 ± 2
	$\Delta H^‡$ 63 ± 2 kJ mol^{-1}, $\Delta S^‡$ 8 ± 6 J K^{-1} mol^{-1}			
	5.2	25	0.3	163 ± 1
			0.4	160 ± 2
			0.6	159 ± 3
			0.8	153 ± 2
	6	25	0.25	187 ± 1
	7			436 ± 1
	8			5385 ± 48

Oxide	pH	k_1/s^{-1}	K/dm^3 mol^{-1}	k_{-1}/dm^3 mol^{-1} s^{-1}
$HON(SO_3)_2^{2-}$ [b]	4.5	0.96 ± 0.09	84 ± 18	0.04 ± 0.02
	5.0	2.0 ± 0.4	27 ± 8	0.04 ± 0.02
	5.2	1.9 ± 0.1	84 ± 15	0.14 ± 0.04
	5.2	1.4 ± 0.1	87 ± 21	0.14 ± 0.04
	5.5	1.5 ± 0.1	62 ± 11	0.17 ± 0.02
	6.0	1.9 ± 0.1	52 ± 3	0.23 ± 0.00

[a] Experimental conditions: ionic strength = 0.75 mol dm^{-3}, reactions followed at 340 < λ < 400 nm, atmospheric pressure. [b] All results at 25 °C, [acac] = 0.25 mol dm^{-3}. At pH 4.0, $k_1K = 37.1 \pm 1.1$ dm^3 mol^{-1} s^{-1}.

plexes produced are reoxidized to Mn^{III}(acac) complexes will be discussed later. It is important to note that the oxidation of $HONH(SO_3)^-$ by $[Mn^{III}(acac)_2(H_2O)(OH)]$ is *ca.* 400 times faster than by $[Mn^{III}(acac)_2(H_2O)_2]^+$. This suggests that the electron-transfer reaction could be substitution controlled, *i.e.* determined by the lability of the co-ordinated solvent molecules. Furthermore, in the case of the reaction with $HONH(SO_3)^-$ no spectral or kinetic evidence for an intermediate complex was observed under the selected experimental conditions, such that substitution can in principle be the rate-determining step. A reaction mechanism that includes the latter possibilities is outlined in Scheme 3, and the corresponding rate law is given in equation (2). From the pH-dependence data it is clear that at pH 5.2 only the $[Mn^{III}(acac)_2(H_2O)_2]^+$ species is kinetically significant.

$$k_{obs} = (k_1KK_1[L][H^+])/([H^+]^2 + K_1[H^+] + K_1K_2[Hacac] + KK_1[L]) + k_{-1} \quad (2)$$



Scheme 3 L = $HONH(SO_3)^-$ or $HON(SO_3)_2^{2-}$

For the reduction by $HONH(SO)_3^-$ no reoxidation of $[Mn^{II}(acac)_2(H_2O)_2]$ occurs due to the absence of $ON(SO_3)_2^{2-}$ (see further Discussion), *i.e.* $k_{-1} \approx 0$, and K is small such that equation (2) simplifies to (3). In this case the observed second-order rate constant, k_1K, was calculated directly from the slope of plots of k_{obs} *versus* $[HONH(SO_3)^-]$ (Fig. 3) according to equation (3), and the results are summarized in Table 1. For the reduction by $HON(SO_3)_2^{2-}$ the data were treated according to equation (2) by plotting $(k_{obs} - k_{-1})^{-1}$ *versus* $[HON(SO_3)_2^{2-}]^{-1}$, and the resulting values for k_1 and K are summarized in Table 1. The magnitude of K is such that it strongly supports the efficient formation of an inner-sphere complex followed by the electron-transfer process.

$$k_{obs} = (k_1KK_1[L][H^+])/([H^+]^2 + K_1[H^+] + K_1K_2[Hacac]) \quad (3)$$

At a fixed pH the rate decreases significantly with increasing [acac] (see Fig. 5 and Table 1). This is in agreement with studies on the reduction of $[Mn^{III}(acac)_3]$ by thiosulfate[15] and sulfur(IV)[6] and confirms that $[Mn^{III}(acac)_3]$ is the least reactive Mn^{III} species towards reduction. The values of k_{obs} at different $[acac]_T$ but at constant $[H^+]$ and $HONH(SO_3)^-$ were fitted by equation (3) using a non-linear least-squares method, and the fits are shown as solid lines in Fig. 5. From this fit it follows that $k_1K = 115 \pm 19$ dm^3 mol^{-1} s^{-1}, which is the average value from the five different data sets in Fig. 5. The latter value agrees fairly well with the value obtained according to equation (3) at 25 °C, pH 5.2 and [acac] = 0.25 mol dm^{-3}.

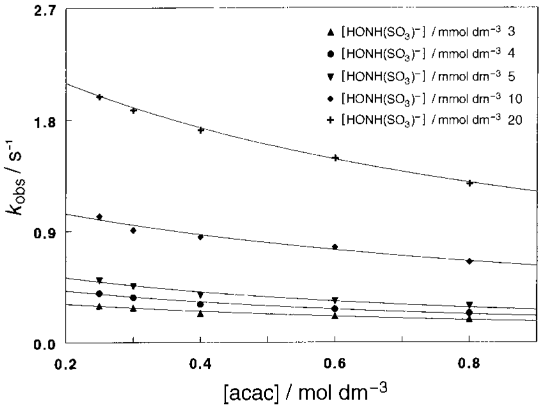


Fig. 5 Plots of k_{obs} *versus* [acac] at different $[HONH(SO_3)^-]$ for the reduction of Mn^{III}(acac) complexes. Experimental conditions as in Fig. 3

The second-order rate constants, k_1K, for the reduction by $HONH(SO_3)^-$ as a function of temperature in Table 1 were used to calculate values for $\Delta H^‡$ and $\Delta S^‡$. These values are

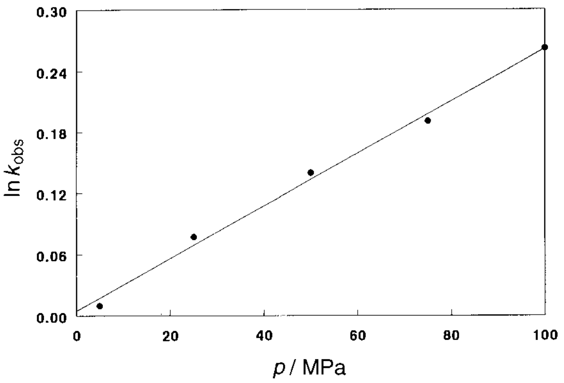


Fig. 6 Pressure dependence of k_{obs} for the reduction of $[\mathrm{Mn^{III}(acac)_2(H_2O)_2}]^+$ by $\mathrm{HONH(SO_3)^-}$. Experimental conditions: $[\mathrm{HONH(SO_3)^-}] = 1 \times 10^{-2}$, $[\mathrm{Mn^{III}}] = 1 \times 10^{-4}$, $I = 0.75$ mol dm^{-3}, pH 5.2, $[\mathrm{acac}]_T = 0.25$ mol dm^{-3}, $T = 25$ °C

also listed in Table 1. In addition, the effect of pressure (up to 100 MPa) on this reaction was studied at pH 5.3 and the results are summarized in Fig. 6, from which it follows that $\Delta V^\ddagger = -5.8 \pm 0.5$ cm^3 mol^{-1}. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are in line with those expected for a negatively charged reductant in combination with a positively charged manganese(III) complex.[22] These redox processes are in general interpreted in terms of a substitution-controlled process. It should, however, be noted that the activation entropy reported here is significantly more positive than those reported for the reduction of $[\mathrm{Mn^{III}(acac)_2(H_2O)_2}]^+$ by thiosulfate,[3] $\mathrm{S^{IV}}$ [6] and the oxalate ion.[23] In most of the latter cases the formation of an intermediate complex species could be observed spectrophotometrically. For the reduction of $\mathrm{Mn^{III}(cydta)}$ by $\mathrm{HONH(SO_3)^-}$ [2d] more negative values for both the activation volume and entropy and smaller values for the activation enthalpy were observed, which point to the formation of $\mathrm{Mn^{III}L\{HONH(SO_3)\}}$ species in a highly ordered transition state. In the present case the activation parameters are composite quantities including contributions from both the complex-formation and the electron-transfer steps in terms of an inner-sphere mechanism. The complex-formation step is accompanied by ligand substitution and charge neutralization, whereas the electron-transfer step involves reduction of the metal centre and oxidation of $\mathrm{HONH(SO_3)^-}$ and $\mathrm{HON(SO_3)_2^{2-}}$. It is reasonable to expect that entropic and volume contributions for both these steps could cancel to some extent and result in the almost zero $\Delta S^\ddagger$ and small negative $\Delta V^\ddagger$ values. A more detailed interpretation of the reported activation parameters seems to be too speculative at the present stage.

Oxidation of $\mathrm{Mn^{II}(acac)}$ by $\mathrm{ON(SO_3)_2^{2-}}$

In order to investigate the oxidation of bis(acetylacetonato)manganese(II) by $\mathrm{ON(SO_3)_2^{2-}}$ the complex was mixed with an excess of $\mathrm{ON(SO_3)_2^{2-}}$ and the UV/VIS spectra monitored as a function of time. The spectral changes showed that $[\mathrm{Mn^{II}(acac)_2(H_2O)_2}]$ is oxidized to $\mathrm{Mn^{III}(acac)}$ by $\mathrm{ON(SO_3)_2^{2-}}$. Ion-chromatographic analyses of the reaction mixture showed that $\mathrm{HON(SO_3)_2^{2-}}$ is formed during the reaction, which further demonstrates that the reaction between $\mathrm{ON(SO_3)_2^{2-}}$ and $[\mathrm{Mn^{II}(acac)_2(H_2O)_2}]$ is a redox process.

Values for k_{obs} were measured as a function of pH under pseudo-first-order conditions with $[\mathrm{Mn^{II}}]$ in excess (SUP 57239). No investigations were performed at pH < 3.5 since the acid-catalysed hydrolysis of $\mathrm{ON(SO_3)_2^{2-}}$ is significant under these conditions.[24] No significant drift in the pH was observed after mixing equivalent volumes of the $\mathrm{Mn^{II}(acac)}$ complex with $\mathrm{ON(SO_3)_2^{2-}}$. In all the cases the absorbance *vs.* time plots at 340 nm are typical for pseudo-first-order reactions and the corresponding plots of $\ln (A_\infty - A_t)$ *versus* time are linear for at least 2–3 half-lives of the reaction.

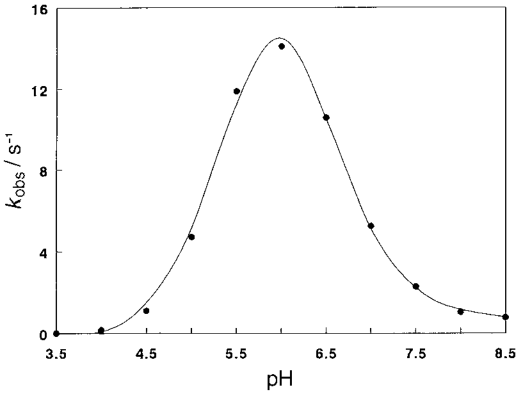


Fig. 7 pH Dependence of k_{obs} for the oxidation of $\mathrm{Mn^{II}(acac)}$ complexes by $\mathrm{ON(SO_3)_2^{2-}}$. Experimental conditions: $[\mathrm{Mn^{II}}] = 1 \times 10^{-3}$, $[\mathrm{ON(SO_3)_2^{2-}}] = 5 \times 10^{-5}$, $[\mathrm{acac}] = 0.25$ mol dm^{-3}, $T = 25$ °C, $I =$ mol dm^{-3}

$$\mathrm{HON(SO_3)_2^-} \overset{K_5}{\rightleftharpoons} \mathrm{ON(SO_3)_2^{2-}} + \mathrm{H^+}$$

$$[\mathrm{Mn^{II}(acac)(Hacac)(H_2O)_3}]^+ \overset{K_6}{\rightleftharpoons} [\mathrm{Mn^{II}(acac)_2(H_2O)_2}] + \mathrm{H_3O^+}$$

$$[\mathrm{Mn^{II}(acac)(Hacac)(H_2O)_3}]^+ + \mathrm{HON(SO_3)_2^-} \xrightarrow{k_e} \text{products}$$

$$[\mathrm{Mn^{II}(acac)_2(H_2O)_2}] + \mathrm{HON(SO_3)_2^-} \xrightarrow{k_f} \text{products}$$

$$[\mathrm{Mn^{II}(acac)_2(H_2O)_2}] + \mathrm{ON(SO_3)_2^{2-}} \xrightarrow{k_g} \text{products}$$

Scheme 4

The pH dependence of the oxidation of $[\mathrm{Mn^{II}(acac)_2(H_2O)_2}]$ by $\mathrm{ON(SO_3)_2^{2-}}$ was studied in the range $3.5 \leqslant \mathrm{pH} \leqslant 8.5$ in the presence of an excess of the complex. The results reported in Fig. 7 indicate a typical bell-shaped pH dependence which suggests that two acid–base equilibria involving three species of different reactivity must be involved in the process. However, pH titrations of both the $\mathrm{Mn^{II}(acac)}$ complex and $\mathrm{ON(SO_3)_2^{2-}}$ revealed no characteristic acid–base equilibria in this pH range, which is consistent with available literature data.[25,26] It has however been reported[26,27] that the redox potential of $\mathrm{ON(SO_3)_2^{2-}}$ increases significantly on decreasing the pH from 11.8 to 6.6, which coincides with the increase in k_{obs} with decreasing pH (>6) as seen in Fig. 7. No further information is available on the nature of the protonated anion radical of $\mathrm{ON(SO_3)_2^{2-}}$.[26] The decrease in k_{obs} with decreasing pH at pH < 6 must be related to protonation of a $\mathrm{Mn^{II}(acac)}$ complex to form a dechelated complex, accompanied by a decrease in the redox activity. It is expected that, because of the neutral charged $[\mathrm{Mn^{II}(acac)_2(H_2O)_2}]$ species, the co-ordinated acac will be much more easily protonated than was the case for $[\mathrm{Mn^{III}(acac)_2(H_2O)_2}]^+$. We therefore suggest the participation of a $[\mathrm{Mn^{II}(acac)(Hacac)(H_2O)_3}]^+$ species that can undergo a subsequent deprotonation reaction as indicated in Scheme 4.

The rate law for the reaction in the presence of an excess of $\mathrm{Mn^{II}}$ is given by equation (4). A non-linear least-squares fit of

$$k_{obs} = [\mathrm{Mn^{II}}]_T(k_e[\mathrm{H^+}]^2 + k_fK_6[\mathrm{H^+}] + k_gK_5K_6)/\{(1 + K_5[\mathrm{H^+}]^{-1})(1 + K_6[\mathrm{H^+}]^{-1})\} \quad (4)$$

the data in Fig. 7 (SUP 57239) resulted in values for $k_e \approx 0$, $k_f = (3.4 \pm 0.9) \times 10^4$, and $k_g = (6 \pm 3) \times 10^2$ dm^3 mol^{-1} s^{-1}, $K_5 = (6 \pm 2) \times 10^{-7}$ and $K_6 = (2.1 \pm 0.8) \times 10^{-6}$ mol dm^{-3}. It follows that the deprotonated $[\mathrm{Mn^{II}(acac)_2(H_2O)_2}]$ complex and the protonated $\mathrm{HON(SO_3)_2^{2-}}$ ligand have the highest redox activity in the investigated pH range. The reaction with the protonated dechelated complex is suggested to account for the decrease in k_{obs} at lower pH. The significantly lower reactivity of the protonated complex species is not so unusual. Similar reactivity patterns have been observed for the oxidation of $HONH(SO_3)^-$ by Mn^{III}(cydta) complexes[2d] and the reduction of NO_2^-,[28] $[Co(NH_3)_5Cl]^{2+}$, $[Co(en)_2(pvp)Cl]^{2+}$ and $[Co(en)_2(py)Cl]^{2+}$ [pvp = poly(4-vinylpyridine), en = ethane-1,2-diamine, py = pyridine][29] by aminopolycarboxylatoiron(II) complexes. The values for K_5 and K_6 deviate slightly from the inflection points in Fig. 7 because $ON(SO_3)_2^{2-}$ exists in solution at pH values where $[Mn^{II}(acac)(Hacac)(H_2O)_2]^+$ has already formed. It is realistic that K_6 could not be detected in the pH titrations due to the high concentrations of acac (= 0.25 mol dm^{-3}) compared to [complex] < 0.01 mol dm^{-3} employed to stabilize the complex in aqueous solution.

The influence of $[Mn^{II}]$ and $[ON(SO_3)_2^{2-}]$ on the rate of oxidation reaction was investigated at the maximum of the pH profile in Fig. 7, *i.e.* pH 6, and at 25 °C. The observed first-order rate constants exhibited a linear dependence on both $[Mn^{II}]$ and $[ON(SO_3)_2^{2-}]$, from which second-order rate constants $(1.4 \pm 0.3) \times 10^4$ and $(1.1 \pm 0.3) \times 10^4$ dm^3 mol^{-1}, respectively, were calculated. The latter value agrees well with that obtained for k_f from the data fit of the k_{obs} values as a function of pH using equation (4) and so supports the proposed mechanism. Analogously to Scheme 3, these are composite values resulting from the complex-formation and the electron-transfer reaction steps, respectively. We also determined the volume of activation at pH 6, *i.e.* where the pH profile in Fig. 7 reaches a maximum, by measuring k_{obs} values for the oxidation of Mn^{II}(acac) by $ON(SO_3)_2^{2-}$ at elevated pressures (up to 100 MPa). The results enable the calculation of $\Delta V^\ddagger = -13.4 \pm 0.7$ cm^3 mol^{-1} from the slope ($= -\Delta V^\ddagger/RT$) of a plot of ln k_{obs} *versus* pressure. The latter value indicates that the formation of the $Mn^{II}L$-$\{ON(SO_3)_2^{2-}\}$ species is characterized by a highly ordered transition state, *i.e.* a decrease in the overall partial molar volume which is usually associated with an increase in the co-ordination number in the transition state. As mentioned above, the value for $\Delta V^\ddagger$ is a composite resulting from the volume changes due to complex-formation and electron-transfer reaction steps, respectively. The oxidation of Mn^{II} to Mn^{III} and the associated increase in electrostriction due to charge creation during this step will largely account for the negative value of $\Delta V^\ddagger$.[30]

The results of this study confirm our previous results[2] on the ion-chromatographic analyses of the redox products for these type of reactions. In accordance with our results for the Mn^{III}-(cydta)[2d] system, only $HONH(SO_3)^-$ and $HON(SO_3)_2^{2-}$ are reactive. The kinetic data in this study confirm the inner-sphere nature of the reactions when SN oxides react with manganese(III) complexes in general. This is the second study in which an activation volume for the oxidation of $HONH(SO_3)^-$ has been reported, and the value reported in this study can be accounted for in terms of an inner-sphere electron-transfer mechanism. It is important to note that oxidation products are generated during the reduction of the trivalent metal-ion species that participate in the reoxidation of the metal to its trivalent state. This has also been observed in our previous study.[2d] The oxidation of bis(acetylacetonato)manganese(II) by such an oxidation product, *viz.* $ON(SO_3)_2^{2-}$, was investigated in more detail in the present study. The results of the reoxidation reaction suggest that it proceeds according to an inner-sphere mechanism. The present study therefore contributes to the available mechanistic information on reactions of manganese-(II) and -(III) complexes with SN oxides in general, and demonstrates the feasibility of redox cycling of the metal complex in such systems.

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