CHAPTER IVA

PALLADIUM (II) CATALYSED OXIDATION OF
ALLYL ALCOHOL BY MANGANESE (III) IN
AQUEOUS SULPHURIC ACID
Palladium(II) catalysed oxidation of allyl alcohol by manganese(III) in aqueous sulphuric acid

Manganese is one of the abundant elements, it constitutes 0.085% of earth's crust. It is one of the trace elements essential to the life of plants and animals. The cells of living things contain minute concentration of manganese and a deficiency of this metal in all organisms studied ranging from bacteria through plants to mammals, inhibits growth and diminishes life expectancy. Manganese deficiency in higher plants causes mottled chlorosis. The normal requirement of human diet has been estimated to be about 4 mg per day and the consumption of tea and coffee provides larger source of metal. Seeds, nuts and cereals also have high manganese content but milk products and sea foods are low. Manganese can activate enzymatic processes. It is also involved in the structures of nucleic acids and it promotes the synthesis of cholesterol.

Manganic(III) can exist as the red manganic ion in the concentrated acid solution. It is a powerful one electron oxidant with an oxidation potential of -1.51V (of Mn(III)/Mn(II) couple) at dilute acid. At low acidities it undergoes disproportionation unless it is stabilised by being complexed with various ligands. Fluoride, sulphate and pyrophosphate have been used for this purpose. The aqueous
solution of manganese(III) are stabilised by the presence of large excess of manganous, Mn(II) and H⁺ ions.

Sulphate complexes to some extent with manganese(III). The sulphate complex of manganese(III) in sulphuric acid is easy to prepare and is stable provided that the acidity is not too low. A small disproportionation into manganese(II) and manganese(IV) of around 3 and 0.3% has been observed in 4.0 and 7.2 mol dm⁻³ sulphuric acid respectively.

\[ 2\text{Mn(III)} \rightarrow \text{Mn(II)} + \text{Mn(IV)} \]

The stabilizing effect of sulphate ions must be due to their effect on disproportionation equilibrium or on the rate of hydrolysis of manganese(IV).

\[ K = \frac{[\text{Mn(II)}]^2[\text{Mn(IV)}]}{[\text{Mn(III)}]^2} \]

Since K is of the order of \(10^{-3}\) in sulphuric acid (4.5 mol dm⁻³) and the effect of the sulphate complexing is to reduce the activity of manganese(III) by a factor of about ten, the rate of precipitation of manganese-dioxide, if proportional to \([\text{Mn(IV)}]^2\), should be reduced ten thousand fold. Indeed, solution of manganic sulphate and manganic pyrophosphate are stable enough to be used as oxidising
agents in volumetric analysis\textsuperscript{7-10}. Other manganese(III) complexes with ligands such as acetate, fluoride have found good use as oxidising agents in hydrocarbon chemistry and as fluorinating agents respectively.

The last decade has been significant development in the elucidation of the mechanisms of manganese(III) oxidation of both organic and inorganic substrates, and many of these are well understood. Kinetic studies involving oxidation of different organic compounds by manganese(III) are available\textsuperscript{11} and similar studies, involving inorganic substances are also available\textsuperscript{12-16}. In view of the high reduction potential and large charge on the ion, manganese(III) oxidations are usually comparatively fast.

The importance of allyl alcohol and palladium(II) are given in Chapters IA and IB. In the oxidation of allyl alcohol, we have observed\textsuperscript{17} that the products of the oxidations were different with different catalysts. Acrolein is the main product of osmium(VIII) catalysed reaction and acrylic acid the main product using palladium(II) catalyst. The allyl alcohol-manganese(III) reaction is catalysed by palladium(II) and can be conveniently studied by spectrophotometry. The effect of chloride as well as acid on the reaction is investigated and the nature of the main active species of catalyst, and oxidant in the title reaction is arrived at.
In this work, we report the results of our study of this reaction.

**EXPERIMENTAL**

Reagent grade chemicals were used and doubly distilled water was employed throughout this work. The manganese(II) solution was obtained by dissolving manganese(II) sulphate (Riedel) in 1.0 mol dm$^{-3}$ sulphuric acid and its concentration was ascertained by standardising with EDTA solution using eriochrome black-T$^{18}$ as indicator at pH 10. The pH was maintained using aqueous NH$_3$/NH$_4$Cl buffer.

The manganese(III) solution in almost all experiments was prepared freshly as it was found to degrade by approximately 3% in 24 hours. It was prepared as below: 3.0 cm$^3$ Conc. sulphuric acid was added in 50 cm$^3$ of 0.1 mol/dm$^{-3}$ manganese(II) sulphate (Riedel) in 3.0 mol dm$^{-3}$ sulphuric acid and cooled. 12.0 cm$^3$ of 0.1 mol dm$^{-3}$ potassium permanganate (E.Merck) solution was added in small quantities of 2.0 cm$^3$ at a time intervals of 3 minutes with constant cooling. After the addition of 8.0 cm$^3$ and 12.0 cm$^3$ potassium permanganate as above 2.0 cm$^3$ of Conc.sulphuric acid was also added. The resultant solution was thoroughly cooled, kept for 6 hours and filtered. In the preparation of manganese(III) solution, special precautions for adequate cooling were
necessary to prevent the formation of precipitates of higher oxides. Solution was standardised with iron(II) solution with addition of 1-2 drops of glacial phosphoric acid to manganese(III) solution to get distinct end point.

The stock solutions of manganese(III) prepared in this way also contained manganese(II) ion in modest concentrations and such manganese(II) concentration was ascertained spectrophotometrically: first by reducing manganese(III) to manganese(II) with sodium bisulfite solution and then total manganese(II) concentration was determined by measuring the absorbance after the addition of formaldoxime reagent at 450 nm ($\varepsilon = 9900\pm1.5\% \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$). The manganese(II) concentration was then obtained from the difference of total manganese(II) and manganese(III) concentrations. Manganese(III) solution was kept in blue bottles as it forms manganese dioxide on exposure to light.

In the visible region, the spectrum of the manganese(III) was scanned and compared with the spectrum of potassium permanganate which shows two maxima whereas manganese(III) shows only one \(^{[\text{Fig.IVA}(i),p.183]}\). The spectrum of manganese(III) agreed with earlier work\(^2\). Also, using the absorbances at particular wavelengths in both the spectra, the concentrations of manganese(III) and potassium
Fig. IVA(1): Spectrum of Mn(III) and MnO$_4^-$ in 5.0 mol dm$^{-3}$ H$_2$SO$_4$

\[
\begin{align*}
\left[\text{Mn(III)}\right] & = 1.0 \times 10^{-3} \text{ mol dm}^{-3} \\
\left[\text{MnO}_4^-=\right] & = 1.7 \times 10^{-4} \text{ mol dm}^{-3}
\end{align*}
\]
permanganate were calculated from the resulting pair of simultaneous equations. The concentration of manganese-(III) found was in the range of $10^{-2}$ mol dm$^{-3}$ whereas the concentration of MnO$_4^-$ found was in the range of $10^{-7}$ mol dm$^{-3}$. The ionic strength was maintained constant with sodium sulphate. Ionic strength was arrived at using calculated free H$^+$, HSO$_4^-$ and SO$_4^{2-}$ concentrations from the acid sulphate equilibrium constant and the added sulphate.

The allyl alcohol and Pd(II) solutions were prepared as given in IB,p.(69). Chloride present in preparing the stock solution of palladium(II) was diluted in the reaction mixture to a concentration of about $2 \times 10^{-4}$ M and under these conditions it was observed that chloride did not affect the rate of the reaction. Under the conditions studied, allyl alcohol-palladium(II) reaction was also very slow.

**Kinetic studies**

Kinetic runs were initiated by mixing the previously thermostatted solutions of manganese(III), allyl alcohol and palladium(II) which also contained equivalent amounts of sulphuric acid and the required amount of sodium sulphate. The reaction was followed by measuring the absorbance of Mn(III) in the reaction mixture at 500 nm in a 1 cm cell in a Hitachi 150-20 spectrophotometer.
The obedience to Beer's law of manganese(III) solution 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 $5.0 \times 10^{-4}$ to $1.0 \times 10^{-2}$ mol dm$^{-3}$ with molar absorbancy index resulting as $\varepsilon = 114 \pm 1.0$% dm$^3$ mol$^{-1}$ cm$^{-1}$ (Fig.IVA(ii), p.186). The value of $\varepsilon$ was found to depend on the concentration of sulphuric acid and it decreased slightly with the decrease in acid concentration. The value of $\varepsilon$ in the presence of 5.0, 4.0, 3.5 and 3.0 mol dm$^{-3}$ sulphuric acid were 114, 114, 112 and 117 dm$^3$ mol$^{-1}$ cm$^{-1}$ ($\pm 1\%$) respectively. The specific rates of reaction were obtained by plots of concentration of manganese(III) vs time, and the rate constants were calculated from the slopes of 1st order plot of $\log [\text{Mn(III)}]$ vs time. An example run is given in Table IVA(i), p.188 and Fig.IVA(iii). Initial rates and rate constants were reproducible within $\pm 4\%$. Temperatures were maintained within $\pm 0.05K$.

RESULTS

Stoichiometry

Different reaction mixtures containing various sets of concentrations of reactants in sulphuric acid media at constant ionic strength were allowed to stand for 24 hours and then analysed for manganese(III). In the conditions
Fig. IVA(ii) : Verification of Beer's law for Mn(III) at 500 nm

\[ \text{[H}_2\text{SO}_4] = 5.0; \ I = 5.60/\text{mol dm}^{-3} \]
Table IVA(i): Sample run of Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in acid medium at 25°C

\[ \begin{align*}
K_{A} &= 1.0 \times 10^{-2}; \quad K_{Mn(III)} = 2.0 \times 10^{-3}; \\
K_{Pd(II)} &= 5.0 \times 10^{-6}; \quad K_{H_{2}SO_{4}} = 5.0; \quad I = 5.60/\text{mol dm}^{-3}
\end{align*} \]

<table>
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<tr>
<th>Time (min)</th>
<th>Absorbance 500 nm</th>
<th>( [\text{Mn(III)}] \times 10^{3} ) mol dm(^{-3} )</th>
</tr>
</thead>
<tbody>
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<td>0.228</td>
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</table>

Error ±4%
Fig.IVA(iii) : Sample run of Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in acid medium

(Conditions as in Table IVA(i), p.187)
the excess allyl alcohol was determined as given in Chapter IA (p. 39). In the conditions $[\text{Mn(III)}] > [\text{AA}]$, the excess Mn(III) was found by measuring its absorbance at 500 nm. The main product was found to be acrolein, identified by spot test.\(^{22}\) The results are given in Table IVA(ii), (p. 190). The results indicated that one mole of allyl alcohol consumed two moles of manganese(III) and the reaction may be represented by the following equation.

$$2\text{Mn(III)} + \text{CH}_2=\text{CHCH}_2\text{OH} \rightarrow 2\text{Mn(II)} + \text{CH}_2=\text{CHCHO} + 2\text{H}^+$$

The concentration of the catalyst, palladium(II) was unchanged at the end of the reaction as found by estimating it spectrophotometrically as palladium azide complex as given in Chapter IB (p. 76).

**Order of the reaction**

The order in oxidant and reductant was determined from log-log plots of initial rates against concentration at constant acid concentration of 5.0 mol dm\(^{-3}\), and constant ionic strength of 5.6 mol dm\(^{-3}\). At a fixed allyl alcohol concentration of 1.0x10\(^{-2}\) mol dm\(^{-3}\), the order in manganese(III) in the concentration range of 5.0x10\(^{-4}\) to 5.0x10\(^{-3}\) mol dm\(^{-3}\) was unity and under similar conditions of acidity, ionic strength and temperature, at a constant manganese(III) concentration
Table IVA(ii): Stoichiometry of Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in acid medium at 25°C

\[ [\text{Pd(II)}] = 5.0 \times 10^{-5}; \quad [\text{H}_2\text{SO}_4] = 5.0; \quad I = 5.60/\text{mol dm}^{-3} \]

<table>
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<tr>
<th>Taken ( [\text{Mn(III)}] \times 10^{-3} )</th>
<th>( [\text{AA}] \times 10^3 )</th>
<th>Found</th>
<th>( [\text{Mn(III)}] \times 10^{-3} )</th>
<th>( [\text{AA}] \times 10^3 )</th>
<th>( [\text{Mn(II)}] \times 10^{-3} )</th>
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Error \( \pm 5\% \)
of $2.0 \times 10^{-3}$ mol dm$^{-3}$, the order in allyl alcohol in the range of $5.0 \times 10^{-3}$ to $5.0 \times 10^{-2}$ mol dm$^{-3}$ was $\approx 0.6$. The results are given in Table IVA(iii) (p. 192) and in Fig. IVA(iv) (p. 193).

**Effect of catalyst**

By keeping other conditions constant, the effect of catalyst in the range of $1.0 \times 10^{-6}$ to $1.0 \times 10^{-5}$ mol dm$^{-3}$ was studied (Table IVA(iv) p. 194). The order with respect to catalyst is unity (Fig. IVA(v) p. 195).

**Effect of acid**

The determination of order in $\sum H^+$ was restricted somewhat to $\sum H^+$ range of 3.0 to 5.5 mol dm$^{-3}$ in view of the instability of the oxidant at lower acid concentration. The reaction was found to be independent of acid concentration (Table IVA(v) p. 196).

**Effect of added products**

By keeping other conditions and concentrations of reactants constant, the effect of initially added product, Mn(II) was studied in the range of $2.0 \times 10^{-3}$ to $1.0 \times 10^{-2}$ mol dm$^{-3}$. It was observed that there was no significant effect of Mn(II) on the rate of the reaction (Table IVA(v)). The effect of acrolein on the reaction could not be studied as it was
Table IVA(iii): Effect of $[\text{Mn(III)}]$ and $[\text{AA}]$ on Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in aqueous acid medium at 25°C

$[\text{Pd(II)}] = 5.0 \times 10^{-6}$; $[\text{H}_2\text{SO}_4] = 5.0$; $I = 5.60/\text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>$[\text{Mn(III)}]$ $x 10^3$</th>
<th>$[\text{AA}] x 10^2$</th>
<th>Rate $x 10^6$</th>
<th>Rate constant $x 10^3$ $s^{-1}$</th>
<th>Exptl.</th>
<th>Calcd*</th>
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Error ±3%

* Rate constant is calculated using $k$ and $K$ as $532 \pm 9 \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1}$ and $188 \pm 5 \text{ dm}^3\text{ mol}^{-1}$ respectively.
Fig.IVA(iv): Order in $[\text{Mn(III)}]$ and $[\text{AA}^{-}]$ catalysed oxidation of allyl alcohol by Mn(III) in acid medium

(Conditions as Table IVA(iii), p.192)

$-\log[\text{AA}]$

$-\log(\text{rate})$

$-\log[\text{Mn(III)}]$
Table IVA(iv) | Effect of catalyst, $[\text{Pd}(\text{II})]$ on Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in aqueous acid medium at 25°C

\[ [\text{AA}] = 1.0 \times 10^{-2}; \quad [\text{Mn(III)}] = 2.0 \times 10^{-3}; \]
\[ [\text{H}_2\text{SO}_4] = 5.0; \quad I = 5.60/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>$[\text{Pd(II)}]$ x10^6 mol dm(^{-3})</th>
<th>Rate x10^6 mol dm(^{-3}) s(^{-1})</th>
<th>Rate constant x10^3 s(^{-1})</th>
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<th>Cald.*</th>
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*Rate constant is calculated using values $k$ and $K$

532±9 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) and 188±5 dm\(^3\) mol\(^{-1}\) respectively.

Error ±4%
Fig. IVA(v) : Order in catalyst $\left[ \text{Pd(II)} \right]$; Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in acid medium.

(Conditions as in Table IVa(iv), p. 194)
Table IVA(v): Effect of $\text{[H}_2\text{SO}_4]$ and product $[\text{Mn(II)}]$ on Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in aqueous acid medium at 25°C

$[\text{AA}] = 1.0 \times 10^{-2}$; $[\text{Mn(III)}] = 2.0 \times 10^{-3}$

$[\text{Pd(II)}] = 5.0 \times 10^{-6}$; $I = 5.60/\text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>$\text{[H}_2\text{SO}_4]$ mol dm$^{-3}$</th>
<th>Rate $\times 10^6$ mol dm$^{-3}$ s$^{-1}$</th>
<th>Rate constant $\times 10^3$ s$^{-1}$</th>
<th>$[\text{Mn(II)}]$ mol dm$^{-3}$</th>
<th>Rate $\times 10^6$ mol dm$^{-3}$ s$^{-1}$</th>
<th>Rate constant $\times 10^3$ s$^{-1}$</th>
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Error ±5%
unstable because of its tendency to readily polymerise; use of stabilising agents was not thought desirable.

**Effect of ionic strength**

The effect of ionic strength from 5.36 to 6.2 mol dm$^{-3}$ was studied. There was no significant change in the reaction rate (Table IVA(vi) (p.198)).

**Effect of temperature**

The reaction was studied at 298,303,308 and 313 K keeping all conditions constant. The data is shown in Table IVA(vi) (p.198). A plot of log $k$ vs $1/T$ is drawn to get activation parameters (Fig.IVA(vi), p.199).

**Test for polymerisation**

Under the reaction conditions as in Table IVA(1) (p.187) the reaction was allowed to take place in presence of 0.01 mol dm$^{-3}$ acrylamide. After the completion of reaction the solution was diluted with methanol and this resulted in the formation of a precipitate.

**Effect of Cl$^-$ and SO$_4^{2-}$ ions**

The added Cl$^-$ and SO$_4^{2-}$ in the range of 2.0x10$^{-4}$ to 2.0x10$^{-3}$ is studied keeping all conditions constant and added Cl$^-$ or SO$_4^{2-}$ do not have any effect on the rate of reaction.
Table IVA(vi): Effect of ionic strength and temperature on Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in aqueous acid medium

\[ [AA] = 1.0 \times 10^{-2}; \quad [\text{Mn(III)}] = 2.0 \times 10^{-3} \]

\[ [\text{Pd(II)}] = 5.0 \times 10^{-6}; \quad [\text{H}_2\text{SO}_4] = 5.0/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Ionic strength ( I ) (Temp. 25°C)</th>
<th>Rate ( 10^6 ) ( \text{mol dm}^{-3} \text{s}^{-1} )</th>
<th>Rate constant ( 10^3 ) ( \text{s}^{-1} ) ( \text{mol dm}^{-3} \text{ s}^{-1} )</th>
<th>Temp. K</th>
<th>Rate constant ( 10^3 ) ( \text{s}^{-1} ) ( \text{mol dm}^{-3} \text{ s}^{-1} )</th>
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<td>6.2</td>
<td>3.70</td>
<td>1.70</td>
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</tr>
</tbody>
</table>

Error ± 4.9%

\[ E_a = 31.5 \pm 2 \text{ kJ mol}^{-1} \]

\[ \Delta S^\pm = -200.0 \pm 10 \text{ J.K}^{-1}\text{mol}^{-1} \]
Fig. IVA(vi): Effect of temperature on Pd(II) catalysed oxidation of allyl alcohol by Mn(III) in acid medium.

(Conditions as in Table IVA(vi), p.198)
DISCUSSION

The manganese(III) oxidation of allyl alcohol catalysed by Pd(II) in sulphuric acid medium follows the approximate rate law (1).

\[
\text{Rate} = k[A]^{0.6} [\text{Mn(III)}]^{1}[\text{Pd(II)}]^{1}
\] (1)

The order in allyl alcohol concentrations being fractional, palladium(II) and manganese(III) orders were unity. Acid and added products do not have any effect on the reaction in the concentration range studied. The rate data are compatible with the reaction going through a substrate-catalyst complex followed by the intervention of oxidant with complex in the rate determining step as shown in Scheme 1.

\[
Pd(II) + AA \xrightarrow{K_c} \text{Complex (C)}
\]

\[
C + Mn(III) \xrightarrow{K} AA + Mn(II) + Pd(II) \quad \text{slow}
\]

\[
AA + Mn(III) \rightarrow \text{Acrolein + Mn(II)} \quad \text{fast}
\]

Scheme 1

Scheme 1 involves the formation of a complex containing catalyst and reductant and scheme 1 also involves the intervention of free radicals. Attempts to obtain spectral
evidence for the complex were not successful. However, the interaction may be feeble and such complex formation between allyl alcohol and palladium(II) has been observed in other studies\(^\text{17}\). The evidence for complex formation is obtained from kinetic study i.e. \(\frac{1}{k_1} \) vs \(\frac{1}{[AA]^7}\) plot is straight line with intercept indicating the complex formation in the mechanism. The observed fractional order in \([AA]_7\), unit order in both \([\text{Mn(III)}]_7\) and \([\text{Pd(II)}]_7\) can be very well be accommodated in Scheme 1 (as seen from rate law (6) also).

The rate of disappearance of Mn(III) with time, \(t\), is given by

\[
-\frac{d[\text{Mn(III)}]_7}{dt} = k[\text{C}]_7[\text{Mn(III)}]_7
\]

(2)

The concentration of the complex \(C\), may be written, from its formation equilibrium (Scheme 1), as in (3) where \([\text{Pd(II)}]_7^T\) and \([\text{AA}]_7^T\) are uncomplexed or free Pd(II) and allyl alcohol concentrations respectively. The total concentration of Pd(II) and allyl alcohol, represented by \([\text{Pd(II)}]_7^T\) and \([\text{AA}]_7^T\) are the sums of concentrations of the free and complexed Pd(II) and allyl alcohol respectively and they are given by (4) and (5).
\[ \sum_{\text{Pd(I)\textsuperscript{2+}}} = \sum_{\text{Pd(I)\textsuperscript{2+}}} + C \]

\[ = \sum_{\text{Pd(I)\textsuperscript{2+}}} + K \sum_{\text{Pd(I)\textsuperscript{2+}}} \sum_{\text{AA}} \]

\[ \sum_{\text{Pd(I)\textsuperscript{2+}}} = \frac{\sum_{\text{Pd(I)\textsuperscript{2+}}} + \sum_{\text{Pd(I)\textsuperscript{2+}}} \sum_{\text{AA}}}{(1 + K \sum_{\text{AA}})} \quad (4) \]

\[ \sum_{\text{AA}} = \sum_{\text{AA}} + K \sum_{\text{Pd(I)\textsuperscript{2+}}} \sum_{\text{AA}} \]

\[ \sum_{\text{AA}} = \frac{\sum_{\text{AA}}}{1 + K \sum_{\text{Pd(I)\textsuperscript{2+}}}} \quad (5) \]

Substituting the \( \sum_{\text{AA}} \) and \( \sum_{\text{Pd(I)\textsuperscript{2+}}} \) in equation (3) and then in (2),

\[
\text{Rate} = \frac{K \sum_{\text{AA}} \sum_{\text{Pd(I)\textsuperscript{2+}}} \sum_{\text{Mn(III)\textsuperscript{2+}}}}{(1 + K \sum_{\text{AA}}) (1 + K \sum_{\text{Pd(I)\textsuperscript{2+}}})} \quad (6)
\]

\[ 1 + K \sum_{\text{Pd(I)\textsuperscript{2+}}} \approx 1 \text{ in view of the low concentration of palladium(II) used.} \]

The rate law (6) can be written as

\[
\frac{\text{Rate}}{\sum_{\text{Mn(III)\textsuperscript{2+}}}} = k' = \frac{k \sum_{\text{AA}} \sum_{\text{Pd(I)\textsuperscript{2+}}}}{(1 + K \sum_{\text{AA}})} \quad (7)
\]

Where \( k' \) is rate constant.

The rate eq. (7) is verified in the form of
\[
\frac{\sqrt{Pd(II)^{7+}}}{k^1} = \frac{1}{k K_{AA^{-7}}} + \frac{1}{k}
\]

A plot of \(\frac{\sqrt{Pd(II)^{7+}}}{k^1}\) vs \(\frac{1}{\sqrt{AA^{-7}}}\) is drawn Fig.IVA(vii) p. 204. From the slope and intercept of such a plot, the value of \(K\), the formation constant of the catalyst-substrate complex, and the \(k\), the rate constant, are found to be around \(188 \pm 5 \text{ dm}^3 \text{ mol}^{-1}\), \(532 \pm 9 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}\) respectively. These values may be further used to find rate constants under different conditions of the reaction. Rate constants calculated in this way are in good agreement with experimentally measured rate constants Table IVA(iii), (iv).p. 192.'s 194.

The lack of an acid effect and sulphate effect indicates that Mn\(^{3+}\)\(_{aq}\) is only active in second step of scheme 1 which is entirely different to the earlier cases\(^{23}\). It is also noteworthy that the reaction is not influenced by chloride ions, to be expected in palladium(II) catalysed reactions. Hence the palladium(II) species involved is Pd\(^{2+}\) and not its chloride complex as in other cases\(^{24}\). Furthermore, since the substrate is neutral, no effect of ionic strength is noticeable.

The observed modest energy of activation and negative entropy of activation supports the involvement of a complex transition state in the reaction.
Fig. IVA(vii) : Verification of rate law (6)

(Conditions as in Table IVA(iii), p.192)
Findings

Palladium(II) catalysed manganese(III) oxidation of allylalcohol is studied and it is understood to go through substrate — Catalyst complex followed by intervention of oxidant with complex in rate determining step. Acid and added products do not have any effect on the reaction. The formation constant and rate constant of decomposition of complex were found.

Importance of Chapter IVA

The title reaction is studied in acid medium. The lack of an acid effect and sulphate effect indicates that Mn$^{3+}_{aq}$ is only active which is entirely different to the earlier cases. It is also noted that the reaction is not influenced by chloride ions to be expected in palladium(II) catalysed reaction. Hence the palladium(II) species involved is Pd$^{2+}$ and not its chloride complex as in other cases. Since the substrate is neutral, no effect of ionic strength is noticeable.
References


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CHAPTER IVB

BROMIDE CATALYSED OXIDATION OF ARSENIC(III)
BY MANGANESE(III) IN ACID MEDIUM
Bromide catalysed oxidation of arsenic(III) by manganese(III) in acid medium

The importance of bridging anions in facilitating electron transfer in inorganic reactions is well known. A chloride ion bridge accelerated mechanism has been found in many exchange reactions including Ce(IV)-Ce(III) exchange\textsuperscript{3a}. In case of redox reactions where halide catalysis is appreciable, what is to be known is whether the catalysis occurs through complexation or is simply an anion effect. In case of oxidation of arsenic(III), antimony(III) and thallium(I)\textsuperscript{3b}, influence of halides is pronounced. Thus in the oxidation of thallium(I) by Mn(III) in presence of chloride\textsuperscript{4}, not only thallium(II) but also species like MnCl\textsubscript{2}\textsuperscript{2+} and Cl\textsubscript{2}⁻ were understood to intervene.

It is well understood that arsenic(III) forms several stable halide complexes. The bromide catalysis of manganese(III)-arsenic(III) reaction has not been studied. The rate acceleration of manganese(III)-arsenic(III) reaction in presence of halide may be due to the formation of arsenic(III)-halide complex, manganese(III)-halide complex or it may simply be due to general anion effect. In view of such possibilities a study of the manganese(III)-arsenic(III) reaction catalysed by bromide in aqueous sulphuric acid was undertaken and the results are furnished here.
EXPERIMENTAL

Reagent grade chemicals were used. A stock solution of sodium bromide (BDH) was prepared by dissolving the required amount in distilled water. A stock solution of arsenic(III) was made by dissolving arsenic(III) oxide (BDH, AR) in 1.0 mol dm\(^{-3}\) sodium hydroxide. The base in the arsenic(III) solution was neutralised by adding the requisite amount of acid in the preparation of the reaction mixture. Arsenic(V) was prepared by dissolving potassium orthoarsenate (Riedel) in water. The rest of experimental details are the same as given in Part A of this Chapter (p. 181).

Kinetic runs

Kinetic runs were initiated by mixing the previously thermostatted solutions of manganese(III) and arsenic(III) which also contained bromide, equivalent amount of sulphuric acid and the required amount of sodium sulphate. The reactions were followed by measuring the absorbance of manganese-(III) in the reaction mixture at different intervals at 500 nm in a 1 cm cell in a Hitachi-150-20 spectrophotometer. The obedience to Beer's law of manganese(III) solution at different acid concentrations had been tested as in Chapter IVA (p. 185). Most of the kinetic runs were studied at 5.0 H\(_2\)SO\(_4\) and 5.6 mol dm\(^{-3}\) ionic strength, obtained from in situ calculated free
H⁺, HSO₄⁻ and SO₄²⁻ and the sulphate added to the solution. The \( \sum H^+ \) values are calculated from added H₂SO₄ concentration and \( \sum SO_4^{2-} \) from sulphate equilibrium constant. Initial rates were obtained from plots of \( \sum Mn(III) \) vs time. Rates of reaction were reproducible to within ±4%. Temperatures were maintained within ±0.05°C.

RESULTS

Stoichiometry

Different reaction mixtures containing various sets of concentrations of reactants with a constant amount of catalyst, bromide (5.0x10⁻⁵ mol dm⁻³), sulphuric acid (5 mol dm⁻³) and ionic strength (5.60 mol dm⁻³) were allowed to react over 24 hours at room temperature and then analysed for manganese(III), arsenic(III) and arsenic(V). Manganese(III) was found by measuring its absorbance at 500 nm. Arsenic(III) was estimated by titration with bromate using methyl orange as indicator and the product arsenic(V) was found iodometrically by titration with thiosulphate. The results were in agreement with the stoichiometry of one mole of arsenic(III) to two moles of manganese(III) reacted as in equation (1). The catalyst (bromide) concentration was found by measuring the amount of precipitate formed with silver nitrate before and
2Mn(III) + As(III) \rightleftharpoons 2Mn(II) + As(V) \tag{1}

after the reaction using a systronics Nephelo Turbidity-meter. The amount of precipitate found before and after the reaction was the same, the agreement was total with an error of less than 1.0%. A sample run is given in Table IVB(i), (p. 213) and Fig.IVB(i) (p. 214).

Order of reaction

The order in oxidant, reductant and catalyst was determined from log-log plots of initial rates against concentrations. Under the conditions of reaction (5.0 mol dm\(^{-3}\) \(\text{H}_2\text{SO}_4\), and \(I = 5.6\) mol dm\(^{-3}\)), the reaction between manganese(III) (5.0x10\(^{-3}\) mol dm\(^{-3}\)) and bromide (5.0x10\(^{-5}\) mol dm\(^{-3}\)) was very slow, the initial rate being 5.0x10\(^{-9}\) mol dm\(^{-3}\) s\(^{-1}\).

At a fixed arsenic(III) concentration of 1.0x10\(^{-2}\), 5.0 mol dm\(^{-3}\) \(\text{H}_2\text{SO}_4\) and \(I = 5.6\) mol dm\(^{-3}\) at 25°C, the order in manganese(III) concentration in the range of 1.3x10\(^{-3}\) to 1.2x10\(^{-2}\) mol dm\(^{-3}\) was unity as shown in Fig.IVB(ii) (p.215) (Table IVB-(ii); p.216). Under similar conditions of acidity, ionic strength and temperature, at a constant manganese(III) concentration of 5.0x10\(^{-3}\) mol dm\(^{-3}\) in the range of 4.0x10\(^{-3}\) to 4.0x10\(^{-2}\) mol dm\(^{-3}\) arsenic(III) concentrations, the order in arsenic(III) was \(\sim 0.6\) as shown in Fig.IVB(ii); (p.215) and
Table IVB(i) : Sample run of bromide catalysed oxidation of As(III) by Mn(III) in acid medium at 25°C

\[
\begin{align*}
\left[\text{As(III)}\right] & = 2.0 \times 10^{-4}; \\
\left[\text{Mn(III)}\right] & = 5.0 \times 10^{-3}; \\
\left[\text{H}_2\text{SO}_4\right] & = 5.0; \\
\left[\text{Br}^-\right] & = 5.0 \times 10^{-5}; \\
\text{I} & = 5.60/\text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Absorbance 500 nm</th>
<th>(\left[\text{Mn(III)}\right]/\text{x}10^3) mol dm(^{-3})</th>
</tr>
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<td>0.570</td>
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<td>12.0</td>
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</table>

Error ±3%
Fig. IVB(i) : Sample run of bromide catalysed oxidation of As(III) by Mn(III) in acid medium.

(Conditions as in Table IVB(i), p. 213)
Fig. IVB(ii): Order in $\text{Mn(III)}^\cdot$ and $\text{As(III)}^\cdot$, bromide catalysed oxidation of $\text{As(III)}$ by $\text{Mn(III)}$ in acid medium.

(Conditions as in Table IVB(ii), p. 216)

<table>
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<tr>
<th>$-\log[\text{As(III)}]$</th>
<th>3.9</th>
<th>4.1</th>
<th>4.3</th>
<th>4.5</th>
<th>4.7</th>
<th>4.9</th>
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<td>$-\log[\text{Mn(III)}]$</td>
<td>2.8</td>
<td>2.6</td>
<td>2.4</td>
<td>2.2</td>
<td>2.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

![Graph showing the relationship between $-\log[\text{As(III)}]$ and $-\log[\text{Mn(III)}]$.]
Table IVB(ii) : Effect of $\sqrt{\text{Mn(III)}}$ and $\sqrt{\text{As(III)}}$ on $\text{Br}^-$
catalysed oxidation of As(III) by Mn(III) in
acid medium at 25°C

$\sqrt{\text{Br}^-} = 5.0 \times 10^{-5}$; $\sqrt{\text{H}_2\text{SO}_4} = 5.0$; $I = 5.60 / \text{mol dm}^{-3}$


<table>
<thead>
<tr>
<th>$\sqrt{\text{Mn(III)}} \times 10^3$ (mol dm$^{-3}$)</th>
<th>$\sqrt{\text{As(III)}} \times 10^2$ (mol dm$^{-3}$)</th>
<th>Rate $\times 10^5$ (mol dm$^{-3}$ s$^{-1}$)</th>
<th>Exptl.</th>
<th>Calcd.*</th>
</tr>
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<td>2.3</td>
<td></td>
</tr>
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<td>1.0</td>
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<td>4.0</td>
<td>11.1</td>
<td>11.1</td>
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</tbody>
</table>

* Initial rates were calculated using $K$ and $k$ as 60.4±6 dm$^3$ mol$^{-1}$ and 627.0±15 dm$^3$ mol$^{-1}$ s$^{-1}$ respectively.

Error ±4%
Table IVB(ii)(p. 216).

**Effect of catalyst**

The effect of catalyst was studied in the range of $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ mol dm$^{-3}$ and the order in catalyst is found to be 0.7 as in Fig.IVB(iii)(p. 218); Table IVB(iii), (p. 219).

**Effect of acid**

The effect of acid concentration on the reaction rate was studied in the range of 3.0 to 5.0 mol dm$^{-3}$. Higher concentration is preferred, since at low acid concentrations the oxidant is unstable. The effect of acid is studied at constant 5.6 mol dm$^{-3}$ ionic strength. There is no significant effect of acid on the initial rate of reaction.

**Effect of products**

The effect of products, arsenic(V) and Mn(II) was studied in the range of $1.0 \times 10^{-3}$ to $1.0 \times 10^{-2}$ and 1.0 to $4.0 \times 10^{-2}$ mol dm$^{-3}$ respectively, keeping all other conditions constant. The arsenic(V) and Mn(II), did not alter the reaction rate significantly (Table IVB(iv);p.220 ).
Fig.IVB(iii) : Order in catalyst $\sqrt{Br^-}$; bromide catalysed oxidation of As(III) by Mn(III) in acid medium.

(Conditions as in Table IVB(iii), p. 219)
Table IVB(iii) : Effect of catalyst, $[\text{Br}^-]$ in bromide catalysed oxidation of $\text{As(III)}$ by $\text{Mn(III)}$ in acid medium at 25°C

\[
\begin{align*}
\left[\text{As(III)}\right] &= 1.0 \times 10^{-2}; \\
\left[\text{Mn(III)}\right] &= 5.0 \times 10^{-3}; \\
\left[\text{H}_2\text{SO}_4\right] &= 5.0; \\
I &= 5.60/\text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>$[\text{Br}^-]$ x 10^5 mol dm^{-3}</th>
<th>$\left[\text{As(III)}\right]$ x 10^{-4} mol dm^{-3}</th>
<th>$\left[\text{AsBr}^{2+}\right]$ x 10^{-6} mol dm^{-3}</th>
<th>$\left[\text{AsBr}^+\right]$ x 10^{-9} mol dm^{-3}</th>
<th>$\left[\text{AsBr}_3\right]$ x 10^{12} mol dm^{-3}</th>
<th>$\left[\text{AsBr}_4^-\right]$ x 10^{16} mol dm^{-3}</th>
<th>Rate x 10^5 mol dm^{-3}s^{-1}</th>
<th>Exptl.</th>
<th>Calcd.*</th>
</tr>
</thead>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
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<td>0.3019</td>
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<td>52.90</td>
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</table>

* Rates were calculated using $K_{eq}$ and $k$ as 60.4±6 dm\(^3\) mol\(^{-1}\) and 627.0±15 dm\(^3\) mol\(^{-1}\)s\(^{-1}\) respectively.

Error ±5%
Table IVB(iv): Effect of added products, [Mn(II)] and [As(V)];
bromide catalysed oxidation of arsenic(III)
by manganese(III) in acid medium, at 25°C

\[ \begin{align*}
  \Gamma_{\text{As(III)}} &= 1.0 \times 10^{-2}; \quad \Gamma_{\text{Mn(III)}} = 5.0 \times 10^{-3}; \\
  \Gamma_{\text{Br}^-} &= 5.0 \times 10^{-5}; \quad \Gamma_{\text{H}_2\text{SO}_4} = 5.0; \quad I = 5.60/\text{mol dm}^{-3}
\end{align*} \]

<table>
<thead>
<tr>
<th>( \sqrt{\text{Mn(II)}} \times 10^2 ) ( \text{mol dm}^{-3} )</th>
<th>( \text{Rate} \times 10^5 ) ( \text{mol dm}^{-3} s^{-1} )</th>
<th>( \text{As(V)} \times 10^3 ) ( \text{mol dm}^{-3} )</th>
<th>( \text{Rate} \times 10^5 ) ( \text{mol dm}^{-3} s^{-1} )</th>
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<td>5.30</td>
</tr>
<tr>
<td>1.0</td>
<td>5.32</td>
<td>1.0</td>
<td>5.32</td>
</tr>
<tr>
<td>2.0</td>
<td>5.38</td>
<td>2.0</td>
<td>5.31</td>
</tr>
<tr>
<td>3.0</td>
<td>5.35</td>
<td>5.0</td>
<td>5.35</td>
</tr>
<tr>
<td>4.0</td>
<td>5.30</td>
<td>10.0</td>
<td>5.33</td>
</tr>
</tbody>
</table>

Error ±4%
Test for polymerisation

Under the reaction conditions as in Table IVB(ii) (p.216), the reaction was allowed to take place in presence of 0.01 mol dm$^{-3}$ acrylamide. After the completion of the reaction, the solution was diluted with methanol and this resulted in the formation of a precipitate.

Effect of temperature

The effect of temperature was studied at 25, 30, 35 and 40°C and is given in Table IVB(v), p.(222). Since the evaluation of rate constants of different steps in the reaction scheme was not possible, the activation parameters were not calculated.

Effect of sulphate

Since manganese(III) can form sulphate complexes, runs were followed with varying sulphate concentrations keeping all other conditions constant in perchlorate perchloric acid media. Added sulphate did not lead to any recognisable effect on the reaction.
Table IVB(v): Effect of temperature on bromide catalysed oxidation of arsenic (III) by manganese (III) in acid medium.

\[ [\text{As(III)}] = 1.0 \times 10^{-2}; \ [\text{Mn(III)}] = 5.0 \times 10^{-3}; \]
\[ [\text{Br}^-] = 5.0 \times 10^{-5}; \ [\text{H}_2\text{SO}_4] = 5.0; \ I = 5.60/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>Rate constant $k \times 10^3$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>3.09</td>
</tr>
<tr>
<td>303</td>
<td>4.20</td>
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<tr>
<td>308</td>
<td>4.88</td>
</tr>
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<td>318</td>
<td>6.30</td>
</tr>
</tbody>
</table>

Error $\pm 5\%$
DISCUSSION

The bromide catalysed oxidation of arsenic(III) by manganese(III) in a strong sulphuric acid follows an approximate rate law shown in equation (2), the orders in arsenic(III) and bromide concentration being fractional. Acid and initial presence of products do not affect the reaction in the concentration ranges studied. The possibility that the orders in two extreme cases $[^\text{oxidant}] \gg [^\text{reductant}]$ and

$$\frac{d}{dt} [\text{Mn}^{3+}] = k [\text{Mn}^{3+}] [\text{As}^{3+}]^{0.57} [\text{Br}^-]^{0.7}$$

would be different as in the case of iodide catalysed cerium(IV) oxidation of arsenic(III)\textsuperscript{7} was also ruled out as it was found in the two extreme cases also that the order remained approximately same with respect to oxidant and reductant concentrations. The rate data are compatible with the reaction going through a substrate-halide complex followed by intervention of arsenic(IV) as shown in Scheme 1.

Although Mn(III) can form MnBr\textsubscript{2}\textsuperscript{+} similar to MnCl\textsubscript{2}\textsuperscript{+}, the fact that its equilibrium constant is small\textsuperscript{8} and that the measured order in Mn(III) is approximately unity shows that MnBr\textsubscript{2}\textsuperscript{+} which is present under the present experimental
conditions to the extent of about 1% may not be involved and aquated Mn(III) might be the active species. Furthermore, experiments with varying sulphate concentrations keeping all other concentrations constant in perchlorate media also showed that sulphate is without influence on the reaction. Hence, sulphate complexes are also not involved. It is well understood that not only species such as AsBr$_3$, AsCl$_3$ have high stability but also equilibrium constants of different SbCl$_{3-x}$ complexes are known to have substantial values, x indicating one to six chlorides. In view of similarity of arsenic(III) and antimony(III) halide complexes, the known

$$\begin{align*}
{\text{As}}^{3+} + {\text{Br}}^- & \rightleftharpoons {\text{AsBr}}^{2+} & K_{\text{eq}} \\
{\text{AsBr}}^{2+} + {\text{Mn}}^{3+} & \rightarrow {\text{As}}^{(IV)} + {\text{Br}}^- + {\text{Mn}}^{2+} & k \text{ slow} \\
{\text{As}}^{(IV)} + {\text{Mn}}^{3+} & \rightarrow {\text{As}}^{(V)} + {\text{Mn}}^{2+} & k \text{ fast}
\end{align*}$$

Scheme 1

equilibrium constants of SbCl$_{3-x}$ may be used to make an approximate estimate of the concentrations of different arsenic(III)-bromide complexes. Such concentrations calculated by an approximate method accounting for the competing equilibria, are shown in Table IVB(iii) (p.219) along with the corresponding experimentally determined rates in the case of different bromide concentrations used.
It was found that a ready parallelism between concentrations and rates occurs only in the case of the species involving only one halide, AsBr²⁺ and not in others - reinforcing the possibility of the latter's participation in the mechanism (as in Scheme 1). In terms of Scheme 1, a rate law may be derived as follows. According to Scheme 1, the concentration of arsenic(III)-bromide complex (AsBr²⁺) is given by eqn.(3).

\[
\left[\text{AsBr}^{2+}\right] = K_{eq}\left[\text{As(III)}\right]^{2}\left[\text{Br}^{-}\right]^{2} \tag{3}
\]

The rate of disappearance of [Mn(III)] with time is given by

\[
\frac{-d[\text{Mn(III)}]}{dt} = k_{eq}\left[\text{AsBr}^{2+}\right]\left[\text{Mn}^{3+}\right]^{2} \tag{4}
\]

Since

\[
\left[\text{As(III)}\right]^{2} = \left[\text{As(III)}\right]^{2} + K_{eq}\left[\text{As(III)}\right]^{2}\left[\text{Br}^{-}\right]^{2}
\]

And

\[
\left[\text{Br}^{-}\right]^{2} = \left[\text{Br}^{-}\right]^{2} + K_{eq}\left[\text{Br}^{-}\right]^{2}\left[\text{As(III)}\right]^{2}
\]

equation (4) becomes eqn.(5).
The rate law (5) accounts for the fractional orders of \( \text{As(III)} \) as well as \( \text{Br}^- \) and may be verified in the form of (6) at constant \( \text{Br}^- \) by plotting left hand side against \( \text{As(III)} \) as shown in Fig.IVB(iv) (p. 227).

\[
\frac{\text{Rate}}{\sqrt{\text{As(III)}}} = \frac{k \frac{\sqrt{\text{Br}^-}}{T} \sqrt{\text{Mn}^{3+} \text{T}}}{1 + k_{eq} \frac{\sqrt{\text{As(III)}}}{T} + k_{eq} \frac{\sqrt{\text{Br}^-}}{T} + k_{eq}^2 \frac{\sqrt{\text{As(III)}}}{T} \sqrt{\text{Br}^-} \text{T}}
\]

The linearity of such a plot verifies scheme 1.

Further confirmation of scheme 1 is had by evaluating \( k_{eq} \) and \( k \) from graph and utilising the latter constants to calculate rates for different situations. \( k_{eq} \) and \( k \) derived from graph were 60.4±6 dm mol\(^{-1}\) and 627.0±15 dm mol\(^{-1}\) s\(^{-1}\) respectively. The calculated rates were found to compare reasonably with the corresponding experimental rates as given in Table IVB(ii), (p.216); (iii) (p.219).

The present reaction has been studied in presence of chloride ions. It is found that the catalytic activity
Fig. IVB(iv): Verification of rate law (3)

(Conditions as in Table IVB(ii), p. 216)
of bromide is more than that of chloride, indicating the case of electron transfer or effectiveness of the bridge decreases in the order \( \text{Br}^- > \text{Cl}^- \) which is in agreement with the work of A.E. Ogard and H. Taube\(^{12}\). The difference in the rates of halogen transfer is expected, for the most polarizable ligand is likely to transfer most easily\(^{13}\). Activation parameters were not calculated as the rates measured corresponded to a multistep mechanism.
Findings

Halide catalysed manganese(III) oxidation of arsenic(III) is studied and it is understood to go through complex such as AsBr$^{2+}$ and through As(IV). No acid or product effect found. A mechanism incorporating such data is written and derived rate law is verified. Some constants involved in the mechanism are derived.

Work advisable

More exact values of the stability constants of different AsBr$^{+3-x}_x$, $x$ indicating one to six bromides would have explained the role of active species better.

Importance of the Chapter IVB

The bromide catalysis of manganese(III)-arsenic(III) reaction occurs through complexation such as AsBr$^{2+}$. Complexation is usual in such cases and may very well be a rule rather than exception. Rates calculated using the derived constants are in reasonable agreement with experimental rates.
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