CHAPTER II

CHROMIUM(III) CATALYSED OXIDATION OF TELLURIUM(IV) BY CERIUM(IV) IN ACID MEDIUM
Chromium(III) catalysed oxidation of tellurium(IV) by cerium(IV) in acid medium

Tellurium is used in the manufacture of coloured glasses or ceramic and enamel pigments, and as bases for phosphors. It is also used as secondary vulcanizing agents for natural rubber and in the form of organo-compounds, as oxidation inhibitors in lubricating oils, other uses which have been described in more detail elsewhere.¹

The oxidation potential of a redox couple such as Ce(IV)/Ce(III) generally depend both on the nature and the concentration of the acid medium in which the oxidation potential is determined.² Thus, for example, the Ce(IV)/Ce(III) oxidation potential in perchloric acid varies from -1.70 to -1.87 V depending on the perchloric acid concentration and from -1.44 to -1.42 depending on the sulphuric acid concentration used. The redox potential of the couple³, Te(VI)/Te(IV) being -1.02 in acid medium, is capable to reduce cerium(IV). The oxidation of tellurium(IV) in acid medium by few oxidants has been studied⁴. The reaction of tellurium(IV)–cerium(IV) in acid medium is known to be catalysed by osmium⁵ and ruthenium⁶.

In sulphuric acid medium, several sulphate complexes of cerium(IV) form but their role has not received attention so far. Thus, the reaction rate increases with acid.
concentration and this effect has not been understood. Although chromium(III) catalysis has been observed in the case of many redox reactions, few of them have been studied.

Thus for example the chromium(III) catalysis of cerium(IV) oxidation of Te(IV) has not received any attention. Among the different chromium oxidation states, chromium(III) and chromium(VI) are stable and chromium(IV) and Cr(V) are unstable. The mechanism of chromium(III) catalysed cerium(IV)-tellurium(IV) reaction is of interest as reactive chromium(IV) and chromium(V) may intervene. Furthermore, whether there is any complex formation between the catalyst and the substrate to be subsequently oxidised by the oxidant is to be examined. These considerations point at the several different mechanisms that may be feasible. In the present work, we have studied the chromium(III) catalysed cerium(IV) oxidation of tellurium(IV) in aqueous acid medium. We have observed that the catalysis is more when we use the mixture of perchloric acid and sulphuric acid.

EXPERIMENTAL

All the chemicals used were of reagent grade and doubly distilled water was used throughout this work. The stock solutions of cerium(IV) were prepared by dissolving a known quantity of cerium(IV) ammonium sulphate (E. Merck) in
1.0 mol dm$^{-3}$ sulphuric acid and allowed to stand for some time. The resulting solution was standardised$^9$ against iron(II) ammonium sulphate using ferroin as indicator. The chromium(III) solutions were obtained by dissolution of chromium(III) potassium sulphate (BDH, Analar), Cr$_2$(SO$_4$)$_3$·K$_2$SO$_4$·2H$_2$O and the concentration of chromium(III) was determined by oxidising it to chromium(VI) with excess persulphate in presence of one or two drops of 1x10$^{-2}$M silver nitrate$^{10}$. The excess persulphate was boiled off and the chromium(VI) thus obtained was determined against iron(II) ammonium sulphate solution. The tellurium(IV) solution was prepared from sodium tellurite (SISCO) and standardised by adding excess of standard cerium(IV) solution and 10 ml of concentrated hydrochloric acid and about 0.05 gm of chromium(III) solution. The solution was boiled for 10 mins, then cooled and back-titrated with standard iron(II) solution, using ferroin indicator.

The cerium(III) and tellurium(VI) solutions were prepared by dissolving cerium(III) acetate (BDH) and telluric acid, H$_6$TeO$_6$ (Fluka) in water. The concentration of cerium(III) was ascertained$^{11}$ by oxidising it to cerium(IV) as performed in Chapter IB (p.70).

The stock solutions were diluted as required and standardised before use in a kinetic run. To maintain the
Kinetic studies

Runs were followed under pseudo first-order conditions where tellurium(IV) was excess over that of cerium(IV) at constant temperature (25±0.05°C). The reaction was initiated by addition of the cerium(IV) solution containing the required amounts of perchloric acid, sulphuric acid and sodium perchlorate to the tellurium(IV) solution which also contained chromium(III). The reaction was followed by measuring the absorption of cerium(IV) in the reaction mixture in a 1 cm cell placed in the thermostatted cell compartment of a Hitachi 150-20 spectrophotometer at 360 nm where the other constituents of the reaction mixture did not absorb significantly. The obedience of cerium(IV) under the conditions (as in the reaction) to Beer's law had earlier been verified in the concentration range of 6×10⁻⁵ to 5.0×10⁻⁴ mol dm⁻³ cerium(IV) at constant concentration of HClO₄ and H₂SO₄ of 0.15 and 0.1 mol dm⁻³ respectively, as shown in fig.II(i), (p.10) and the molar absorptivity, ε, was 3150 ±1.5% dm³ mol⁻¹ cm⁻¹.

The reaction mixtures, in all runs contained a constant amount of sulphuric acid (0.15 mol dm⁻³) and perchloric acid (0.10 mol dm⁻³) since the effectiveness of catalyst is maximum.
Fig. II (1) : Verification of Beer's law for Ce(IV) at 360 nm, $\sqrt{\text{HClO}_4} = 0.10$, $\sqrt{\text{H}_2\text{SO}_4} = 0.15$/mol dm$^{-3}$.
in the mixtures of these two acids compared to the individual acids. The effect of acid was studied by changing the concentration of perchloric acid keeping the sulphuric acid concentration constant.

The initial rates were measured from the slopes of the tangents at the initial stages of concentration time curves as in earlier Chapter IA (p. 40). The first order plots of log (a-x) vs time were linear to about 80% of reaction in most of the runs. The data of an example run are given in Table II (i) (p. 104) and Fig. II (ii). The first order rate constant, k, was calculated from the slope of the plot, using the equation,

\[ k = \frac{2.303 \times \text{slope}}{t} \]

Kinetic data were reproducible in all cases within ±4%.

RESULTS

Stoichiometry

Different sets of concentrations of reactants and catalyst in 0.1 mol dm\(^{-3}\) perchloric acid, 0.15 mol dm\(^{-3}\) sulphuric acid at a constant ionic strength of 0.6 mol dm\(^{-3}\) were kept to react for over 24 hrs at 25°C and then analysed for cerium(IV), tellurium(IV) and cerium(III). The oxidant, cerium(IV) was found by measuring its absorption at 360 nm and tellurium(IV) and cerium(III) were estimated by the methods.
Table II(i) : Sample run of Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C

\[ \left[ Te(IV) \right] = 1.0 \times 10^{-3}; \left[ Ce(IV) \right] = 1.0 \times 10^{-4}; \]
\[ \left[ Cr(III) \right] = 5.0 \times 10^{-5}; \left[ HClO_4 \right] = 0.10; \]
\[ \left[ H_2SO_4 \right] = 0.15; \quad I = 0.60/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Absorbance 360 nm</th>
<th>( \left[ Ce(IV) \right] \times 10^4 ) mol dm(^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.315</td>
<td>1.00</td>
</tr>
<tr>
<td>5.0</td>
<td>0.287</td>
<td>0.91</td>
</tr>
<tr>
<td>10.0</td>
<td>0.259</td>
<td>0.82</td>
</tr>
<tr>
<td>15.0</td>
<td>0.239</td>
<td>0.76</td>
</tr>
<tr>
<td>20.0</td>
<td>0.217</td>
<td>0.69</td>
</tr>
<tr>
<td>30.0</td>
<td>0.169</td>
<td>0.54</td>
</tr>
<tr>
<td>40.0</td>
<td>0.149</td>
<td>0.47</td>
</tr>
<tr>
<td>50.0</td>
<td>0.125</td>
<td>0.40</td>
</tr>
<tr>
<td>60.0</td>
<td>0.106</td>
<td>0.34</td>
</tr>
<tr>
<td>70.0</td>
<td>0.086</td>
<td>0.27</td>
</tr>
<tr>
<td>75.0</td>
<td>0.079</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Error ±4%
Fig.II(ii) : Sample run of Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C

(Conditions as in Table II(i), p.103)

\[ -\log [\text{Ce(IV)}] \]

\[ \text{time (min)} \]
given in experimental section. The results are given in Table II(ii), (p.106). The stoichiometry was found to be in the ratio of 2:1 of oxidant to reductant.

\[
\text{Te(IV)} + 2\text{Ce(IV)} \rightarrow \text{Cr(III)} \rightarrow \text{Te(VI)} + 2\text{Ce(III)} \tag{1}
\]

The concentration of the catalyst, chromium(III), was unchanged at the end of the reaction as found by measuring the absorbance of the reaction mixture at 583 nm.

**Reaction order**

The orders, as found from log-log plots of initial rates vs concentrations, were \( \sim 0.95 \) in the case of cerium(IV) and \( \sim 0.4 \) for tellurium(IV) in the concentration range of \( 3.0 \times 10^{-5} \) to \( 3.0 \times 10^{-4} \) mol dm\(^{-3} \) and \( 5 \times 10^{-4} \) to \( 5 \times 10^{-3} \) mol dm\(^{-3} \) respectively at constant 0.1 mol dm\(^{-3} \) perchloric acid and 0.15 mol dm\(^{-3} \) sulphuric acid, ionic strength of 0.60 mol dm\(^{-3} \) and catalyst, Cr(III), of \( 5.0 \times 10^{-5} \) mol dm\(^{-3} \). The results are shown in table II(iii) (p.107) and fig.II(iii) (p.108). An order of approximately unity for cerium(IV) was also derived from the constancy of rate constants at different concentrations of cerium(IV) and from runs under conditions where the \( \frac{[\text{oxidant}]}{[\text{reductant}]} \). First order plots under such conditions are linear over 80% of the reaction for different initial cerium-IV concentrations (Fig.II(ii), p. 104).
Table II(ii): Stoichiometry of Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C

\[ \text{[Cr(III)] = 5.0 \times 10^{-4}; } \] 
\[ \text{[HClO}_4] = 0.10; \]  
\[ \text{[H}_2\text{SO}_4] = 0.15; \]  
\[ I = 0.60/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Taken</th>
<th>Found</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{[Ce(IV)]} \times 10^2 \text{ mol dm}^{-3} ]</td>
<td>[ \text{[Te(IV)]} \times 10^2 \text{ mol dm}^{-3} ]</td>
<td>[ \text{[Ce(III)]} \times 10^2 \text{ mol dm}^{-3} ]</td>
<td>[ \text{[Te(IV)]} \times 10^2 \text{ mol dm}^{-3} ]</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>0.0</td>
<td>1.98</td>
</tr>
<tr>
<td>3.0</td>
<td>2.0</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
<td>0.0</td>
<td>3.97</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>0.0</td>
<td>1.98</td>
</tr>
<tr>
<td>4.0</td>
<td>0.5</td>
<td>2.98</td>
<td>1.0</td>
</tr>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Error ±5%
Table II (iii) : Effect of $[\text{Ce(IV)}]$ and $[\text{Te(IV)}]$ on Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C

$[\text{Cr(III)}] = 5.0 \times 10^{-5} \; \text{mol dm}^{-3}$; $[\text{HClO}_4] = 0.10 \; \text{mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 0.15 \; \text{mol dm}^{-3}$; $I = 0.60 \; \text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>$\text{Ce(IV)} \times 10^4$ mol dm$^{-3}$</th>
<th>$\text{Te(IV)} \times 10^3$ mol dm$^{-3}$</th>
<th>Initial Rate $\times 10^8$ mol dm$^{-3}$s$^{-1}$</th>
<th>Rate constant $\times 10^4$ s$^{-1}$</th>
<th>Exptl.</th>
<th>Calcd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>1.0</td>
<td>1.77</td>
<td>3.11</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>1.0</td>
<td>3.40</td>
<td>3.11</td>
<td>3.11</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>5.30</td>
<td>3.11</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.0</td>
<td>6.50</td>
<td>3.10</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>8.61</td>
<td>3.11</td>
<td>3.15</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>12.5</td>
<td>3.12</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>4.0</td>
<td>1.85</td>
<td>1.84</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.7</td>
<td>4.9</td>
<td>2.41</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>5.3</td>
<td>3.10</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>2.5</td>
<td>7.7</td>
<td>5.30</td>
<td>5.25</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>3.75</td>
<td>8.7</td>
<td>6.40</td>
<td>6.33</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>5.0</td>
<td>9.58</td>
<td>7.08</td>
<td>6.92</td>
<td></td>
</tr>
</tbody>
</table>

Error $\pm4\%$
Fig. II(iii): Order in \( \text{Ce(IV)} \) and \( \text{Te(IV)};\text{Cr(III)} \)
catalysed oxidation of \( \text{Te(IV)} \) by \( \text{Ce(IV)} \)
in acid medium at 25°C
(Conditions as in Table II(iii), p.107)
\[-\log[\text{Ce(IV)}]\]
Effect of catalyst

The effect of chromium(III) concentration on the reaction was studied in the range of $1.0 \times 10^{-5}$ to $1.5 \times 10^{-4}$ mol dm$^{-3}$ with keeping all other concentrations constant as given in Table II(iv) (p. 110). The order with respect to chromium(III) was found to be less than unity ($\approx 0.7$) from log-log plots (Fig.II(iv), p. 111).

Effect of initially added products

The effect of added products, cerium(III) and tellurium(VI), was studied in the concentration range of $1.0 \times 10^{-4}$ to $1.0 \times 10^{-3}$ mol dm$^{-3}$ with keeping all conditions constant as given in Table II(v) (p. 112). It was found that while added cerium(III) did not have any significant effect on the reaction, increasing concentration of added tellurium(VI), retarded the reaction with an approximate order of $\approx 0.3$ (Fig.II(iv), p. 111).

Effect of acid

The effect of acid concentration was studied by varying the amount of perchloric acid in the reaction mixture between $2.5 \times 10^{-2}$ and $2.0 \times 10^{-1}$ mol dm$^{-3}$ at constant sulphuric acid concentration of $0.15$ mol dm$^{-3}$ and ionic strength of $0.6$ mol dm$^{-3}$ and all other reactant concentrations were constant.
Table II (iv): Effect of catalyst, [Cr(III)] on Cr(III)
catalysed oxidation of Te(IV) by Ce(IV) 
in acid medium at 25°C.

\[
\begin{align*}
[\text{Te(IV)}] &= 1.0 \times 10^{-4}; \\
[\text{Ce(IV)}] &= 1.0 \times 10^{-3}; \\
[\text{H}_2\text{SO}_4] &= 0.15; \\
[\text{HClO}_4] &= 0.10; \\
I &= 0.60/\text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>( [\text{Cr(III)}] \times 10^5 )</th>
<th>Initial Rate ( \times 10^8 )</th>
<th>Rate constant ( \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol dm(^{-3} )</td>
<td>mol dm(^{-3} ) s(^{-1} )</td>
<td>s(^{-1} )</td>
</tr>
<tr>
<td>0.0</td>
<td>0.50</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>1.52</td>
<td>0.80</td>
</tr>
<tr>
<td>1.5</td>
<td>2.20</td>
<td>1.30</td>
</tr>
<tr>
<td>3.0</td>
<td>3.71</td>
<td>1.90</td>
</tr>
<tr>
<td>5.0</td>
<td>5.00</td>
<td>3.11</td>
</tr>
<tr>
<td>7.0</td>
<td>6.94</td>
<td>4.31</td>
</tr>
<tr>
<td>9.0</td>
<td>8.05</td>
<td>4.90</td>
</tr>
<tr>
<td>15.0</td>
<td>9.92</td>
<td>9.20</td>
</tr>
</tbody>
</table>

Error \( \pm 5\% \)
Fig. II(iv): Order in $\text{Cr(III)}$ and product, $\text{Te(VI)}$; Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C

(Conditions as in Table II(iv), p. 110 and Table II(v), p. 112)

$-\log[\text{Te(VI)}]$
Table II (v) : Effect of products, $[\text{Te(\text{VI})}]$ and $[\text{Ce(\text{III})}]$, on Cr(\text{III}) catalyzed oxidation of Te(\text{IV}) by Ce(\text{IV}) in acid medium at 25°C.

$\left[\text{Te(\text{IV})}\right] = 1.0 \times 10^{-3}; \quad \left[\text{Ce(\text{IV})}\right] = 1.0 \times 10^{-4};$

$\left[\text{Cr(\text{III})}\right] = 5.0 \times 10^{-5}; \quad \left[\text{H}_2\text{SO}_4\right] = 0.15; \quad \left[\text{HClO}_4\right] = 0.10; \quad I = 0.69 \text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>$\left[\text{Te(\text{VI})}\right] \times 10^4$</th>
<th>Initial rate $\times 10^8$ mol dm$^{-3}$s$^{-1}$</th>
<th>Rate constant $\times 10^4$ mol dm$^{-3}$s$^{-1}$</th>
<th>$\left[\text{Ce(\text{III})}\right] \times 10^4$</th>
<th>Rate constant $\times 10^8$ mol dm$^{-3}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.30</td>
<td>3.12</td>
<td>0.0</td>
<td>5.31</td>
</tr>
<tr>
<td>1.0</td>
<td>5.16</td>
<td>2.82</td>
<td>1.0</td>
<td>5.32</td>
</tr>
<tr>
<td>2.0</td>
<td>3.98</td>
<td>2.50</td>
<td>2.0</td>
<td>5.30</td>
</tr>
<tr>
<td>3.0</td>
<td>3.50</td>
<td>2.24</td>
<td>3.0</td>
<td>5.31</td>
</tr>
<tr>
<td>5.0</td>
<td>3.06</td>
<td>1.95</td>
<td>5.0</td>
<td>5.30</td>
</tr>
<tr>
<td>7.0</td>
<td>2.59</td>
<td>1.86</td>
<td>7.0</td>
<td>5.33</td>
</tr>
<tr>
<td>9.0</td>
<td>2.15</td>
<td>1.62</td>
<td>9.0</td>
<td>5.31</td>
</tr>
<tr>
<td>10.0</td>
<td>2.18</td>
<td>1.44</td>
<td>10.0</td>
<td>5.34</td>
</tr>
</tbody>
</table>

Error ±4%
The rate of the reaction increases with increase in $\mathcal{H}^+$. From the plot of log rate versus log $\mathcal{H}^+$, the order in $\mathcal{H}^+$ were found to be fractional (~0.8) (Fig. II(v) (p. 114) and Table II(vi) (p. 115)). A constant amount of sulphuric acid present in all reaction mixtures apart from varying perchloric acid concentration enables formation of hydrolysed as well as different sulphate complexes of cerium(IV) such as Ce(0H)$^{3+}$, CsO$^{2+}$, Ce(SO$^4$)$_2^+$, HCe(SO$^4$)$_3^-$ and H$_3$Ce(SO$^4$)$_4^-$ as shown in equations (2) - (6).

\[
\begin{align*}
\text{Ce}^{4+} + \text{H}_2\text{O} & \rightleftharpoons \text{Ce(OH)}^{3+} + \text{H}^+ & K_{\text{OH}} & (2) \\
\text{Ce}^{4+} + \text{SO}_4^{2-} & \rightleftharpoons \text{Ce(SO}_4^2)^{2+} & K_1 & (3) \\
\text{Ce(SO}_4^2)^{2+} + \text{SO}_4^{2-} & \rightleftharpoons \text{Ce(SO}_4^2)^{2+} & K_2 & (4) \\
\text{Ce(SO}_4^2)^{2+} + \text{H}_2\text{O} & \rightleftharpoons \text{HCe(SO}_4^3)^{3-} & K_3 & (5) \\
\text{HCe(SO}_4^3)^{3-} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{Ce(SO}_4^2)^{2+} & K_4 & (6)
\end{align*}
\]

The total cerium(IV) concentration, $\sum_{\text{Ce(IV)}}$, is the sum of the different cerium(IV) species, Ce(OH)$^{3+}$, Ce(SO$^4$)$_2^+$, Ce(SO$^4$)$_2^-$, HCe(SO$^4$)$_3^-$, H$_3$Ce(SO$^4$)$_4^-$, and uncomplexed Ce$^{4+}$, the complexes having the cumulative equilibrium constants, $K_{\text{OH}}$, $\beta_1$, $\beta_2$, $\beta_3$ and $\beta_4$ respectively as shown in equation (7), where $\beta_1 = K_1$, $\beta_2 = K_1K_2$, $\beta_3 = K_1K_2K_3$, $\beta_4 = K_1K_2K_3K_4$. 

$113$
Fig. II(v) : Order in $\sum H^+$; Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C

(Conditions as in Table II(vi), p.115)
Table II(vi) : Variation of the different Ce(IV) species* with $\sqrt{H^+}$ on Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C.

$[\text{Te(IV)}] = 1.0 \times 10^{-3}$; $[\text{Ce(IV)}] = 1.0 \times 10^{-4}$; $[\text{Cr(III)}] = 5.0 \times 10^{-5}$; $I = 0.60/\text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>$[\text{HClO}_4]$</th>
<th>$[\text{H}^+]$</th>
<th>$[\text{SO}_4^{2-}]$</th>
<th>$[\text{HSO}_4^{-}]$</th>
<th>$x_0 \times 10^2$</th>
<th>$x_{\text{OH}} \times 10^2$</th>
<th>$x_1 \times 10^1$</th>
<th>$x_2 \times 10^3$</th>
<th>$x_3 \times 10^4$</th>
<th>$x_4 \times 10^5$</th>
<th>Initial rate $\times 10^8$</th>
<th>mol dm$^{-3}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.226</td>
<td>0.0513</td>
<td>0.0982</td>
<td>1.14</td>
<td>7.58</td>
<td>2.26</td>
<td>5.09</td>
<td>2.80</td>
<td>1.81</td>
<td>3.78</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>0.248</td>
<td>0.0485</td>
<td>0.101</td>
<td>1.24</td>
<td>7.51</td>
<td>2.32</td>
<td>4.95</td>
<td>3.01</td>
<td>1.85</td>
<td>4.20</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0.293</td>
<td>0.043</td>
<td>0.107</td>
<td>1.45</td>
<td>7.39</td>
<td>2.41</td>
<td>4.62</td>
<td>2.95</td>
<td>1.89</td>
<td>5.20</td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>0.334</td>
<td>0.034</td>
<td>0.116</td>
<td>1.69</td>
<td>7.57</td>
<td>2.22</td>
<td>3.36</td>
<td>2.33</td>
<td>2.01</td>
<td>5.80</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>0.385</td>
<td>0.035</td>
<td>0.115</td>
<td>1.86</td>
<td>7.24</td>
<td>2.53</td>
<td>3.95</td>
<td>2.79</td>
<td>2.03</td>
<td>6.25</td>
<td></td>
</tr>
</tbody>
</table>

Error ±4%

* $x_0$, $x_{\text{OH}}$, $x_1$, $x_2$, $x_3$ and $x_4$ are the fractions of total Ce(IV) species, Ce$^{4+}$, Ce(OH)$^{3+}$, Ce(SO$_4$)$^{2+}$, Ce(SO$_4$)$_2^-$, HCe(SO$_4$)$_3^-$ and H$_3$Ce(SO$_4$)$_4^-$ respectively.
\[
\begin{align*}
\ln \left( \frac{[\text{Ce(IV)}]}{[\text{Ce(III)}]} \right) &= \ln \left( \frac{[\text{Ce(IV)}]}{[\text{Ce(III)}]} \right) \left( 1 + \frac{K_{\text{OH}}}{[\text{H}^+]} + \beta_1 [\text{SO}_4^{2-}] + \beta_2 [\text{SO}_4^{2-}]^2 + \beta_3 [\text{SO}_4^{2-}]^3 + \beta_4 [\text{SO}_4^{2-}]^4 \right) \\
&+ \beta_5 [\text{SO}_4^{2-}]^5 + \beta_6 [\text{SO}_4^{2-}]^6 + \beta_7 [\text{SO}_4^{2-}]^7 + \beta_8 [\text{SO}_4^{2-}]^8 + \beta_9 [\text{SO}_4^{2-}]^9 + \beta_{10} [\text{SO}_4^{2-}]^{10}
\end{align*}
\]

The reported values of $\beta_1$ to $\beta_4$ and $K_{\text{OH}}$ being 384.62, 169.49, 101.7, 203.4 and 15 respectively. The approximate concentration of Ce(OH)$_3^+$ as well as the sulphate complexes are calculable from the concentrations of dissolved Ce$^{4+}$, H$^+$, HSO$_4^-$ and SO$_4^{2-}$. The in situ H$^+$ and HSO$_4^-$ concentrations were calculated from the dissolved sulphuric acid and the acid sulphate dissociation constant. The formation of Ce(OH)$_2^+$ occurs to a much smaller extent in comparison with the others and is therefore neglected. The results of such calculations are given in Table II(vi) (p.115). These results are utilized to draw fig.II(vi) (p.117) and it is seen that, of the different species concentrations, the variation of only the concentration of H$_3$Ce(SO$_4$)$_4^-$ with acidity shows any parallelism with variation of rate with acidity.

**Effect of dielectric constant and ionic strength**

The effect of changing dielectric constant on the reaction was studied by increasing the acetic acid content in the medium at constant ionic strength and all other reactant
Fig. II(vi): Effect of acid concentration on the different Ce(IV) species and also on the initial rates.

(Conditions as in Table II(vi), p. 115)
concentrations were constant. The effect of solvent polarity on the rate constant is tabulated in Table II(vii) (p.119).

The plot of \( \log k \) vs. \( 1/D \) was found to be linear with negative slope (Fig.II(vii)(p.120)). Since the dielectric constants of aqueous acetic acid are not available in literature, they were computed from the values of pure liquids\(^{14}\) from equation (8).

\[
D = V_1 D_1 + V_2 D_2
\]  

(8)

where \( V_1 \) and \( V_2 \) are the volume fractions and \( D_1 \) and \( D_2 \) are the dielectric constants of water and acetic acid respectively.

Increasing ionic strength by increasing the concentration of sodium perchlorate results in an increase in the rate of reaction which is shown in Table II(vii) (p.119). The plot of \( \log k \) versus \( I^\dagger \) is linear with positive slope (Fig.II(vii), p.120).

Effect of temperature

The effect of temperature on the reaction was studied by following the reaction at different temperatures (Table II-(viii), p.121), and the plot of \( \log k \) vs \( 1/T \) was found to be linear as shown in Fig.II(viii)(p.122). The activation energy and entropy of activation were calculated from the slope of Fig.II(viii) using the equation as in Chapter IIA (p. 56) and were listed in Table II(viii) (p.121).
Table II(vii) : Effect of polarity of solvent and ionic strength on Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C.

\[ [\text{Te(IV)}] = 1.0 \times 10^{-3}; [\text{Ce(IV)}] = 1.0 \times 10^{-4}; [\text{Cr(III)}] = 5.0 \times 10^{-5}; \]
\[ [\text{H}_2\text{SO}_4] = 0.15; [\text{HClO}_4] = 0.10; I = 0.60/\text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>HAC/water percentage</th>
<th>Dielectric constant</th>
<th>Rate constant ( x 10^8 )</th>
<th>Ionic strength ( x 10^4 )</th>
<th>Rate constant ( x 10^8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>78.0</td>
<td>5.20</td>
<td>3.12</td>
<td>0.55</td>
</tr>
<tr>
<td>10.0</td>
<td>71.3</td>
<td>3.35</td>
<td>2.69</td>
<td>0.60</td>
</tr>
<tr>
<td>20.0</td>
<td>64.2</td>
<td>2.39</td>
<td>2.34</td>
<td>0.75</td>
</tr>
<tr>
<td>30.0</td>
<td>57.0</td>
<td>2.83</td>
<td>2.13</td>
<td>0.85</td>
</tr>
<tr>
<td>40.0</td>
<td>49.5</td>
<td>1.91</td>
<td>1.81</td>
<td>0.95</td>
</tr>
<tr>
<td>50.0</td>
<td>42.7</td>
<td>1.83</td>
<td>1.71</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Error ±5%
Fig.II(vii): Effect of ionic strength and solvent polarity on Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C

(Conditions as in Table II(vii), p.119)

\[ \sqrt{I} \]
Table II(viii) : Effect of temperature on Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium at 25°C.

\[
\begin{align*}
\sqrt{[\text{Te(IV)}]} &= 1.0 \times 10^{-3}; \\ \sqrt{[\text{Ce(IV)}]} &= 1.0 \times 10^{-4}; \\ \sqrt{[\text{Cr(III)}]} &= 5.0 \times 10^{-5}; \\ \sqrt{[\text{H}_2\text{SO}_4]} &= 0.15; \\ \sqrt{[\text{HClO}_4]} &= 0.10; \\ I &= 0.60/\text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Temp.K</th>
<th>Rate constant (x10^4) s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>3.11</td>
</tr>
<tr>
<td>303</td>
<td>5.62</td>
</tr>
<tr>
<td>308</td>
<td>7.94</td>
</tr>
<tr>
<td>313</td>
<td>10.0</td>
</tr>
<tr>
<td>318</td>
<td>14.1</td>
</tr>
</tbody>
</table>

\(E_a = 50.0 \pm 2k\ J\ mol^{-1}\)

\(\Delta S^\ddagger = -151.8 \pm 10\ JK^{-1}\ mol^{-1}\)

\text{Error} \pm 4\%.
Fig. II(viii): Effect of temperature on Cr(III) catalysed oxidation of Te(IV) by Ce(IV) in acid medium.

(Conditions as in Table II(viii), p. 121)
The rate law for the reaction follows from the experimental results as shown in (9).

$$-\frac{d[\text{Ce(IV)}]}{dt} = k[\text{Ce(IV)}]^0.4[\text{Cr(III)}]^0.7[H^+]^0.8[\text{Te(VI)}]^{-0.3}$$  \hfill (9)

**DISCUSSION**

The experimental results incorporated in (9) are well accommodated by rate law (10).

$$\text{Rate} = \frac{kK[\text{Ce(IV)}]^7[\text{Cr(III)}]^7[\text{Te(IV)}]^7}{1 + K[\text{Te(IV)}]^7 + K[\text{Cr(III)}]^7}$$  \hfill (10)

In the denominator, a term $k^2[\text{Te(IV)}]^7[\text{Cr(III)}]^7$ is left out since its value is negligible compared to 1, in view of low concentrations of tellurium(IV) and chromium(III) used in the experiments. The mechanism of scheme 1, in agreement with (10), may be written where a substrate - catalyst complex ($C_1$) may be expected in view of the orders in tellurium(IV) and chromium(III) concentrations being less than unity. The complex ($C_1$) gets oxidised by one equivalent of cerium(IV) to give the complex ($C_2$). Attempts to obtain spectral evidence of such
complexes was in vain, no appreciable change resulting in the spectra of the reductant and the catalyst in presence of one another. A feeble interaction is probably involved.

\[
\begin{align*}
\text{Te(IV)} + \text{Cr(III)} & \xrightleftharpoons[K]{} \text{Complex (C}_1) \\
\text{C}_1 + \text{Ce(IV)} & \xrightarrow[k]{} \text{Ce(III)} + \text{Complex (C}_2) \quad \text{Slow} \\
\text{C}_2 + \text{Ce(IV)} & \rightarrow \text{Te(VI)} + \text{Cr(III)} + \text{Ce(III)} \quad \text{fast} \\
\text{Ce(III)} + \text{Te(VI)} & \rightarrow \text{Ce(III).Te(VI) (Complex)} \quad \text{fast}
\end{align*}
\]

Scheme 1

However, the evidence for complex formation is obtained kinetically (The plot of \(1/k\) vs \(1/\text{[Te(IV)]}\) is linear with intercept). Such complex formation between the catalyst and substrate has also been observed in other studies\(^{15}\). The rate law of the catalysed reaction can be understood in terms of the mechanism of scheme 1 where a catalyst-substrate complex formation is followed by its oxidation in succeeding steps.

The rate law (10) can be derived from Scheme 1 as follows. The rate of disappearance of cerium(IV) is given by (11).
The concentration of the complex, \( C_1 \), may be written, from its formation equilibrium (Scheme 1), as in (12) where \( \sum \text{Cr(III)} f \) and \( \sum \text{Te(IV)} f \) are the uncomplexed or free chromium(III) and tellurium(IV) concentrations respectively.

\[
\sum \text{Cr(III)} f \sum \text{Te(IV)} f = k \sum \text{Cr(III)} f \sum \text{Te(IV)} f
\]  

(12)

The total concentrations of chromium(III) and tellurium(IV), represented as \( \sum \text{Cr(III)} T \) and \( \sum \text{Te(IV)} T \), are the sums of the concentrations of the free and the complexed chromium(III) and tellurium(IV) respectively and they are given by (13) and (14).

\[
\sum \text{Cr(III)} T = \sum \text{Cr(III)} f + \sum \text{Cr(III)} f
\]

or

\[
\sum \text{Cr(III)} T = \sum \text{Cr(III)} f + k \sum \text{Cr(III)} f \sum \text{Te(IV)} f
\]  

(13)

\[
\sum \text{Te(IV)} T = \sum \text{Te(IV)} f + k \sum \text{Te(IV)} f \sum \text{Cr(III)} f
\]

(14)

Therefore, the concentrations of free chromium(III) and tellurium(IV) may be seen to result from (13) and (14) as (15) and (16) respectively.
\[ \sum \text{Cr(III)}_2^7 = \frac{\sum \text{Cr(III)}_4^7}{(1+K_4^7 \sum \text{Te(IV)}_7^7)} \]  \hspace{1cm} (15)

\[ \sum \text{Te(IV)}_7^7 = \frac{\sum \text{Te(IV)}_4^7}{(1+K_4^7 \sum \text{Cr(III)}_7^7)} \]  \hspace{1cm} (16)

Use of expressions for \( \sum \text{Cr(III)}_7^7 \) and \( \sum \text{Te(IV)}_7^7 \) from (15) and (16) in (12) gives \( \sum \text{C}_1^{-7} \) which is used in (11), and rate law (10) results.

The active species involved in the mechanism can be understood as follows. The variation of rate, with acidity was shown in results section to parallel the trend of variation of the concentrations of the species \( \text{H}_3\text{Ce(SO}_4)_4^- \) with acidity (Table II(vi) (p. 115) and Fig. II(vi) (p. 117). The plot of rate\(_{\text{cat}}^\sum \text{H}^+\sum \) is linear passing through the origin (Fig. II(v) (p.114) indicating that a protonated oxidant species is active. Although the concentrations calculated in the manner indicated in the results section are approximate in view of the competitive multiequilibria involved, the parallelism between the variation of \( \text{H}_3\text{Ce(SO}_4)_4^- \) concentration and rate with acidity are noteworthy. This oxidant species is more important than others.

The chromium(III) catalyst has a fractional order in the reaction presumably due to its active species being the
labile ion-pair complex, $\text{Cr}^{3+}\cdot\text{SO}_4^{2-}$ with a low equilibrium constant\textsuperscript{12,16}. Inner sphere complexes of chromium(III) are unlikely to be of much importance in the oxidation. This species is similar to the cases that observed in earlier studies\textsuperscript{12,17}.

Under the acid concentrations, used in the reaction, it has reported\textsuperscript{18} that tellurium(IV) will be present as $\text{TeO(OH)}^+$. The mechanism of scheme will, therefore, involve the above species as shown below in Scheme 2,

\[
\begin{align*}
\text{H}_2\text{TeO}_3 + H^+ & \underset{K_1}{\overset{K_1}{\rightleftharpoons}} \text{TeO(OH)}^+ + \text{H}_2\text{O} \\
\text{Ce}^{4+} + 2\text{SO}_4^{2-} + \text{HHSO}_4^- + H^+ & \rightleftharpoons \text{H}_3\text{Ce(SO}_4)_4^- \\
\text{Cr}^{3+} + \text{SO}_4^{2-} & \rightleftharpoons \text{Cr}^{3+}\cdot\text{SO}_4^{2-} \quad K_{IP} \\
\text{Cr}^{3+}\cdot\text{SO}_4^{2-} + \text{TeO(OH)}^+ & \overset{K}{\rightleftharpoons} \text{Complex (C}_1) \\
\text{C}_1 + \text{H}_3\text{Ce(SO}_4)_4^- & \overset{k_{\text{slow}}}{\underset{\text{fast}}{\rightleftharpoons}} \text{Ce(III)} + \text{C}_2 \\
\text{C}_2 + \text{H}_3\text{Ce(SO}_4)_4^- & \rightarrow \text{Te(VI)} + \text{Cr(III)} + \text{Ce(III)}
\end{align*}
\]

Scheme 2

Therefore, in terms of the active species, the rate law (10) takes the form (17).
Rate =

\[
\frac{kK^3 Ce(SO_4)^2^- \cdot \sum Cr^{3+} \cdot SO_4^{2-} \cdot \sum TeO(OH) \cdot \sum}{1+K^3 Ce(OH) \cdot \sum K^2 Cr^3+ \cdot SO_4^{2-} \cdot \sum K^2 TeO(OH) \cdot \sum K^2 Cr^3+ \cdot SO_4^{2-} \cdot \sum}
\]

\[
\ldots \quad (17)
\]

Substituting the value for \( \sum Ce^{4+} \) from (7), equation (18) becomes (19).

\[
\sum H^3 Ce(SO_4)^2^- \cdot \sum = \beta_4 \sum Ce^{4+} \sum SO_4^{2-} \sum HSO_4^- \cdot \sum H^+ \cdot \sum 
\]

\[
\ldots \quad (18)
\]

\[
\sum H^3 Ce(SO_4)^2^- = \frac{\beta_4 \sum Ce(IV) \sum SO_4^{2-} \sum HSO_4^- \cdot \sum H^+ \cdot \sum \cdot 1+K_{OH} \sum H^+ \cdot \sum + \beta_1 \sum SO_4^{2-} \sum + \beta_2 \sum SO_4^{2-} \sum + \beta_3 \sum SO_4^{2-} \sum \sum HSO_4^- \cdot \sum \sum HSO_4^- \sum \sum H^+ \cdot \sum}{1+K_{OH} \sum H^+ \sum + \beta_1 \sum SO_4^{2-} \sum + \beta_2 \sum SO_4^{2-} \sum + \beta_3 \sum SO_4^{2-} \sum \sum HSO_4^- \sum \sum H^+ \sum}
\]

\[
(19)
\]

From the third equilibrium of scheme 2, equation (20) results.

\[
\sum Cr^{3+} \cdot SO_4^{2-} \cdot \sum = K_{IP} \sum Cr^{3+} \sum \cdot \sum SO_4^{2-} \sum 
\]

\[
(20)
\]

But total chromium(III) is given as

\[
\sum Cr^{III} \sum = \sum Cr^{3+} \sum \cdot (1+K_{IP} \sum SO_4^{2-} \sum)
\]

Therefore,
Substituting eqn. (21) in (20), eqn. (22) results in:

\[
\left[ \text{Cr(III)} \right]_f = \frac{\int \text{Cr(III)} \, \mathrm{d}T}{1 + K_{IP} \int \text{SO}_4^{2-} \, \mathrm{d}T}
\]  

Substituting eqn. (21) in (20), eqn. (22) results in:

\[
\int \text{Cr}^{3+} \cdot \text{SO}_4^{2-} \, \mathrm{d}T = \frac{K_{IP} \int \text{Cr(III)} \, \mathrm{d}T \int \text{SO}_4^{2-} \, \mathrm{d}T}{1 + K_{IP} \int \text{SO}_4^{2-} \, \mathrm{d}T}
\]  

Now \( \text{TeO(OH)}^+ = K_1 \int \text{H}_2\text{TeO}_3^- \, \mathrm{d}H^+ \)

\[
\int \text{Te(IV)} \, \mathrm{d}T = \int \text{H}_2\text{TeO}_3^- (1 + K_1 \int \text{H}^+ \, \mathrm{d}T)
\]

\[
\int \text{H}_2\text{TeO}_3^- \, \mathrm{d}T = \frac{\int \text{Te(IV)} \, \mathrm{d}T}{1 + K_1 \int \text{H}^+ \, \mathrm{d}T}
\]  

Substituting eqn. (24) in (23),

\[
\text{TeO(OH)}^+ = \frac{K_1 \int \text{Te(IV)} \, \mathrm{d}T}{1 + K_1 \int \text{H}^+ \, \mathrm{d}T}
\]  

Substituting equations (19), (22) and (25) in equation (17), we obtain,
Rate =

\[
\frac{kK \beta_4 K_{IP} K_{Ce(IV)} K_{Cr(III)} K_{Te(IV)} K_{SO_4^{2-}} K_{HSO_4^{-}} K_{H^+}}{(1 + K_{OH}) + \beta_1 K_{SO_4^{2-}} + \beta_2 K_{SO_4^{2-}} K_{SO_4^{2-}} + \beta_3 K_{SO_4^{2-}} K_{HSO_4^{-}} K_{HSO_4^{-}} K_{H^+}^2} \times
\]

\[
+ \beta_4 K_{SO_4^{2-}} K_{HSO_4^{-}} K_{HSO_4^{-}} K_{H^+}^2
\]

\[
(1 + K_{IP} K_{SO_4^{2-}}) (1 + K_{IP} K_{H^+})
\]

The effect of ionic strength and solvent may be understood on the basis of an essentially ionic reactions (Scheme 2).

Finally, for the verification of rate law (10) of Scheme 1, is rearranged in the form of (27), and verified by plotting left hand side, against \(1/K_{Te(IV)}\) which should be linear.
\[ \frac{[\text{Cr(III)}]}{k'} = \frac{1}{[\text{Te(IV)}]} \left( \frac{1}{kk'} + \frac{[\text{Cr(III)}]}{k} \right) + \frac{1}{k} \]

where, 
\[ k' = \text{Rate/}[\text{Ce(IV)}] \]

This is found to be so as shown in Fig.II(ix) (p.132). From the slope and intercept of such a plot, the values of formation constant of the complex, \( K \) and the rate constant of decomposition of complex \( k \), were calculated. The values result as \( 460 \pm 10 \text{ mol}^{-1}\text{dm}^3 \text{ and } 20 \pm 1 \text{ dm}^3 \text{mol}^{-1}\text{s}^{-1} \) respectively. Using these values, rates under different conditions were calculated. It is found that such calculated rate constants agree with the experimental rate constants (Tables II(iii) & (iv) (p. 110).

The fact that retardation of reaction occurs in the presence of tellurium(VI) only, is probably due to a formation of complex between Ce(III) and Te(VI) as given in last step of scheme 1 which is also observed in earlier work\(^{19}\). The modest activation energy and sizable negative entropy of activation support a complex transition state in the reaction.
Fig. II(ix) : Verification of rate law (10)

(Conditions as in Table II(iii), p.107)
Findings

The chromium(III) catalysed oxidation of tellurium(IV) by cerium(IV) reaction in acid medium proceeds through substrate-catalyst complex. The effectiveness of catalyst is maximum in the mixture of acids (HClO₄+H₂SO₄) compared to the individual acids. The active species of cerium(IV), tellurium(IV) and chromium(III) were understood to be as, H₃Ce(SO₄)₄⁺, TeO(OH)⁺ and Cr³⁺.SO₄²⁻ respectively under the reaction conditions studied.

Importance of the results of Chapter II

A mechanism in terms of the active species of oxidant, reductant and catalyst is proposed and rate law derived. Reaction constants involved in the mechanism are obtained. Rate constants calculated using the derived constants are in reasonable agreement with the experimental rate constants. The retardation of rate of the reaction by one of the products, i.e. tellurium(VI), is probably due to a formation of a complex between cerium(III) and tellurium(VI).
References

1 K. W. Begnall,
"The Chemistry of Selenium, Tellurium and Polonium",

2 W. H. Richardson,
"Ceric ion oxidation of organic compounds", in
Oxidation in organic chemistry, Part A, AP, NY, London,
p.244 (1965), edited by K. B. Wiberg.

3 M. C. Day and J. Selbin,
"Theoretical Inorganic Chemistry",

4 L. S. A. Dikshitulu and D. Satyanarayana,
J. Inorg. Nucl. Chem., 38, 1843 (1976);
L. S. A. Diskhitulu, V. Hanumantharao and S. N. Dindi,
Indian J. Chem., 19A, 203 (1980);
R. Rambabu, P. Vani and L. S. A. Diskhitulu,

5 L. S. A. Diskhitulu, V. Hanumantharao and P. Vani,

6 L. S. A. Diskhitulu, V. Hanumantharao and P. Vani,

7 S. E. Kharzeova and V. V. Serebrennikov,
Russ. J. Inorg. Chem., 12, 1601 (1967);
K. T. Bugaenko and H. Kuam-lin,
Ibid, 8, 1299 (1963).
8 S.A. Chimatadar, S.T. Nandibewoor, M.I. Sambrani and J.R. Raju, 
S.R. Kampli, S.T. Nandibewoor and J.R. Raju, 
Indian J. Chem., 29A, 908 (1990); 
G.S. Gokavi and J.R. Raju, 
Oxidation Communication 11, 205 (1988).

9 Vogel's "Text Book of Quantitative Inorganic Analysis", 

10 Ref. 9 p.361.

11 Ref. 9 p. 368.

12 S.A. Chimatadar, S.T. Nandibewoor, M.I. Sambrani, 
and J.R. Raju, 

13 F.Ya. Kulba, Yu. B. Yakovlev and V.E. Mironov, 

14 Hand Book of Chemistry and Physics, 
Edited by C.D. Hodgman, Chemical Rubber, Publishing 

15 S.R. Kampli, S.T. Nandibewoor, M.I. Sambrani 
and J.R. Raju, 
Polish. J. Chem., 65, 1203 (1991); 
K.K. Sengupta and B. Basu, 
Indian J. Chem., 15, 108 (1977);
15 S.K.Upadhyay and M.C.Agrawal, Indian J. Chem., 19, 478 (1980);

16 N.Foge, J.M.Tai and J.Yarborough, J. Am. Chem. Soc., 84, 1145 (1962);
M.J.Weaver and F.C.Anson, J. Phys. Chem., 80, 1861 (1976);


18 L.S.A.Dikshitulu and D.Satyanarayana, J. Inorg. Nucl. Chem., 38, 1843 (1976);