PART-I

Catalysed Reactions
CHAPTER II
RUTHENIUM(III) MEDIATED CERIUM(IV) OXIDATION OF THALLIUM(I) IN AQUEOUS SULPHURIC ACID - A KINETIC AND MECHANISTIC STUDY

The slow reaction between cerium(IV) and thallium(I) has been studied in acid medium\(^1\). A number of catalysts such as silver(I)\(^2,3\), platinum\(^4\) and manganese(IV)\(^5\) are used as catalyst in the cerium(IV)-thallium(I) reaction. The slow cerium(IV) oxidation of thallium(I) is facilitated by a minute amount (10\(^{-6}\) mol dm\(^{-3}\)) of ruthenium(III) in aqueous sulphuric acid. The platinum and ruthenium(III) is known to be an efficient catalyst in several redox reactions\(^6,8\). The catalysed mechanism can be quite complicated due to the formation of different intermediate complexes, free radicals and various oxidation states of ruthenium.

The redox potentials of different couples\(^9\) involved in the reactions in an acid medium make the ruthenium(III) catalysis for oxidation of thallium(I) by cerium(IV) more feasible. In sulphuric acid and sulphate media cerium(IV) and thallium(I) forms several complexes\(^10,13\), but their role has not received much attention so far. Thus the reaction rate increases as the acid and sulphate concentration increases, but these effects are not understood. Hence we have investigated the effect of sulphate and acid on the ruthenium(III) catalysed oxidation of thallium(I) by cerium(IV) to determine the active species of catalyst, oxidant and substrate, and to arrive at a plausible mechanism. The results of the title reaction are reported in this chapter.
EXPERIMENTAL

Materials

Reagent grade chemicals and double distilled water were used throughout. The stock solution of 0.01 mol dm$^{-3}$ of cerium(IV) in 0.1 dm$^3$ volumetric flask was obtained by dissolving (0.6326 g) cerium(IV) ammonium sulphate (E. Merck) in 1 mol dm$^{-3}$ of sulphuric acid. The solution was standardised$^{14}$ by taking 0.025 dm$^3$ of cerium(IV) stock solution into a 0.25 dm$^3$ conical flask, added 0.025 dm$^3$ of 0.5 mol dm$^{-3}$ sulphuric acid. The contents were titrated against standard iron(II) ammonium sulphate solution using ferroin as an indicator. The thallium(I) solution of 0.1 mol dm$^{-3}$ in 0.1 dm$^3$ volumetric flask was obtained by dissolving (2.5240 g) thallous sulphate (BDH) in water. The solution of thallium(I) was standardised$^{15}$ by taking 0.02 dm$^3$ of the stock solution into a 0.25 dm$^3$ reagent bottle, added 0.06 dm$^3$ of concentrated hydrochloric acid and 0.005 dm$^3$ of chloroform. The contents were titrated against standard 0.25 mol dm$^{-3}$ of potassium iodate, until the violet colour of the organic layer just disappears. The ruthenium(III) solution was made by dissolving ruthenium trichloride (S. d. fine-Chem.) in 0.20 mol dm$^{-3}$ hydrochloric acid and its concentration was ascertained by EDTA titration$^{16,17}$. Dilute solutions of ruthenium(III) were made from the stock solution as required. The cerium(III) solution was prepared by dissolving cerium(III) acetate (BDH) in water. The thallium(III) sulphate solution was obtained by dissolving thallium(III) oxide (BDH) in aqueous sulphuric acid. Sodium sulphate and sulphuric acid were used to provide the required ionic strength and acidity respectively, except in the case of effect of added sulphate, in which sodium perchlorate and perchloric acid were used to maintain the...
ionic strength and acidity.

**Kinetics**

The kinetics were followed at 30 ± 0.1°C, unless otherwise stated. Reaction was initiated by mixing the cerium(IV) solution, containing the required amounts of sulphuric acid and sodium sulphate to the thallium(I) solution, the latter also containing ruthenium(III). The reaction was generally followed under pseudo-first order conditions, with ten fold excess in thallium(I) concentration, by measuring the absorbance of cerium(IV) concentration in the mixture at 360 nm in a 1 cm cell placed in the thermostatted compartment of an Varian Cary-50 Bio Uv-visible spectrophotometer. Beer's law had been verified earlier between $5.0 \times 10^{-5}$ and $3.0 \times 10^{-4}$ mol dm$^{-3}$ of cerium(IV) concentrations at 360nm under the reaction conditions. The extinction co-efficient, \( e \), was found to be $3500 \pm 50$ dm$^{-3}$ mol$^{-1}$ cm$^{-1}$ (Fig. II(i)(p.30)). Kinetic runs were followed upto about 80 % completion of the reaction and good first order kinetics were observed. During the reaction it was found that cerium(IV) also oxidised the catalyst, ruthenium(III), appreciably. Hence a correction for the ruthenium(III) oxidation was also applied in the case of each run by studying a parallel blank run under similar conditions in the absence of the thallium(I).

A sample run is given in Table II(i)(p.31). The rate constants, \( k_{obs} \) were calculated from the plots of log[cerium(IV)] versus time. The pseudo-first order plots were linear over 70% completion of the reaction and are shown in Fig. II(ii)(p.32). Rate constants were reproducible within ± 5%.
Fig. II(i)

Verification of Beer's law for cerium(IV) concentrations at 360 nm in 0.50 mol dm$^{-3}$ sulphuric acid at 30$^\circ$C
Table II(i)

Ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

\[ [\text{Ce(IV)}] = 1.0 \times 10^{-4} \; ; \quad [\text{Tl(I)}] = 5.0 \times 10^{-3} \; ; \]
\[ [\text{Ru(III)}] = 5.0 \times 10^{-6} \; ; \quad [\text{H}_2\text{SO}_4] = 0.50 \; ; \]
\[ I = 1.60 / \text{mol dm}^{-3} \]

<table>
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<tr>
<th>Time (min)</th>
<th>O.D. in presence of thallium(I)</th>
<th>O.D. in absence of thallium(I)</th>
<th>Corrected O.D.</th>
<th>([\text{Ce(IV)}] \times 10^5)</th>
<th>(5 + \log[\text{Ce(IV)}])</th>
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</table>
Ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

(Conditions as in Table II(i)(p.31))

\[ [\text{Ce(IV)}] \times 10^4 = (1) 0.5, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0, (6) 5.0 \text{ / mol dm}^{-3} \]
RESULTS

Stoichiometry

Different sets of concentrations of reactants and ruthenium(III), in 0.50 mol dm$^{-3}$ sulphuric acid at constant ionic strength, 1.60 mol dm$^{-3}$, were kept for over 6 h at 30°C in a closed container. When [Ce(IV)] > [Tl(I)], the remaining cerium(IV) concentration was assayed by measuring the absorbance at 360 nm, whereas under the conditions, [Tl(I)] > [Ce(IV)], when cerium(IV) had fully reacted, the remaining thallium(I) concentration was determined by titration with iodate$^{15}$. Cerium(III) was oxidised to cerium(IV) with peroxodisulphate and then determined quantitatively by spectrophotometer. The results showed that two moles of cerium(IV) were required to oxidise one mole of thallium(I) as in equation 1 (Table II(ii)(p.34)).

$$2 \text{Ce(IV)} + \text{Tl(I)} \rightarrow 2 \text{Ce(III)} + \text{Tl(III)}$$ (1)

Reaction order

The order with respect to each of reductant, catalyst and acid was determined by the slopes of log$k_{obs}$ versus log(concn.) plots. The orders were obtained by varying the concentrations of reductant, catalyst and acid in turn while keeping the others constant.

Effect of [cerium(IV)]

At constant ionic strength, I = 1.60 mol dm$^{-3}$, sulphuric acid concentration of 0.50 mol dm$^{-3}$ and ruthenium(III) concentration of 5.0×10$^{-6}$ mol dm$^{-3}$, the cerium(IV) concentration was varied. The order with respect to cerium(IV) in the 5.0×10$^{-5}$ - 5.0×10$^{-4}$ mol dm$^{-3}$ concentration range was found to be unity, since the rate
Table II(ii)

Stoichiometry* of ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

\[
[Ru(\text{III})] = 5.0 \times 10^{-6} \quad [\text{H}_2\text{SO}_4] = 0.50 \quad I = 1.60 \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Taken [Ce(IV)] \times 10^4</th>
<th>Taken [Tl(I)] \times 10^4</th>
<th>[Ce(IV)] \times 10^4</th>
<th>[Ce(III)] \times 10^4</th>
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*All concentrations are in mol dm\(^{-3}\)
Constants, $k_{obs}$, were constant for different initial cerium(IV) concentrations (Table II(iii)(p.36)). The parallel linear plots over 70% completion of the reaction for different initial cerium(IV) concentrations also indicate the first order with respect to cerium(IV) (Fig. II(ii)(p.32)).

**Effect of [thallium(I)]**

The concentration of thallium(I) was varied in the range of $5.0 \times 10^{-4}$ and $5.0 \times 10^{-3}$ mol dm$^{-3}$ keeping the concentration of oxidant, acid and catalyst constant at a fixed ionic strength of 1.60 mol dm$^{-3}$ (Table II(iii)(p.36)). The data led to the plots of log $k_{obs}$ versus log(concn.) and the order with respect thallium(I) concentration was determined. At lower thallium(I) concentration order with respect to thallium(I) was found to be less than unity, 0.33 (Fig. II(iii)(p.37)), and at higher thallium(I) concentration the reaction was found to be independent of thallium(I) concentration. The order in thallium(I) concentration changes from first order to zero order as the thallium(I) concentration varies.

**Effect of [ruthenium(III)]**

At constant oxidant, reductant and acid concentrations of $1.0 \times 10^{-4}$, $5.0 \times 10^{-3}$ and 0.50 mol dm$^{-3}$, respectively, and at $I = 1.60$ mol dm$^{-3}$, the ruthenium(III) concentration was varied between $1.0 \times 10^{-6}$ and $1.0 \times 10^{-5}$ mol dm$^{-3}$ (Table II(iii)(p.36)). The order in ruthenium(III) concentration was found to be unity (Fig. II(iii)(p.37)).
Table II(iii)

Effect of cerium(IV), thallium(I) and ruthenium(III) concentrations on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

\[ \text{[H}_2\text{SO}_4\text{]} = 0.50 \ ; \quad \text{I} = 1.60 / \text{mol dm}^{-3} \]

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<tr>
<th>([\text{Ce(IV)}] \times 10^4) (mol dm(^{-3}))</th>
<th>([\text{Ti(I)}] \times 10^3) (mol dm(^{-3}))</th>
<th>([\text{Ru(III)}] \times 10^6) (mol dm(^{-3}))</th>
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36
Fig. II(iii)

Order with respect to thallium(I) and ruthenium(III) concentrations on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

(Conditions as in Table II(iii)(p.36))
**Effect of initially added products**

The effect of initially added products, cerium(III) and thallium(III), was studied in the $5.0 \times 10^{-5} - 5.0 \times 10^{-4}$ mol dm$^{-3}$ concentration range, keeping the ionic strength, reactant concentrations and other conditions constant. It was observed that, both the cerium(III) and thallium(III) products did not have any significant effect on the reaction rate.

**Effect of varying acidity**

At fixed ionic strength (3.10 mol dm$^{-3}$) and with other conditions remaining constant, the rate was found to increase with increasing acidity (Table II(iv)(p.42)). Sulphuric acid, H$_2$SO$_4$, has a high first ionisation constant and in solution, exists almost completely as H$^+$ and HSO$_4^-$ species. However, HSO$_4^-$, has modest ionisation properties and hence, it becomes necessary to evaluate the *in situ* H$^+$ ion concentration in our reactant solutions especially in view of the high sulphate concentration used and the importance of HSO$_4^-$ equilibria. The *in situ* H$^+$ ion concentration in the sulphuric acid-sulphate media has been calculated using the known ionisation constant$^{18}$ of acid sulphate as in an earlier study$^{12}$. An example calculation of H$^+$ ion concentration is given below. From the knowledge of the added sulphate and acidity, the concentration of HSO$_4^-$ was calculated from the quadratic equation applicable to this case and the actual H$^+$ ion concentration in solution. Thus in the case of 0.03 mol dm$^{-3}$ added sulphate (to maintain the ionic strength constant) and acidity of 1.0 mol dm$^{-3}$.

\[
\begin{align*}
H^+ + SO_4^{2-} & \rightleftharpoons HSO_4^- ; \\
(a - x) & \quad (b - x) \quad x \\
K = \frac{[HSO_4^-]}{[H^+][SO_4^{2-}]} & 
\end{align*}
\]
where ‘a’ and ‘b’ are the concentrations of acid, \((1.0 + 1.0) = 2.0 \text{ mol dm}^{-3}\) and sulphate, \((1.0 + 0.03) = 1.03 \text{ mol dm}^{-3}\) respectively and ‘x’ that of bisulphate,

\[
8.3 = \frac{x}{(a-x)(b-x)} \quad \text{or} \quad 8.3x^2 - 26.149x + 17.098 = 0
\]

\[
[\text{HSO}_4^-] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

Thus,

\[
[H^+] = (a-x) = (2.0 - 0.9261) = 1.0739
\]

and

\[
[\text{SO}_4^{2-}] = (b-x) = (1.03 - 0.9261) = 0.1039
\]

Similarly, other \(H^+\) ion concentrations were calculated. The order with respect to \(H^+\) ion concentration was found to be less than unity from the plot of \(\log k_{\text{obs}}\) versus \(\log[H^+]\) (Fig. II(iv)(p.43)). The fractional order of \(H^+\) ion concentration might have arisen due to its role of being involved in the formation of cerium(IV) complexes in aqueous sulphuric acid. Cerium(IV) is known to form several complexes in acid-sulphate media such as \(\text{CeSO}_4^{2+}, \text{Ce(SO}_4)_2, \text{Ce(SO}_4)_2(\text{HSO}_4^-)\) and \(\text{H}_3\text{Ce(SO}_4)_4^-\) as shown in equilibria (2)-(6)

\[
\begin{align*}
\text{Ce}^{4+} + \text{H}_2\text{O} & \rightleftharpoons \text{Ce(OH)}^{3+} + \text{H}^+ \quad K_{\text{OH}} \quad (2) \\
\text{Ce}^{4+} + \text{SO}_4^{2-} & \rightleftharpoons \text{CeSO}_4^{2+} \quad K_1 \quad (3) \\
\text{CeSO}_4^{2+} + \text{SO}_4^{2-} & \rightleftharpoons \text{Ce(SO}_4)_2 \quad K_2 \quad (4) \\
\text{Ce(SO}_4)_2 + \text{HSO}_4^- & \rightleftharpoons \text{Ce(SO}_4)_2 \text{HSO}_4^- \quad K_3 \quad (5) \\
\text{Ce(SO}_4)_2 \text{HSO}_4^- + \text{HSO}_4^- + \text{H}^+ & \rightleftharpoons \text{H}_3\text{Ce(SO}_4)_4^- \quad K_4 \quad (6)
\end{align*}
\]
The Ce(OH)$_3^+$ species may also be present. Since the total cerium(IV) is distributed between different species with the equilibrium constants, $\beta_1=K_1 = 384.62$, $\beta_2=K_1K_2 = 169.49$, $\beta_3=K_1K_2K_3 = 101.17$, $\beta_4=K_1K_2K_3K_4 = 203.4$, and $K_{\text{OH}} = 15$ characterising such equilibria, the approximate concentrations of such species may be calculated from equation (7) from the concentrations of the dissolved cerium(IV) and acid sulphate, as also the competing equilibria and their constants$^{12}$.

\[
[\text{Ce(IV)}]_t = [\text{Ce}^{4+}]_f \\
\times \left\{1 + \frac{K_{\text{OH}}}{[\text{H}^+]} + \beta_1[\text{SO}_4^{2-}] + \beta_2[\text{SO}_4^{2-}]^2 + \beta_3[\text{SO}_4^{2-}]^2[\text{HSO}_4^-] + \beta_4[\text{SO}_4^{2-}]^2[\text{HSO}_4^-][\text{H}^+]\right\}
\] (7)

In equation (7) the subscripts 't' and 'f' stands for total and free respectively.

The formation of Ce(OH)$_2^{2+}$, occurs to a much smaller extent and is therefore neglected. A sample calculation of different cerium(IV) species in 1.0 mol dm$^{-3}$ H$_2$SO$_4$ is given below:

\[
[H^+] = 1.0739; \quad [SO_4^{2-}] = 0.1039 \text{ mol dm}^{-3}
\]

\[
[\text{Ce(IV)}]_t = 1.0 \times 10^{-4}
\]

\[
= [\text{Ce}^{4+}]_f \times \{1 + (15 / 1.0739) + 384.62 (0.1039) + 169.49 (0.1039)^2 \\
+ 101.17 (0.1039)^2 (0.9261) + 203.4 (0.1039)^2 (0.9261)^2 (1.0739)\}\n\]

\[
= [\text{Ce}^{4+}]_f \times \{1 + 13.9678 + 39.9620 + 1.8297 + 1.0114 + 2.0224\}\n\]

\[
= [\text{Ce}^{4+}]_f \times 59.7933
\]

\[
\therefore [\text{Ce}^{4+}]_f = 1.0 \times 10^{-4} / 59.7933 = 1.6724 \times 10^{-6}
\]

But, $\alpha_0 = [\text{Ce}^{4+}]_f / 1.0 \times 10^{-4} = 1.6724 \times 10^{-6} / 1.0 \times 10^{-4} = 1.6724 \times 10^{-2}$
Similarly,

\[
[Ce(OH)^3+] = 1.6724 \times 10^{-6} \times 13.9678 = 2.3360 \times 10^{-5} \quad ; \quad \alpha_{OH} = 0.2336
\]

\[
[CeSO_4^{2+}] = 1.6724 \times 10^{-6} \times 39.9620 = 6.6834 \times 10^{-5} \quad ; \quad \alpha_1 = 6.6834 \times 10^{-1}
\]

\[
[Ce(SO_4)_2] = 1.6724 \times 10^{-6} \times 1.8297 = 3.0599 \times 10^{-6} \quad ; \quad \alpha_2 = 3.0599 \times 10^{-2}
\]

\[
[HCe(SO_4)_3] = 1.6724 \times 10^{-6} \times 1.01144 = 1.6915 \times 10^{-6} \quad ; \quad \alpha_3 = 1.6915 \times 10^{-2}
\]

\[
[H_3Ce(SO_4)_4]^2^- = 1.6724 \times 10^{-6} \times 2.0223 = 3.3822 \times 10^{-6} \quad ; \quad \alpha_4 = 3.3822 \times 10^{-2}
\]

where \(\alpha_0, \alpha_{OH}, \alpha_1, \alpha_2, \alpha_3\) and \(\alpha_4\) are the fractions of total cerium(IV) of the species \(Ce^{4+}, Ce(OH)^{3+}, CeSO_4^{2+}, Ce(SO_4)_2, HCe(SO_4)_3\) and \(H_3Ce(SO_4)_4\) respectively. The results are given in Table II(iv)(p.42) and these values are used to draw Fig. II(v)(p.44).

**Effect of added sulphate**

The rate of reaction increased with increase in sulphate concentration (Table II(v)(p.46)). This is ascribable to the formation of thallium(I) sulphate complexes. The order in sulphate concentration under the experimental condition was \(ca\ 0.98\). Thallium(I) is known to form sulphate complexes\(^1\) of formula \(Tl(H_2O)_n SO_4^{2-}\). The cumulative stability constants \(\beta_5 = K_5\) and \(\beta_6 = K_5K_6\) being 0.33 and 0.13 respectively as shown in the following equilibria.

\[
Tl^- + SO_4^{2-} \rightleftharpoons Tl(SO_4)^- \quad K_5 \quad (8)
\]

\[
Tl(SO_4)^- + SO_4^{2-} \rightleftharpoons Tl(SO_4)_2^{3-} \quad K_6 \quad (9)
\]

The approximate concentrations of such species may be calculated, based on equation (10), from the concentrations of the dissolved thallium(I) and sulphate with their competing equilibria\(^12,19,20\).

\[
[Tl(I)]_t = [Tl(I)]_f \{1 + \beta_5 [SO_4^{2-}] + \beta_6 [SO_4^{2-}]^2\} \quad (10)
\]

41
Table II(iv)

Variation of different cerium(IV) species* with H⁺ ion concentration on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

\[
\begin{align*}
[\text{Ce(IV)}] &= 1.0 \times 10^{-4} ; \\
[\text{Tl(I)}] &= 5.0 \times 10^{-3} ; \\
[\text{Ru(III)}] &= 5.0 \times 10^{-6} ; \\
I &= 1.60 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>[\text{H}_2\text{SO}_4] (\text{mol dm}^{-3})</th>
<th>[\text{H}^+] (\text{mol dm}^{-3})</th>
<th>\alpha_0 \times 10^3</th>
<th>\alpha_{0H}</th>
<th>\alpha_1 \times 10</th>
<th>\alpha_2 \times 10^2</th>
<th>\alpha_3 \times 10^2</th>
<th>\alpha_4 \times 10^3</th>
<th>k_{\text{obs}} \times 10^3 (\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.025</td>
<td>0.937</td>
<td>0.562</td>
<td>3.083</td>
<td>11.61</td>
<td>1.213</td>
<td>0.107</td>
<td>0.32</td>
</tr>
<tr>
<td>0.2</td>
<td>0.059</td>
<td>1.619</td>
<td>0.412</td>
<td>4.290</td>
<td>13.03</td>
<td>2.651</td>
<td>3.072</td>
<td>0.54</td>
</tr>
<tr>
<td>0.5</td>
<td>0.280</td>
<td>5.002</td>
<td>0.268</td>
<td>5.964</td>
<td>8.156</td>
<td>3.501</td>
<td>12.19</td>
<td>1.20</td>
</tr>
<tr>
<td>0.7</td>
<td>0.554</td>
<td>9.073</td>
<td>0.246</td>
<td>6.421</td>
<td>5.207</td>
<td>2.629</td>
<td>24.78</td>
<td>1.74</td>
</tr>
<tr>
<td>1.0</td>
<td>1.074</td>
<td>16.72</td>
<td>0.234</td>
<td>6.683</td>
<td>3.600</td>
<td>1.692</td>
<td>33.82</td>
<td>2.46</td>
</tr>
</tbody>
</table>

*\alpha_0, \alpha_{0H}, \alpha_1, \alpha_2, \alpha_3, and \alpha_4 are the fractions of total cerium(IV) of the species Ce⁴⁺, Ce(OH)³⁺, CeSO₄²⁺, Ce(SO₄)₂, Ce(SO₄)₂HSO₄⁻ and H₃Ce(SO₄)₄⁻, respectively.
Effect of variation of acid concentration on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

(Conditions as in Table II(iv)(p.42))
Effect of acid concentration on different cerium(IV) species and also on the rate constants of ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

(Conditions as in Table II(iv)(p.42))
For example,

\[
\begin{align*}
[\text{HSO}_4^-] &= 0.0160; [\text{H}^+] = 0.4839 \text{ and } [\text{SO}_4^{2-}] = 0.00399, \\
[\text{Tl(I)}]_i &= [\text{Tl(I)}]_f \left(1 + \beta_5 [\text{SO}_4^{2-}] + \beta_6 [\text{SO}_4^{2-}]^2 \right), \\
[\text{Tl(SO}_4^-)] &= 4.9934 \times 10^{-3} \times 1.3167 \times 10^{-3} = 6.571 \times 10^{-6}, \\
[\text{Tl(SO}_4^{2-})^2] &= 4.9934 \times 10^{-3} \times 2.0696 \times 10^{-6} = 1.03344 \times 10^{-8}.
\end{align*}
\]

Variations in the concentrations of such species with increase in \([\text{SO}_4^{2-}]\) are shown in Table II(v)(p.46) along with the rate constants. The results of such calculations are used to draw Fig. II(vi)(p.47).

**Effect of added chloride**

The effect of added chloride ions on the reaction in the \(5.0 \times 10^{-4} - 5.0 \times 10^{-3}\) mol dm\(^{-3}\) concentration range was studied while keeping all the other concentrations constant. It was observed that the added chloride ions do not have any significant effect on the rate of reaction.

**Effect of dielectric constant and ionic strength**

The effect of dielectric constant was studied by varying the acetic acid-water (v/v) content in the reaction mixture with all other conditions being maintained constant. Since the dielectric constants of aqueous acetic acid are not available in the literature, they were computed from the pure liquid values as follows\(^{21}\): The dielectric constant of reaction medium at various compositions of acetic acid-water (v/v) were calculated by using the following equation at constant ionic strength and other reactant concentrations constant. The values are given in Table II(vi)(p.49).

\[
D = D_1V_1 + D_2V_2
\]
Table II(v)
Variation of different thallium(I) species* with sulphate concentration on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

\[
[\text{Ce(IV)}] = 1.0 \times 10^{-4} ; \quad [\text{Tl(I)}] = 5.0 \times 10^{-3} ;
\]

\[
[\text{Ru(III)}] = 5.0 \times 10^{-6} ; \quad [\text{HClO}_4] = 0.50 ;
\]

\[
I = 1.60 / \text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Added sulphate $[\text{SO}_4^{2-}] \times 10^2$ (mol dm$^{-3}$)</th>
<th>Free sulphate $[\text{HSO}_4^-] \times 10^2$ (mol dm$^{-3}$)</th>
<th>$\alpha_5 \times 10^3$</th>
<th>$\alpha_6 \times 10^3$</th>
<th>$\alpha_7 \times 10^5$</th>
<th>$k_{obs} \times 10^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.601</td>
<td>0.399</td>
<td>9.982</td>
<td>1.314</td>
<td>0.2067</td>
</tr>
<tr>
<td>4.0</td>
<td>3.181</td>
<td>0.819</td>
<td>9.973</td>
<td>2.695</td>
<td>0.8696</td>
</tr>
<tr>
<td>6.0</td>
<td>4.739</td>
<td>1.261</td>
<td>9.958</td>
<td>4.173</td>
<td>2.0868</td>
</tr>
<tr>
<td>8.0</td>
<td>6.272</td>
<td>1.728</td>
<td>9.943</td>
<td>5.676</td>
<td>3.8686</td>
</tr>
<tr>
<td>10.0</td>
<td>7.780</td>
<td>2.220</td>
<td>9.927</td>
<td>7.272</td>
<td>6.3598</td>
</tr>
</tbody>
</table>

* $\alpha_5$, $\alpha_6$ and $\alpha_7$ are the fractions of total thallium(I) of the species Tl$^+$, Tl(SO$_4$)$^-$ and Tl(SO$_4$)$_2^{3-}$ respectively.
Fig. II(vi)

Effect of sulphate concentration on different thallium(I) species and also on the rate of ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

(Conditions as in Table II(v)(p.46))
where $V_1$ and $V_2$ are the volume fractions and $D_1$ and $D_2$ are dielectric constants of water and acetic acid as 78.5 and 6.15 at 30°C.

For example at 20% acetic acid,

$$D = 78.5 \times \frac{80}{100} + 6.15 \times \frac{20}{100} = 64.03$$

It was found that an increase in the percentage of acetic acid content in the reaction medium, keeping the reactant concentrations and other conditions constant, increases the reaction rate. No reaction of the solvent with the oxidant occurred under the experimental conditions employed. The Fig II(vii)(p.50) shows the plot of $\log k_{\text{obs}}$ versus $1/D$, which is linear with positive slope.

The increase in the ionic strength from 1.60 to 3.50 mol dm$^{-3}$, by increase in the concentration of sodium sulphate, caused the decrease in the rate of the reaction (Table II(vi)(p.49)). A plot of $\log k_{\text{obs}}$ versus $\sqrt{I}$ is linear with negative slope as shown in Fig. II(vii)(p.50).

**Effect of added ions**

At constant reactant concentrations and with other conditions constant, ions such as manganese(II), chloride and nitrate did not have any significant effect on the rate of the reaction. However, added sulphate increases the reaction rate.

**Effect of temperature**

The activation parameters for the reaction were studied by using linear regression analysis (also known as the method of least squares)\textsuperscript{22}. In generalized notation, the formula for a straight line is

$$y = ax + b.$$

The most tractable form of linear regression analysis assumes that values of the
Table II(vi)

Effect of variation of dielectric constant (D) and ionic strength (I) on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

\[
\begin{align*}
[\text{Ce(IV)}] &= 1.0 \times 10^{-4} ; \\
[\text{TI(I)}] &= 5.0 \times 10^{-3} ; \\
[\text{Ru(III)}] &= 5.0 \times 10^{-6} ; \\
[\text{H}_2\text{SO}_4] &= 0.50 ; \\
I &= 1.60 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>% of acetic acid – water (v/v)</th>
<th>D</th>
<th>1/D x 10^3</th>
<th>(k_{\text{obs}} \times 10^4) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.50</td>
<td>12.739</td>
<td>2.40</td>
</tr>
<tr>
<td>10</td>
<td>71.26</td>
<td>14.032</td>
<td>2.65</td>
</tr>
<tr>
<td>20</td>
<td>64.03</td>
<td>15.618</td>
<td>3.10</td>
</tr>
<tr>
<td>30</td>
<td>56.79</td>
<td>17.607</td>
<td>3.65</td>
</tr>
<tr>
<td>40</td>
<td>49.56</td>
<td>20.178</td>
<td>4.84</td>
</tr>
<tr>
<td>50</td>
<td>42.33</td>
<td>23.627</td>
<td>6.44</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
[\text{Ce(IV)}] &= 1.0 \times 10^{-4} ; \\
[\text{TI(I)}] &= 5.0 \times 10^{-3} ; \\
[\text{Ru(III)}] &= 5.0 \times 10^{-6} ; \\
[\text{H}_2\text{SO}_4] &= 0.50 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>I</th>
<th>(\sqrt{I})</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.60</td>
<td>1.265</td>
<td>2.40</td>
</tr>
<tr>
<td>2.00</td>
<td>1.414</td>
<td>1.86</td>
</tr>
<tr>
<td>2.50</td>
<td>1.581</td>
<td>1.37</td>
</tr>
<tr>
<td>3.00</td>
<td>1.732</td>
<td>0.99</td>
</tr>
<tr>
<td>3.50</td>
<td>1.870</td>
<td>0.72</td>
</tr>
</tbody>
</table>
Fig. II(vii)

Effect of variation of dielectric constant(D) and ionic strength(I) on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium at 30°C

(Conditions as in Table II(vi)(p.49))
independent variables ‘x’ are known without error and that experimental error is manifested only in values of the dependent variable ‘y’. Most sets of kinetic data approximate this situation, in as much as times of observation are more accurately measurable than the chemical or physical quantities related to reactant concentrations. The straight line selected by common linear regression analysis is that which minimises the sum of the squares of the derivatives of the ‘y’ variable from the line.

The slope ‘a’ and intercept ‘b’ parameters for the above equation can be calculated by linear regression analysis by any of several mathematically equivalent but different looking experiments. Most familiar are

Slope:  \[ a = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2} \]

Intercept:  \[ b = \frac{\sum y \sum x^2 - \sum x \sum xy}{n \sum x^2 - (\sum x)^2} \]

where ‘n’ is number of data points and the summation are for all data points in the set.

These data were subjected to least squares analysis.

The rate of the reaction was measured at different temperatures under varying thallium(I) concentration keeping other conditions constant. The rate constants \( k \), of the slow step of Scheme 1 were obtained from the intercepts of the plots of \( 1/k_{\text{obs}} \) versus \( 1/[\text{Tl(I)}] \) at five different temperatures. The data are subjected to least square analysis and are tabulated in Table II(vii a)(p.53). The activation parameters were evaluated from the plot of \( \log k_{\text{obs}}(y^*_{\text{cal}}) \) versus \( 1/T \) as shown in Fig. II(viii)(p.54) and are listed in Table II(vii b)(p.53). The activation energy of the reaction is calculated by

\[ E_a = -2.303 \times R \times \text{slope} \]
The entropy of activation is calculated by

\[
\frac{\Delta S^\#}{4.576} = \log k - 10.753 - \log T + \frac{E_a}{4.576}
\]

where \( k \) is in \( \text{sec}^{-1} \), \( T \) is in Kelvin and \( E_a \) is in \( \text{cal mol}^{-1} \). The enthalpy of activation is calculated by

\[
\Delta H^\# = E_a - RT
\]

The free energy of activation is calculated by

\[
\Delta G^\# = \Delta H^\# - T\Delta S^\#
\]

and the \( \log A \) is calculated by

\[
k = A e^{-\frac{E_a}{RT}}
\]

\[
\log A = \log k + \frac{E_a}{2.303RT}
\]

The uncatalysed reaction was carried out at 25, 30, 35, 40 and 45 °C. The pseudo-first order rate constants and the activation parameters are given in Table II(viii a) and (viii b) (p.55) respectively.

DISCUSSION

The cerium(IV) oxidation of thallium(I) is slow in aqueous sulphuric acid and under the present experimental conditions, the first order rate constant, \( k_{obs} \) is \( 2.74 \times 10^{-5} \) s\(^{-1}\). However, the reaction occurs with reasonable rates in the presence of ruthenium(III) in aqueous sulphuric acid. In the presence of perchloric acid, ruthenium(III) catalysis is not that much efficient, possibly due to the presence of active cerium(IV) species as Ce(OH)\(^{3+}\) in such media\(^{23}\). Hence the study was undertaken in sulphuric acid medium. The reaction between thallium(I) and cerium(IV) in presence of ruthenium(III) in aqueous sulphuric acid has a
### Table II(vii)

(a) Effect of variation of temperature on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium

\[
\begin{align*}
[\text{Ce(IV)}] &= 1.0 \times 10^{-4} ; & [\text{TI(I)}] &= 5.0 \times 10^{-3} ; \\
[\text{Ru(III)}] &= 5.0 \times 10^{-6} ; & [\text{H}_2\text{SO}_4] &= 0.50 ; \\
I &= 1.60 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Temperature 1/T x 10^3 k x 10^2</th>
<th>log k</th>
<th>log k (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K) (K^{-1}) (x)</td>
<td>(dm^3 mol^{-1}s^{-1}) (y)</td>
<td>(y*) (cal)</td>
</tr>
<tr>
<td>298 3.3560 2.87</td>
<td>-1.5421</td>
<td>-1.5215</td>
</tr>
<tr>
<td>303 3.3000 5.26</td>
<td>-1.2790</td>
<td>-1.3189</td>
</tr>
<tr>
<td>308 3.2470 7.24</td>
<td>-1.1403</td>
<td>-1.1231</td>
</tr>
<tr>
<td>313 3.1950 11.6</td>
<td>-0.9355</td>
<td>-0.9334</td>
</tr>
</tbody>
</table>

* Calculated

(b) Activation parameters with respect to slow step of Scheme 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_a</td>
<td>73 ± 4 kJ mol^{-1}</td>
</tr>
<tr>
<td>\Delta H^&quot;</td>
<td>71 ± 3 kJ mol^{-1}</td>
</tr>
<tr>
<td>\Delta S^&quot;</td>
<td>40 ± 2 JK^{-1} mol^{-1}</td>
</tr>
<tr>
<td>\Delta G^&quot;</td>
<td>59 ± 2 kJ mol^{-1}</td>
</tr>
<tr>
<td>log A</td>
<td>10 ± 1</td>
</tr>
</tbody>
</table>
Effect of variation of temperature on the ruthenium(III) mediated oxidation of thallium(I) by cerium(IV) in aqueous sulphuric acid medium

(Conditions as in Table II(vii)(p.53))
(a) Effect of variation of temperature on the uncatalysed reaction between thallium(I) and cerium(IV) in aqueous sulphuric acid medium

\[
[\text{Ce(IV)}] = 1.0 \times 10^{-4} ; \\
[\text{Tl(I)}] = 5.0 \times 10^{-3} ; \\
[\text{H}_2\text{SO}_4] = 0.50 ; \\
I = 1.60 / \text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(1/T \times 10^3)</th>
<th>(k \times 10^5) (dm(^3) mol(^{-1}) s(^{-1}))</th>
<th>(\log k)</th>
<th>(\log k^{(y*cal)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>3.3560</td>
<td>1.17</td>
<td>-4.9318</td>
<td>-4.9102</td>
</tr>
<tr>
<td>303</td>
<td>3.3000</td>
<td>2.74</td>
<td>-4.5622</td>
<td>-4.5959</td>
</tr>
<tr>
<td>308</td>
<td>3.2470</td>
<td>5.04</td>
<td>-4.2976</td>
<td>-4.2919</td>
</tr>
<tr>
<td>313</td>
<td>3.1950</td>
<td>10.0</td>
<td>-4.000</td>
<td>-3.9919</td>
</tr>
<tr>
<td>318</td>
<td>3.1447</td>
<td>19.2</td>
<td>-3.7167</td>
<td>-3.7125</td>
</tr>
</tbody>
</table>

(b) Activation parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a)</td>
<td>(105 \pm 3 \text{ kJ mol}^{-1})</td>
</tr>
<tr>
<td>(\Delta H^\ddagger)</td>
<td>(103 \pm 3 \text{ kJ mol}^{-1})</td>
</tr>
<tr>
<td>(\Delta S^\ddagger)</td>
<td>(1.6 \pm 0.1 \text{JK}^{-1} \text{mol}^{-1})</td>
</tr>
<tr>
<td>(\Delta G^\ddagger)</td>
<td>(102 \pm 5 \text{ kJ mol}^{-1})</td>
</tr>
<tr>
<td>(\log A)</td>
<td>(14 \pm 1)</td>
</tr>
</tbody>
</table>

55
stoichiometry of 1:2 with unit order each in cerium(IV), ruthenium(III) and less than unit order each in thallium(I) and H⁺ ion concentrations. No effect of initially added products was observed. The results suggest that thallium(I) first reacts with catalyst ruthenium(III) to give a complex, which then reacts in a slow step with cerium(IV) to give the cerium(III) product, the intermediate thallium(II) and regenerating the catalyst ruthenium(III). The intermediate thallium(II) reacts in a further fast step with another mole of cerium(IV) to give the products thallium(III) and cerium(III). These experimental results can be accommodated in Scheme 1:

\[
\begin{align*}
\text{Tl(I)} + \text{Ru(III)} & \rightleftharpoons \text{Complex (C,)} \\
\text{Complex(C,) + Ce(IV)} & \overset{\text{slow}}{\rightarrow} \text{Tl(II) + Ce(III) + Ru(III)} \\
\text{Tl(II) + Ce(IV)} & \overset{\text{fast}}{\rightarrow} \text{Tl(III) + Ce(III)}
\end{align*}
\]

Scheme 1

The evidence for complex formation was obtained from the UV-visible spectrum of both thallium(I) and ruthenium(III)-thallium(I) mixture in which a bathochromic shift of thallium(I) from 227 to 231 nm and hyperchromicity at 231 nm, occurred. This was also evident from the Michaelis-Menten plot (Fig. II(ix)p.59)) and such complex formation between substrate and catalyst has also been observed in other studies²⁴,²⁵. Since oxidation of thallium(I) by cerium(IV) is a non-complementary reaction, it may occur by the intervention of reactive thallium(II) species. The formation of intermediate thallium(II) is also in accordance with earlier work¹,²⁶-²⁸. The intervention of thallium(II) in many cases of oxidation reaction of
thallium(I) in acid solutions is well established\textsuperscript{1,23} although its intervention is difficult to detect, since it is very short-lived\textsuperscript{13}.

From Scheme 1, including the observed orders in thallium(I), cerium(IV) and ruthenium(III), the rate law may be derived as follows:

Rate $= k [C_1] [\text{Ce(IV)}]$

$$= k K_7 [\text{Tl(I)}] [\text{Ce(IV)}] [\text{Ru(III)}]$$

(11)

The total concentration of thallium(I), $[\text{Tl(I)}]_t$, is given by

$$[\text{Tl(I)}]_t = [\text{Tl(I)}]_f + C_1$$

(12)

Where subscripts ‘$t$’ and ‘$f$’ stand for the total and free respectively.

$$[\text{Tl(I)}]_t = [\text{Tl(I)}]_r + K_7 [\text{Tl(I)}]_r [\text{Ru(III)}]_r$$

$$= [\text{Tl(I)}]_r (1 + K_7 [\text{Ru(III)}]_r).$$

Therefore,

$$[\text{Tl(I)}]_r = \frac{[\text{Tl(I)}]_t}{(1 + K_7 [\text{Ru(III)}]_r)}$$

(13)

Similarly,

$$[\text{Ru(III)}]_r = \frac{[\text{Ru(III)}]_t}{(1 + K_7 [\text{Tl(I)}]_r)}$$

(14)

Substituting for $[\text{Tl(I)}]_r$ and $[\text{Ru(III)}]_r$ from equations (13) and (14) in equation (11) leads to the following rate law (15), which explains the observed orders in thallium(I), cerium(IV) and ruthenium(III).

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = \frac{k K_7 [\text{Tl(I)}] [\text{Ce(IV)}] [\text{Ru(III)}]}{(1 + K_7 [\text{Ru(III)}]) (1 + K_7 [\text{Tl(I)}])}$$

(15)

In view of the low concentrations of ruthenium(III) used, the term $(1+K_7[\text{Ru(III)}])$ in the denominator of the rate law (15) approximates to unity.
Hence,
\[
\text{Rate} = -\frac{d[\text{Ce(IV)}]}{dt} = \frac{k K_7 [\text{Tl(I)}][\text{Ce(IV)}][\text{Ru(III)}]}{(1 + K_7 [\text{Tl(I)}])} \tag{16}
\]

Or
\[
\frac{\text{Rate}}{[\text{Ce(IV)}]} = k_{obs} = \frac{k K_7 [\text{Tl(I)}][\text{Ru(III)}]}{1 + K_7 [\text{Tl(I)}]}
\]

The rate law (16) may be rearranged to equation (17) which is suitable for verification.
\[
\frac{[\text{Ru(III)}]}{k_{obs}} = \frac{1}{k K_7 [\text{Tl(I)}]} + \frac{1}{k} \tag{17}
\]

According to equation (17), the plot of the L.H.S. versus \(1/[\text{Tl(I)}]\) should be linear, and is found to be so in Fig. II(ix)(p.59). The slope and intercept of such plot lead to the values of \(k = (5.26 \pm 0.24) \times 10^2 \text{ dm}^3 \text{ mol}^{-1}\text{s}^{-1}\) and \(K_7 = (1.45 \pm 0.05) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}\). Using these values, rates under different experimental conditions were calculated and compared with experimental data. Experimental and calculated values are agree reasonably well (Table II(iii)(p.36)).

The active species involved in the mechanism can be understood as follows:

The variation of rate with acidity was shown in the Results section, to parallel the trend of variation of concentration of the \(H_3\text{Ce(SO}_4\text{)}_4^-\) species with acidity (Table II(iv) (p.42); Fig.II(v)(p.44)). Although the variation of uncomplexed cerium(IV), i.e. \([\text{Ce}^{4+}]_r\) also parallels the acidity and rate, \(H_3\text{Ce(SO}_4\text{)}_4^-\) is considered to be the most active species since the plot of rate versus \([H_2\text{SO}_4]\) is linear passing through the origin (Fig. II(iv)(inset) (p.43)) indicating that the protonated oxidant species is more active than the unprotonated species. Thallium(I) has been shown to exist as \(\text{Tl(SO}_4\text{)}^-\) and \(\text{Tl(SO}_4\text{)}_2^{3-}\) in aqueous sulphate media\(^{13}\). Oxidations of thallium(I) are greatly
Fig. II(ix)

Verification of rate law (16) in the form of (17)

(Conditions as in Table II(iii)(p.36))
facilitated in sulphuric acid media and reason may be that thallium(I) sulphate complexes are actively involved. The variation of the rate with sulphate ion was shown in the 'Results section' in Table II(v)(p.46); Fig. II(vi)(p.47). Both the sulphate complexes of thallium(I), Tl(SO$_4$)$_{-}$ and Tl(SO$_4$)$_{2-}$ parallel the rate. However, the order in sulphate concentration is ca.0.98. Due to this reason, the active species of thallium(I) is considered to be as Tl(SO$_4$)$_{-}$ in such media.

The use of RuCl$_3$ as homogeneous catalyst in both acidic and alkaline media is of recent interest. In dilute acid and chloride solutions the salt yields complex ions$^{29,30}$ such as [Ru(H$_2$O)$_6$]$^{3+}$, [Ru(H$_2$O)$_5$Cl]$^{2+}$, [Ru(H$_2$O)$_6$Cl$_2$]$^{+}$, [RuCl$_6$]$^{3-}$, [RuCl$_4$]$^{-}$, and [Ru(H$_2$O)$_2$Cl$_4$]$^{-}$. The various chloride complexes of ruthenium(III) are possible$^{31}$ on prolonged standing or heating in presence of high acid concentration. The existence of such complexes seems to be remote due to the negligible effect of chloride ions on the reaction rate and in view of the low concentration of acid used in this study. The electronic spectrum of the ruthenium(III) solution used is similar to that reported$^{32-34}$ for the [Ru(H$_2$O)$_6$]$^{3+}$ spectrum. Hence [Ru(H$_2$O)$_6$]$^{3+}$ has been considered to be the active species of ruthenium(III) under our experimental conditions. In alkaline media, ruthenium(III) is known to exist as its hydroxylated species$^{32-34}$ ([Ru(OH)$_x$(H$_2$O)$_{6-x}$]$^{3-x}$) where x < 6). The mechanism of Scheme 1 will therefore involve the species as shown in Scheme 2
\[
\text{Tl}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{Tl} (\text{SO}_4)^- \\
\text{Ce}^{4+} + 2\text{SO}_4^{2-} + 2\text{HSO}_4^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{Ce} (\text{SO}_4)^- \\
\text{Tl} (\text{SO}_4)^+ + \text{Ru(II)}(\text{H}_2\text{O})_{6}^{3+} \rightleftharpoons \text{Complex (C2)} + \text{H}_2\text{O} \\
\text{Complex(C2)} + \text{H}_3\text{Ce} (\text{SO}_4)^- \overset{\text{H}^+}{\longrightarrow} \text{H}_4\text{Ce} (\text{SO}_4)^+ + \text{TlSO}_4 + \text{Ru(II)}(\text{H}_2\text{O})_{6}^{3+} \\
\text{TlSO}_4 + \text{H}_3\text{Ce} (\text{SO}_4)^- + \text{H}^+ \overset{\text{fast}}{\longrightarrow} \text{Tl} (\text{SO}_4)^+ + \text{H}_4\text{Ce} (\text{SO}_4)^- \\
\text{Scheme 2}
\]

The probable structure of the complex (C2) is as follows:

\[
\begin{array}{c}
\text{OH}_2 \\
\text{O} \quad \text{S} \quad \text{O} \\
\text{OH}_2 \\
\text{O} \\
\end{array}
\]

Therefore, in terms of active species, the rate law (16) takes the form (18)

\[
\text{Rate} = \frac{kK_8 \left[ \text{H}_3\text{Ce} (\text{SO}_4)^- \right] \left[ \text{Tl} (\text{SO}_4)^- \right] \left[ \text{Ru(III)} \right]}{1 + K_8 \left[ \text{Tl} (\text{SO}_4)^- \right]} \\
\text{(18)}
\]

But,

\[
\left[ \text{H}_3\text{Ce} (\text{SO}_4)^- \right] = \beta_4 \left[ \text{Ce}^{4+} \right]_f \left[ \text{SO}_4^{2-} \right]^2 \left[ \text{HSO}_4^- \right]^2 \left[ \text{H}^+ \right] \\
\text{(19)}
\]

Substituting the value for \([\text{Ce(IV)}]_f\) from equation. (7), equation. (19) becomes equation (20)

\[
\left[ \text{H}_3\text{Ce} (\text{SO}_4)^- \right] = \frac{\beta_4 \left[ \text{Ce}^{4+} \right]_f \left[ \text{SO}_4^{2-} \right]^2 \left[ \text{HSO}_4^- \right]^2 \left[ \text{H}^+ \right]}{1 + \frac{K_{\text{OH}}}{[\text{H}^+]} + \beta_1 \left[ \text{SO}_4^{2-} \right] + \beta_2 \left[ \text{SO}_4^{2-} \right]^2 + \beta_3 \left[ \text{SO}_4^{2-} \right]^2 \left[ \text{HSO}_4^- \right] + \beta_4 \left[ \text{SO}_4^{2-} \right]^2 \left[ \text{HSO}_4^- \right]^2 \left[ \text{H}^+ \right]} \\
\text{(20)}
\]
From the first equilibrium step of Scheme 2, we have

\[ \text{TI(SO}_4^-) = K_5 [\text{TI}^+] [\text{SO}_4^{2-}] \]  

(21)

But, the total TI(I) is given by

\[
\begin{align*}
[\text{TI(I)}]_t &= [\text{TI(I)}]_f + \text{TI(SO}_4^-) \\
&= [\text{TI(I)}]_f + K_5 [\text{TI(I)}] [\text{SO}_4^{2-}] \\
&= [\text{TI(I)}]_f (1 + K_5 [\text{SO}_4^{2-}])
\end{align*}
\]

Therefore

\[
[\text{TI(I)}]_f = \frac{[\text{TI(I)}]_t}{1 + K_5 [\text{SO}_4^{2-}]}  
\]

(22)

Substituting equation (18) in equation (17),

\[ \text{TI(SO}_4^-) = \frac{K_5 [\text{TI(I)}] [\text{SO}_4^{2-}]}{(1 + K_5 [\text{SO}_4^{2-}])} \]

(23)

Substitution of equations (20) and (23) in equation (18), yields equation (24)

\[
\text{Rate} = \frac{k \beta_5 K_5 K_8 [\text{Ce(IV)}] [\text{TI(I)}] [\text{Ru(III)}] [\text{SO}_4^{2-}]^3 [\text{HSO}_4^{-}]^2 [\text{H}^+]}{1 + \frac{K_{\text{OH}}}{[\text{H}^+]} + \beta_3 [\text{SO}_4^{2-}] + \beta_4 [\text{SO}_4^{2-}]^2 + \beta_5 [\text{SO}_4^{2-}]^3 [\text{HSO}_4^{-}] + \beta_6 [\text{SO}_4^{2-}]^3 [\text{HSO}_4^{-}]^2 [\text{H}^+]}
\]

\[
\left\{ 1 + K_5 [\text{SO}_4^{2-}] \right\}
\]

(24)

The effect of ionic strength and dielectric constant are on the right direction since two oppositely charged species are involved in the slow step as in Scheme 2. The modest activation energy and sizable entropy of activation supports a complex transition state in the reaction. The difference in the activation parameters for the catalysed and uncatalysed reactions accounts for the catalytic effect on the reaction.
The ruthenium(III) catalyst alters the reaction path by lowering the energy of activation i.e. it provides an alternative path way for the reaction. The observed modest enthalpy of activation and relatively low entropy of activation value and higher rate constant of slow step indicate that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by the results of earlier work.

**FINDINGS**

The cerium(IV) oxidation of thallium(I) has exhibited a stoichiometry of 2:1 in an aqueous sulphuric acid medium. A minute amount ($10^{-6}$ mol dm$^{-3}$) of ruthenium(III) is sufficient to catalyse the reaction. The reaction is first order in [cerium(IV)] in the presence of ruthenium(III) catalyst. The order in [thallium(I)] varies from zero to unity, whereas that in [ruthenium(III)] is unity. Increase in sulphuric acid concentration accelerates the reaction rate. The added products cerium(III) and thallium(III) do not significantly affects the reaction rate. The active species of catalyst, substrate and oxidant are $[\text{Ru(H}_2\text{O)}_6]^3+$, $\text{Tl(SO}_4)^-$ and $\text{H}_2\text{Ce(SO}_4)^4-$, respectively. Possible mechanisms are proposed and the reaction constants involved have been determined.

**IMPORTANCE OF CHAPTER II**

The reaction between cerium(IV) and thallium(I) is very slow in sulphuric acid media. Ruthenium(III) acts as an efficient catalyst especially in sulphuric acid, which is not the case in perchloric acid. Ruthenium(III) catalyses the reaction with a measurable velocity at a concentration of $10^{-6}$ mol dm$^{-3}$. The active species involved in the mechanism play an important role in the reaction.
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