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Manganese(III) oxidation of arsenic(III)/antimony(III) in aqueous sulphuric acid

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The noncomplementary manganese(III) oxidation of arsenic(III)/antimony(III) has been studied in aqueous sulphuric acid medium and is found to follow a complex rate law. Both Mn^{3+} and $MnOH^{2+}$ are active in the oxidation which is also influenced by Mn^{2+} and not by As(V). Some reaction constants have been obtained.

The studies on kinetics of oxidation of inorganic species by Mn(III) are scanty[1]. In view of the high reduction potential of Mn(III) (1.51 V in dilute acid) and large charge on the ion, Mn(III) oxidations are usually rather fast and this, in part, accounts for the comparatively less number of studies involving inorganic reductants. The oxidation of As(III)/Sb(III) by Mn(III) has not been studied. In the following, we report the results of our study of this reaction.

Materials and Methods

Reagent grade chemicals were used. Doubly distilled water was used throughout this work. While the stock solution of As(III) was made by dissolving As(III) oxide (BDH, AR) in 1.0 mol dm^{-3} sodium hydroxide, that of antimony(III) was made by dissolving Sb(III) oxide (AR) in 10 mol dm^{-3} sulphuric acid. The solutions were standardised with potassium bromate[3]. The base in the As(III) solution was neutralised by adding the requisite amount of acid during the preparation of the reaction solution. The Mn(III) solution was freshly prepared for each kinetic run. The Mn(III) solution was prepared by addition of a 0.10 mol dm^{-3} potassium permanganate solution to a solution of Mn(II) sulphate (0.10 mol dm^{-3}) (Riedel) dissolved in 3.0 mol dm^{-3} sulphuric acid[4] and was then standardised with iron(II) solution. The ionic strength in kinetic runs was maintained constant with sodium sulphate.

Kinetic runs were intiated by mixing pre-equilibrated reactant solutions which also contained equivalent amounts of sulphuric acid and the required amount of sodium sulphate. The reaction between Mn(III) and As(III)/Sb(III) was followed by measuring the absorbance of Mn(III) in the reaction mixture at 500 nm in a 1 cm cell on a Bausch and Lomb Spectronic 2000 spectrophotometer. The obedience to Beer's law of Mn(III) solutions under the reaction conditions (5.0 mol dm^{-3} sulphuric acid and $I = 5.6$ mol dm^{-3}) had earlier been tested in the concentration range of 5.0×10^{-4} to 1.0×10^{-2} mol dm^{-3} with $\varepsilon = 114$ ($\pm 1.0\%$). The spectrum of Mn(III) in the visible region agreed with that of earlier work[5]. The value of ε was found to be depend on $[H_2SO_4]$ acid and it decreased slightly with the decrease in [acid]: the value of ε in presence of 5.0, 4.0, 3.5 and 3.0 mol dm^{-3} sulphuric acid were 114, 114, 112, 107 ($\pm 1\%$) respectively. Rates of reaction were reproducible within $\pm 4\%$.

Results

Stoichiometry: Different reaction mixtures containing various sets of concentrations of the reactants in sulphuric acid-sulphate media were allowed to stand for 24 hr and then analysed for Mn(III), As(III)/Sb(III) and As(V)/Sb(V) by measuring the absorbance at 500 nm, by titration with bromate and by iodometric titration respectively. The results indicated that one mole of As(III)/Sb(III) consumed two moles of Mn(III) in accordance with Eq. (1).

$$2Mn(III) + As(III) = 2Mn(II) + As(V) \qquad \ldots (1)$$

Reaction order: Rate data for different sets of concentrations of reactants are presented in Table 1. At fixed [As(III)] (5.0×10^{-3} mole dm^{-3}), $[H_2SO_4]$ (5.0 mol dm^{-3}) and at $I = 5.6$ mol dm^{-3} (obtained from the *in situ* calculated free H^+, HSO_4^- etc. concentrations in reaction solution) and 25°C, the order in [Mn(III)] (1.0×10^{-3} to 9.0×10^{-3} mol dm^{-3}) was ~1.2 and under similar

Table 1 – Rate data of Mn(III)-As(III)/Sb(III) reactions in aqueous sulphuric acid at 25°C ($I = 5.6$ mol dm^{-3})^a

$[Mn^{3+}] \times 10^3$ (mol dm^{-3})	$[As^{3+}] \times 10^3$ (mol dm^{-3})^a	$[H^+]^d$ (mol dm^{-3})	Rate × 10^6 (mol dm^{-3} s^{-1})^{b,c}	
			Exp.	Calc.
1.0 (1.1)	5.0 (2.6)	5.1	0.58 (3.3)	0.75 (5.1)
3.0 (3.1)	5.0 (2.6)	5.1	2.3 (11.0)	2.3 (14.0)
5.0 (5.0)	5.0 (2.6)	5.1	4.0 (20.0)	3.8 (23.0)
8.0 (7.0)	5.0 (2.6)	5.1	7.4 (33.0)	6.0 (33.0)
11.0 (9.0)	5.0 (2.6)	5.1	9.0 (44.0)	8.3 (42.0)
5.0 (5.0)	2.0 (2.5)	5.1	1.5 (20.0)	1.5 (23.0)
5.0 (5.0)	4.0 (5.0)	5.1	4.0 (43.0)	3.8 (45.0)
5.0 (5.0)	8.0 (7.5)	5.1	5.9 (53.0)	6.0 (67.0)
5.0 (5.0)	12.0 (10.0)	5.1	8.6 (83.0)	9.0 (90.0)
5.0 (5.0)	20.0 (12.5)	5.1	14.0 (111.0)	15.0 (112.0)
5.0 (5.0)	5.0 (2.6)	2.4	6.6 (35.0)	5.9 (38.0)
5.0 (5.0)	5.0 (2.6)	3.1	5.5 (29.0)	4.9 (32.0)
5.0 (5.0)	5.0 (2.6)	3.7	4.9 (26.0)	4.5 (29.0)
5.0 (5.0)	5.0 (2.6)	4.4	4.5 (23.0)	4.2 (26.0)

(a) Values in parentheses refer to [Sb(III)].

[b] Values in parentheses refer to Mn(III)-Sb(III) system at 27°C.

(c) All rates are initial rates; rates in case of Mn^{3+}-Sb^{3+} were obtained by construction of the initial parts of the C versus t plots, since the reaction is rather fast in the latter case in the earlier stages.

(d) $[H^+]$ values are calculated from added $[H_2SO_4]$ and $[SO_4^{2-}]$ and the acid sulfate equilibrium constant[9].

Table 2 – Effect of product Mn(II) on the Mn(III)-As(III)/Sb(III) in aqueous sulphuric acid at 25°C ($I = 5.6$ mol dm^{-3}; $[H^+] = 5.1$ mol dm^{-3})^a

$[Mn^{3+}] \times 10^3$ (mol dm^{-3})	$[As^{3+}] \times 10^3$ (mol dm^{-3})	$[Mn^{2+}] \times 10^3$ (mol dm^{-3})	Rate × 10^6 (mol dm^{-3} s^{-1})
5.0 (5.0)	5.0 (2.6)	0 (0)	4.0 (20.0)
5.0 (5.0)	5.0 (2.6)	5 (2)	3.6 (18.0)
5.0 (5.0)	5.0 (2.6)	10 (6)	3.1 (16.0)
5.0 (5.0)	5.0 (2.6)	20 (10)	2.5 (15.0)
5.0 (5.0)	5.0 (2.6)	40 (20)	2.0 (11.0)
— (5.0)	— (2.6)	— (30)	— (10.0)

(a) Entries in parentheses refer to Mn^{3+}-Sb^{3+} reaction at 27°C.

conditions of acidity, I and temperature, at a constant [Mn(III)] (5.0×10^{-3} mol dm^{-3}), the order in As(III)/Sb(III) in the range of 2.5×10^{-3} to 2.0×10^{-2} mol dm^{-3} was ~0.90. The determination of the order in $[H^+]$ was restricted somewhat to $[H^+]$ range of 2.4 to 5.1 mol dm^{-3} at constant I of 5.6 mol dm^{-3} used, in view of the instability of the oxidant at lower [acid] and was found to be approximately −0.8. The reaction orders were found from log-log plots of initial rates against concentrations.

Product effect: Other conditions and concentrations of reactants used being constant, the effect of the initial addition of the products was studied in the range of 0 to 3.0×10^{-2} mol dm^{-3} of Mn(II) of As(V)/Sb(V) and it was found that Mn(II) retarded the reaction with an order of ~0.3 (Table 2); As(V)/Sb(V) added initially did not influence the reaction significantly.

Discussion

The manganese(III) oxidation of As(III) (or Sb(III) in a strong sulphuric acid medium follows the approximate rate law (2). The Mn(III)-Sb(III) case was also studied along with Mn(III)-As(III) because of the added interest in that the

$$\mathrm{Rate} = k[Mn^{3+}]_T^{1.2}[As^{3+}]^{1.0}[H^+]^{-0.8}[Mn^{2+}]^{-0.3} \ldots \quad (2)$$

Mn(III)-Sb(III) system is strongly susceptible to influences of halides[6] and the results largely parallel those of the Mn(III)-As(III) reaction. The reaction rate is lowered by increasing acidity and this indicates that the active oxidant may be a hydrolysed species[7] such as $MnOH^{2+}$; species such as $MnHSO_4^{2+}$ is also present in considerable amounts in sulphuric acid solution[7]. However, studies in strong perchloric acid and sulphuric acid media have shown the importance of $MnOH^{2+}$ as an oxidant to the exclusion of other species like $MnHSO_4^{2+}$. In the present case, Mn_f^{3+} and $MnOH^{2+}$ both seem to be active as indicated by the results presented in Table 3. This is also confirmed from the plot of rate versus $1/[H^+]$ which gives an intercept indicating the likelihood of two active species, one protonated and the other de-

Table 3 – Effect of varying [acid] on Mn(III)-As(III)/Sb(III) reactions in aqueous sulphuric acid at 25°C

$[Mn(III)] = 5.0 \times 10^3$ mol dm^{-3}; $[As(III)]([Sb(III)]) = 5.0 \times 10^{-3}$ (2.6×10^{-3}) mol dm^{-3}; $I = 5.6$ mol dm^{-3}

$[H_2SO_4]$	$[H^+]$	$[HSO_4^-]$	$[SO_4^{2-}]$	$[Mn^{3+}]_f \times 10^4$	$[Mn(OH)^{2+}] \times 10^4$	$[Mn(HSO_4)^{2+}] \times 10^3$	Rate $\times 10^6$ mol dm^{-3} s^{-1}
3.0	2.4	3.6	0.18	6.2	2.5	4.1	6.6 (35.0)
3.5	3.1	3.9	0.16	5.8	1.8	4.2	5.5 (29.0)
4.0	3.7	4.3	0.14	5.4	1.4	4.3	4.9 (26.0)
4.5	4.4	4.6	0.13	5.1	1.1	4.4	4.5 (23.0)
5.0	5.1	5.0	0.12	4.8	0.91	4.4	4.0 (20.0)

Rates in parenthesis refer to Mn^{3+}-Sb^{3+} reaction at 27°C.
All concentration terms are in mol dm^{-3}.

$$\begin{array}{lr}
Mn^{3+} + H_2O \rightleftharpoons MnOH^{2+} + H^+ & (K_h) \\
Mn^{3+} + As(III) \rightleftharpoons Mn^{2+} + As(IV) & (k_1, k_{-1}) \\
Mn^{3+} + As(IV) \rightarrow Mn^{2+} + As(V) & (k_2) \\
MnOH^{2+} + As(III) \rightleftharpoons Mn^{2+} + As(IV) & (k_3, k_{-3}) \\
MnOH^{2+} + As(IV) \rightarrow Mn^{2+} + As(V) & (k_4)
\end{array}$$

Scheme 1

protonated. As regards As(III), it is almost exclusively present as undissociated H_3AsO_3 (written in Scheme 1 simply as As(III)), its dissociation[8] being extremely small ($K = 2 \times 10^{-10}$). In terms of such species, the mechanism shown in Scheme 1 may be written in accordance with results obtained. The rate law derived for Scheme 1 (see appendix) is represented by Eq. (3).

$$-d[Mn^{3+}]_T/dt = \frac{(k_2[H^+]+k_4K_h)(k_1[H^+]+k_3K_h)[Mn^{3+}]_T^2\,[As(III)]}{([H^+]+K_h)^2(k_{-1}+k_3)[Mn^{2+}]+([H^+]+K_h)(k_2[H^+]+k_4K_h)[Mn^{3+}]_T} \quad \ldots\ldots (3)$$

A plot of $([Mn^{3+}]_T[As^{3+}])$/(rate) against $[Mn^{2+}]$/(rate) against $[Mn^{2+}]/[Mn^{3+}]_T$ should be linear at constant acidity according to Eq. (3) and this is found to be the case at different acidities as shown in Fig. 1. From the slopes and intercepts at the different acidities, as seen from a rearranged form of rate law (3), a plot of (intercept/slope) $([H^+] + K_h)$ against $[H^+]$ leads to values of $k_2/(k_{-1} + k_3)$ and $k_4/(k_{-1} + k_{-3})$. Likewise, k_1 and k_3 are obtained from a plot of $([H^+] + K_h)$/(intercept) versus $[H^+]$. These values are as follows: k_1 and k_3 are respectively 0.036 and 0.28 dm^3 mol^{-1} s^{-1} in the case of Mn^{3+}-As^{3+} reaction (k_1 and k_3 respectively are 0.20 and 4.6 dm^3 mol^{-1} s^{-1} for Mn^{3+}-Sb^{3+} case). The values of $(k_2/k_{-1} + k_{-3})$ and $(k_4/k_{-1} + k_{-3})$ are respectively 0.96 and 1.6 in respect of Mn^{3+}-As^{3+} reaction and 1.0 and 1.4 in the Mn^{3+}-Sb^{3+} case. It is noteworthy that $MnOH^{2+}$ is more effective as an oxidant than the free Mn^{3+} itself.

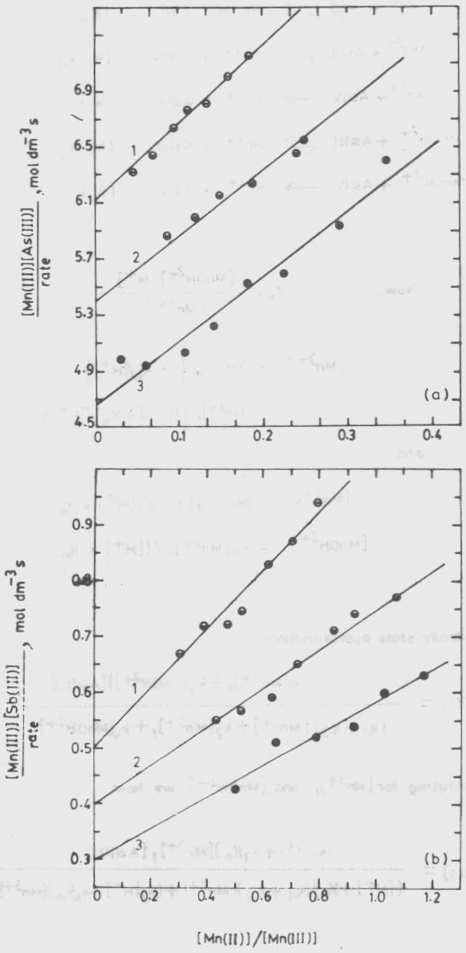

Fig. 1 – (a) Plot of $([Mn^{3+}]_T\ [As^{3+}])$/rate versus $[Mn^{2+}]/[Mn^{3+}]_T$, (b) Plot of $([Mn^{3+}]_T\ [Sb^{3+}])$/rate versus $[Mn^{2+}]/[Mn^{3+}]_T$ at [acid] = 3.0 mol dm^{-3} (●), 3.5 mol dm^{-3} (◒) and 4.5 mol dm^{-3} (⊖); [Other conditions are the same as in Table 1]

A test of rate law (3) is also made by employing the values of the constants obtained as above. Rates calculated using such values in Eq. (3) with appropriate conditions as in Table 1 compare reasonably satisfactorily with the corresponding experimental rates in both Mn^{3+}-As^{3+} and Mn^{3+}-Sb^{3+} cases (Table 1).

A plot of 1/rate versus $[Mn^{+2}]$ should be linear with an intercept on the rate axis according to Eq. (3) and this is found to be so, which also verifies the rate law (3).

APPENDIX

$$Mn^{3+} + H_2O \rightleftharpoons MnOH^{2+} + H^+ \qquad (K_h)$$

$$Mn^{3+} + As(III) \rightleftharpoons Mn^{2+} + As(IV) \qquad (k_1, k_{-1})$$

$$Mn^{3+} + As(IV) \longrightarrow Mn^{2+} + As(V) \qquad (k_2)$$

$$MnOH^{2+} + As(III) \rightleftharpoons Mn^{2+} + As(IV) \qquad (k_3, k_{-3})$$

$$MnOH^{2+} + As(IV) \longrightarrow Mn^{2+} + As(V) \qquad (k_4)$$

Now,
$$K_h = \frac{[MnOH^{2+}][H^+]}{[Mn^{3+}]}$$

$$[Mn^{3+}]_T = [Mn^{3+}]_f \{1 + K_h/[H^+]\}$$
$$= [Mn^{3+}]_f \{([H^+]+K_h)/[H^+]\}$$

and

$$[Mn^{3+}]_f = [Mn^{3+}]_T[H^+]/([H^+]+K_h)$$
$$[MnOH^{2+}] = K_h[Mn^{3+}]_T/([H^+]+K_h)$$

By steady state approximation,

$$[As(IV)] = \frac{(k_1[Mn^{3+}]_f + k_3[MnOH^{2+}])[As(III)]}{(k_{-1}+k_{-3})[Mn^{2+}] + k_2[Mn^{3+}]_f + k_4[MnOH^{2+}]}$$

Substituting for $[Mn^{3+}]_f$ and $[MnOH^{2+}]$ we have

$$[As(IV)] = \frac{(k_1[H^+]+k_3K_h)[Mn^{3+}]_T[As(III)]}{([H^+]+K_h)(k_{-1}+k_{-3})[Mn^{2+}] + (k_2[H^+]+k_4K_h)[Mn^{3+}]_T}$$

The reaction rate is given by

$$\text{Rate} = -d[Mn^{3+}]_T/dt$$
$$= 2(k_2[Mn^{3+}]_f + k_4[MnOH^{2+}])[As(IV)]$$

Substituting for $[Mn^{3+}]_f$, $[MnOH^{2+}]$ and $[As(IV)]$,

$$-d[Mn^{3+}]/dt = \frac{2(k_2[H^+]+k_4K_h)[Mn^{3+}]_T[As(IV)]}{([H^+]+K_h)}$$

$$= \frac{2(k_2[H^+]+k_4K_h)(k_1[H^+]+k_3K_h)[Mn^{3+}]_T[As(III)]}{([H^+]+K_h)^2(k_{-1}+k_{-3})([Mn^{2+}]/[Mn^{3+}]_T) + ([H^+]+K_h)(k_2[H^+]+k_4K_h)}$$

(after rearranging)

Rearrangement gives

$$\frac{[Mn^{3+}]_T[As(III)]}{(\text{rate})} = \underbrace{\left\{\frac{([H^+]+K_h)^2(k_{-1}+k_{-3})}{2(k_2[H^+]+k_4K_h)(k_1[H^+]+k_3K_h)}\right\}}_{\text{Slope I}}\frac{[Mn^{2+}]}{[Mn^{3+}]_T} + \underbrace{\frac{([H^+]+K_h)}{2(k_1[H^+]+k_3K_h)}}_{\text{Intercept I}}$$

Further,
$$\frac{([H^+]+K_h)}{\text{Intercept I}} = 2k_1[H^+] + 2k_3K_h$$

Thus, a plot of $([H^+]+K_h)$/ Intercept I versus $[H^+]$ leads to values of k_1 & k_3 from a knowledge of K_h.

Again,

$$\left(\frac{\text{Intercept I}}{\text{slope I}}\right)([H^+]+K_h) = \left(\frac{k_2}{k_{-1}+k_{-3}}\right)[H^+] + \left(\frac{k_4K_h}{k_{-1}+k_{-3}}\right)$$

from the plot of left hand side versus $[H^+]$, values of $k_2/(k_{-1}+k_{-3})$ & $k_4/(k_{-1}+k_{-3})$ become known.

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