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

S R Kampli, S T Nandibewoor, M I Sambrani & J R Raju*
Department of Chemistry, Karnataka University, Dharwad 580 003

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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 Mn³⁺ and MnOH²⁺ are active in the oxidation which is also influenced by Mn²⁺ 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. 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. 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 and was then standardised with iron(II) solution. The ionic strength in kinetic runs was maintained constant with sodium sulphate.

Kinetic runs were initiated 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 ε = 114 (± 1.0%). The spectrum of Mn(III) in the visible region agreed with that of earlier work. The value of ε was found to be depend on [H₂SO₄] 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 (± 1%) respectively. Rates of reaction were reproducible within ± 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).

\[
2\text{Mn(III)} + \text{As(III)} = 2\text{Mn(II)} + \text{As(V)}
\]  

(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), [H₂SO₄] (5.0 mol dm⁻³) and at I=5.6 mol dm⁻³ (obtained from the in situ calculated free H⁺, HSO₄⁻ 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 conditions.
Table 1 - Rate data of Mn(III)-As(III)/Sb(III) reactions in aqueous sulphuric acid at 25°C ($I = 5.6$ mol dm$^{-3}$)$^a$

<table>
<thead>
<tr>
<th>$[\text{Mn}^3+] \times 10^3$ (mol dm$^{-3}$)</th>
<th>$[\text{As}^3+] \times 10^3$ (mol dm$^{-3}$)</th>
<th>$[\text{H}^+] \times 10^3$ (mol dm$^{-3}$)</th>
<th>Rate $\times 10^6$ (mol dm$^{-3}$ s$^{-1}$)$^a$</th>
<th>Exp.</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 (1.1)</td>
<td>5.0 (2.6)</td>
<td>5.1</td>
<td>0.58 (3.3)</td>
<td>0.75 (5.1)</td>
<td></td>
</tr>
<tr>
<td>3.0 (3.1)</td>
<td>5.0 (2.6)</td>
<td>5.1</td>
<td>2.3 (11.0)</td>
<td>2.3 (14.0)</td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>5.0 (2.6)</td>
<td>5.1</td>
<td>4.0 (20.0)</td>
<td>3.8 (23.0)</td>
<td></td>
</tr>
<tr>
<td>8.0 (7.0)</td>
<td>5.0 (2.6)</td>
<td>5.1</td>
<td>7.4 (33.0)</td>
<td>6.0 (33.0)</td>
<td></td>
</tr>
<tr>
<td>11.0 (9.0)</td>
<td>5.0 (2.6)</td>
<td>5.1</td>
<td>9.0 (44.0)</td>
<td>8.3 (42.0)</td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>2.0 (2.5)</td>
<td>5.1</td>
<td>1.5 (20.0)</td>
<td>1.5 (23.0)</td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>4.0 (5.0)</td>
<td>5.1</td>
<td>4.0 (43.0)</td>
<td>3.8 (45.0)</td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>8.0 (7.5)</td>
<td>5.1</td>
<td>5.9 (53.0)</td>
<td>6.0 (67.0)</td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>12.0 (10.0)</td>
<td>5.1</td>
<td>8.6 (83.0)</td>
<td>9.0 (90.0)</td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>20.0 (12.5)</td>
<td>5.1</td>
<td>14.0 (111.0)</td>
<td>15.0 (112.0)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$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$_2$SO$_4$] and [SO$_4^{2-}$] and the acid sulfate equilibrium constant$^e$.

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$^{-3}$)$^a$

<table>
<thead>
<tr>
<th>$[\text{Mn}^3+] \times 10^3$ (mol dm$^{-3}$)</th>
<th>$[\text{As}^3+] \times 10^3$ (mol dm$^{-3}$)</th>
<th>$[\text{Mn}^2+] \times 10^3$ (mol dm$^{-3}$)</th>
<th>Rate $\times 10^6$ (mol dm$^{-3}$ s$^{-1}$)$^a$</th>
<th>Exp.</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 (5.0)</td>
<td>5.0 (2.6)</td>
<td>0 (0)</td>
<td>4.0 (20.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>5.0 (2.6)</td>
<td>5 (2)</td>
<td>3.6 (18.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>5.0 (2.6)</td>
<td>10 (6)</td>
<td>3.1 (16.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>5.0 (2.6)</td>
<td>20 (10)</td>
<td>2.5 (15.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 (5.0)</td>
<td>5.0 (2.6)</td>
<td>40 (20)</td>
<td>2.0 (11.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- (5.0)</td>
<td>- (2.6)</td>
<td>- (30)</td>
<td>- (10.0)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

conditions of acidity, I and temperature, at a constant [Mn(III)] ($5.0 \times 10^{-3}$ mol dm$^{-3}$), the order in As(III)/Sb(III) in the range of $2.5 \times 10^{-3}$ to $2.0 \times 10^{-2}$ mol dm$^{-3}$ was $\sim 0.90$. 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 $\sim 0.8$. 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 $3.0 \times 10^{-2}$ 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 $\sim 0.3$ (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 conditions of acidity, I and temperature, at a constant [Mn(III)] ($5.0 \times 10^{-3}$ mol dm$^{-3}$), the order in As(III)/Sb(III) in the range of $2.5 \times 10^{-3}$ to $2.0 \times 10^{-2}$ mol dm$^{-3}$ was $\sim 0.90$. 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 $\sim 0.8$. 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 $3.0 \times 10^{-2}$ 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 $\sim 0.3$ (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 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$^{2+}$ 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 × 10⁻² mol dm⁻３; [As(III)]/([Sb(III)]) = 5.0 × 10⁻³ (2.6 × 10⁻³) mol dm⁻３; l = 5.6 mol dm⁻３

<table>
<thead>
<tr>
<th>[H₂SO₄]</th>
<th>[H⁺]</th>
<th>[HSO₄⁻]</th>
<th>[SO₄²⁻]</th>
<th>[Mn³⁺] × 10⁴</th>
<th>[Mn(OH)²⁺] × 10⁴</th>
<th>[Mn(HSO₄)²⁺] × 10³</th>
<th>Rate × 10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>2.4</td>
<td>3.6</td>
<td>0.18</td>
<td>6.2</td>
<td>2.5</td>
<td>4.1</td>
<td>6.6 (35.0)</td>
</tr>
<tr>
<td>3.5</td>
<td>3.1</td>
<td>3.9</td>
<td>0.16</td>
<td>5.8</td>
<td>1.8</td>
<td>4.2</td>
<td>5.5 (29.0)</td>
</tr>
<tr>
<td>4.0</td>
<td>3.7</td>
<td>4.3</td>
<td>0.14</td>
<td>5.4</td>
<td>1.4</td>
<td>4.3</td>
<td>4.9 (26.0)</td>
</tr>
<tr>
<td>4.5</td>
<td>4.4</td>
<td>4.6</td>
<td>0.13</td>
<td>5.1</td>
<td>1.1</td>
<td>4.2</td>
<td>4.5 (23.0)</td>
</tr>
<tr>
<td>5.0</td>
<td>5.1</td>
<td>5.0</td>
<td>0.12</td>
<td>4.8</td>
<td>0.91</td>
<td>4.4</td>
<td>4.0 (20.0)</td>
</tr>
</tbody>
</table>

Rates in parenthesis refer to Mn³⁺-Sb³⁺ reaction at 27°C.
All concentration terms are in mol dm⁻３.

Mn³⁺ + H₂O ⇌ MnOH²⁺ + H⁺  \((K_h)\)
Mn³⁺ + As(III) ⇌ Mn²⁺ + As(IV) \((k₁, k_{-1})\)
Mn³⁺ + As(IV) → Mn²⁺ + As(V) \((k₂)\)
MnOH²⁺ + As(III) ⇌ Mn²⁺ + As(IV) \((k₃, k_{-₃})\)
MnOH²⁺ + As(IV) → Mn²⁺ + As(V) \((k₄)\)

Scheme 1

protonated. As regards As(III), it is almost exclusively present as undissociated H₃AsO₃ (written in Scheme 1 simply as As(III)), its dissociations 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).

A plot of \([\text{[Mn}³⁺]/\text{[As}³⁺])/\text{(rate)}\) against \([\text{Mn}²⁺]/[\text{Mn}³⁺]\) 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 \([\text{rate}]/\text{[As}³⁺]\) versus \([\text{Mn}³⁺]+K_h]\) leads to values of \(k₂/(k_{-₁}+k₃)\) and \(k₄/(k_{-₁}+k_{-₃})\). Likewise, \(k₁\) and \(k₃\) are obtained from a plot of \([\text{rate}]/\text{Mn}²⁺]\) versus \([\text{H}⁺]+K_h]\) of \(\text{[As}³⁺]\). These values are as follows: \(k₁\) and \(k₃\) are respectively 0.036 and 0.28 dm³ mol⁻¹ s⁻¹ in the case of Mn³⁺-As³⁺ reaction \((k₁\) and \(k₃\) respectively are 0.20 and 4.6 dm³ mol⁻¹ s⁻¹ for Mn³⁺-Sb³⁺ case). The values of \(k₂/(k_{-₁}+k₃)\) and \(k₄/(k_{-₁}+k_{-₃})\) are respectively 0.96 and 1.6 in respect of Mn³⁺-As³⁺ reaction and 1.0 and 1.4 in the Mn³⁺-Sb³⁺ case. It is noteworthy that MnOH²⁺ is more effective as an oxidant than the free Mn³⁺ itself.
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 \( \frac{1}{\text{rate}} \) versus \([\text{Mn}^{2+}]\) 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**

\[
\begin{align*}
\text{Mn}^{3+} + \text{H}_2\text{O} & \rightleftharpoons \text{MnOH}^{2+} + \text{H}^+ \\
\text{Mn}^{3+} + \text{As(III)} & \rightleftharpoons \text{Mn}^{2+} + \text{As(IV)} \\
\text{Mn}^{3+} + \text{As(IV)} & \rightleftharpoons \text{Mn}^{2+} + \text{As(V)} \\
\text{MnOH}^{2+} + \text{As(III)} & \rightleftharpoons \text{Mn}^{2+} + \text{As(IV)} \\
\text{MnOH}^{2+} + \text{As(IV)} & \rightleftharpoons \text{Mn}^{2+} + \text{As(V)}
\end{align*}
\]

Now, \( \frac{1}{k_\text{t}} = \frac{[\text{MnOH}^{2+}][\text{H}^+]}{[\text{Mn}^{3+}]} \)

and \( \frac{[\text{Mn}^{3+}]}{[\text{MnOH}^{2+}]} = \frac{[\text{Mn}^{3+}][\text{H}^+]}/([\text{Mn}^{3+}]+K_\text{t}) \)

By steady state approximation,

\[
\text{As(IV)} = \frac{(k_1[\text{Mn}^{3+}] + k_2[\text{MnOH}^{2+}])[\text{As(III)}]}{(k_1 + k_3)[\text{Mn}^{3+}] + k_2[\text{MnOH}^{2+} + k_3[\text{MnOH}^{2+}]}
\]

Substituting for \([\text{Mn}^{3+}]_1 \) and \([\text{MnOH}^{2+}] \) we have

\[
\text{As(IV)} = \frac{(k_1[\text{H}^+] + k_3K_\text{t})[\text{Mn}^{3+}]_1[\text{As(III)}]}{([\text{H}^+] + K_\text{t})[k_1 + k_3][\text{Mn}^{3+}]_1 + (k_1[\text{H}^+] + k_3K_\text{t})[\text{Mn}^{2+}]_1}
\]

The reaction rate is given by

\[
\frac{-\text{d}[\text{Mn}^{2+}]/\text{d}t}{\text{rate}} = \frac{2[k_2[\text{H}^+] + k_3K_\text{t}][\text{Mn}^{3+}]_1[\text{As(IV)}]}{([\text{H}^+] + K_\text{t})}
\]

\[
\text{rate} = 2[k_2[\text{H}^+] + k_3K_\text{t}][\text{Mn}^{3+}]_1[\text{As(IV)}]
\]

Substituting for \([\text{Mn}^{3+}]_1, [\text{MnOH}^{2+}] \) and \([\text{As(IV)}] \),

\[
\text{rate} = \frac{2(k_1[\text{H}^+] + k_3K_\text{t})[\text{Mn}^{3+}]_1[\text{As(III)}]}{([\text{H}^+] + K_\text{t}) + (k_3[\text{H}^+] + k_2K_\text{t})}
\]

\( \text{rate} \) is found to be so, which also verifies the rate law (3).

**References**