CHAPTER IVA
OSMIUM(VIII) CATALYSED CERIUM(IV) OXIDATION OF ALLYL ALCOHOL IN AQUEOUS SULPHURIC ACID
In recent years the use of transition metal ions such as osmium, ruthenium, iridium either alone or as binary mixtures as catalysts in the oxidation of several redox processes is of considerable interest. The catalytic activity of these ions is due to the presence of vacant d-orbitals which readily accommodate electrons temporarily and coupled with this is the normal redox potential of the oxidised and reduced form of the catalyst.

Csanyi\(^1\) has suggested that osmium(VIII) can be used as a catalyst in acid, neutral and alkaline media. The normal potentials of the Os(VI)/Os(VIII) and Os(IV)/Os(VIII) couples in alkaline media are \(-0.3\) and \(-0.1\) V respectively\(^2\), while the normal potential of the Os(IV)/Os(VIII) couple in acid medium is as high\(^2\) as \(-1.0\) V. Hence, Os(VIII) may be a more powerful catalyst in acid. The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed by Agrawal and Upadhyay\(^3\).

Though the mechanism of catalysis depends on the nature of substrate, oxidant and other experimental conditions, it has been shown that\(^4\) metal ions act as catalysts by one of these different paths like formation of a complex with reactants or oxidation of the substrate.
itself or through formation of free radicals etc. In general, in osmium(VIII) catalysed oxidations, either osmium(VIII) oxidises the substrate directly or via a 1:1 complex with substrate where the role of the oxidant is to regenerate osmium(VIII).

Osmium(VIII) is used as a catalyst in the alkaline medium for many reasons and the behaviour of osmium(VIII) in alkaline medium is reasonably well understood. But there are very few reports on the catalysis by osmium(VIII) in acid medium and, further, the nature of the osmium(VIII) species in acid is also not clear. It may be mentioned here that a small number of organic molecules like alcohols and ketones in acid media are oxidised by mild oxidants like chloramine-T and periodate in presence of osmium(VIII) as catalyst. Apart from these, some inorganic systems have also been studied.

Allyl alcohol finds a number of industrial applications in the preparation of resins, plasticisers, pharmaceuticals and many organic compounds. Kinetic studies on the oxidation of allyl alcohol with different oxidants such as potassium permanganate, chromic acid, vanadium(V), manganese pyrophosphate, chloramine-T, silver(II) have been reported.
Cerium(IV) oxidation of allyl alcohol in nitric acid as well as in sulphuric acid medium has also been reported. Cerium(IV) oxidation of alcohols proceeds through formation of an oxidant - alcohol complex. The oxidation of organic compounds by cerium(IV) is subject to catalysis by inorganic metal ions such as ruthenium(III), silver(I) and chromium(III). The catalysis by ruthenium(III), silver(I) and chromium(III) of cerium(IV) oxidation of alcohols proceeds via formation of a catalyst-substrate complex followed by subsequent oxidation. In both the uncatalysed and catalysed oxidations of allyl alcohol by cerium(IV), the catalyst being chromium(III) and palladium(II), the product was acrylic acid. But, in the osmium(VIII) catalysed cerium(IV)-allyl alcohol reaction, acrolein was found to be the product. Thus, interest in this reaction centres on the specificity of catalytic action and the role of osmium(VIII) in acid medium.

EXPERIMENTAL

The details of preparation of solutions and standardisation were as given in chapter IA, IB and IIB. In the kinetic runs, acidity and ionic strength were maintained using sulphuric acid and sodium sulphate respectively. The study of the effect of ionic strength
was also made by use of sodium perchlorate.

**Kinetic Runs**

Almost all kinetic runs were followed under pseudo-first order conditions at constant temperature (27 ± 0.1°C) with the concentration of allyl alcohol in a large excess over that of the oxidant. The reaction was initiated by the addition of the required amount of cerium(IV) solution to the allyl alcohol solution which also contained osmium(VIII), sulphuric acid and sodium sulphate. The reaction was followed by measuring the decrease in the absorbance of cerium(IV) solution as a function of time at 360 nm using matched 1 cm quartz cells in a Hitachi 150-20 Spectrophotometer. The application of Beer's law for cerium(IV) under the reaction conditions had earlier been verified in the concentration range of 2.0x10^-5 to 3.0x10^-4 mol dm^-3 in 0.50 mol dm^-3 sulphuric acid (Fig.IV A(i), p.215). The resulting molar absorbancy index, ε, was found to be 3500 ± 2% dm^3 mol^-1 cm^-1. Under the conditions of this study, osmium(VIII) or its intermediates in the reaction solution did not absorb at 360 nm and hence did not interfere. Rates were obtained from tangents at the initial portions of concentration versus time curves. Rates of duplicate runs agreed within ± 4%. Temperature was maintained
Fig. IVA(i) : Verification of Beer's law for Ce(IV) in 0.50 mol dm\(^{-3}\) H\(_2\)SO\(_4\) at 360 nm.
constant within \(\pm 0.1^\circ C\).

**Stoichiometry**

Reaction mixtures containing different sets of reactant concentrations at constant acidity and ionic strength were kept for 24 hours at 27°C and then analysed for cerium(IV) by measuring its absorbance at 360 nm. Under the conditions of \([AA] > [Ce(IV)]\), when cerium(IV) had fully reacted, the unreacted allyl alcohol was estimated\(^{14}\) by addition of excess chloramine-T followed by iodometric analysis of the excess chloramine-T. The product, cerium(III), could be analysed by oxidation to cerium(IV) and then finding the cerium(IV) by titration against iron(II). The other main product was acrolein as found by a spot test\(^{15}\) as follows. After completion of the reaction, the solution was treated with concentrated hydrochloric acid and one drop of 6\% (V/V) hydrogen peroxide. To the resulting solution, a few drops of phloroglucinol in alcohol were added. A pink colour formation identified acrolein. The test for acrylic acid was negative. The results were in agreement with two moles of cerium(IV) being utilised per mole of allyl alcohol (Table IV A(1); p.217).

\[
2 \text{Ce(IV)} + \text{CH}_2=\text{CHCH}_2\text{OH} \xrightarrow{\text{Os(VII)}} 2\text{Ce(III)} + \text{CH}_2=\text{C(CHO)} + 2\text{H}^+ 
\]

\(\text{(1)}\)
Table-IVA(i): Stoichiometry of Osmium(VIII) catalysed cerium(IV) allyl alcohol reaction at 27°C.

\[ [\text{H}_2\text{SO}_4] = 0.20, \quad I = 0.90/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Taken ( [\text{Ce(IV)}] \times 10^3 )</th>
<th>Found ( [\text{AA}] \times 10^3 )</th>
<th>Found ( [\text{Ce(III)}] \times 10^3 )</th>
<th>Found ( [\text{AA}] \times 10^3 )</th>
<th>Found ( [\text{Ce(IV)}] \times 10^3 )</th>
</tr>
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<tbody>
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<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
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</tr>
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<td>4.0</td>
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<td>4.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>1.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
</tr>
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<td>3.0</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>0.5</td>
<td>1.0</td>
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<td>1.0</td>
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<tr>
<td>4.0</td>
<td>0.5</td>
<td>3.0</td>
<td>-</td>
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</tbody>
</table>

\# All concentrations are in mol dm\(^{-3}\).
RESULTS

Reaction Order

The orders were found from log-log plots of initial rates versus concentrations. The order in cerium(IV) was around unity and the order in allyl alcohol was around 0.90 in the concentration ranges of $3.0 \times 10^{-5}$ to $3.0 \times 10^{-4}$ mol dm$^{-3}$ and $1.0 \times 10^{-3}$ to $1.4 \times 10^{-2}$ mol dm$^{-3}$ respectively at a constant concentration of osmium(VIII) of $4.0 \times 10^{-7}$ mol dm$^{-3}$, all other conditions being constant. The results are shown in table IVA(ii)(p.219) and fig.IVA(ii)(p.220). The order in the catalyst concentration, osmium(VIII), between $1.0 \times 10^{-7}$ to $2.0 \times 10^{-6}$ mol dm$^{-3}$, all other conditions being constant, was nearly unity(Table IVA(iii),p.221) and fig.IVA(iii); p.222). It was also noted that the first order plot of log [Ce(IV)] versus time was not linear which may be due to the association of acrolein with cerium(IV) (see Discussion).

Effect of added product

The effect of added product, cerium(III), was studied in the concentration range of $0.3 \times 10^{-4}$ to $2.0 \times 10^{-4}$ mol dm$^{-3}$ at an ionic strength of 0.90 mol dm$^{-3}$ and sulphuric acid concentration of 0.20 mol dm$^{-3}$ at
Table IV A(ii) : Effect of [Ce(IV)] and [AA] on Os(VIII) catalysed oxidation of allyl alcohol by cerium(IV) at 27°C.

\[ \text{[H}_2\text{SO}_4] = 0.20, \quad I = 0.90, \quad \text{[Os(VIII)]} = 4.0 \times 10^{-7} \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[Ce(IV)]x10^4 mol dm^{-3}</th>
<th>[AA]x10^3 mol dm^{-3}</th>
<th>(Ini. rate)x10^7 mol dm^{-3}s^{-1}</th>
<th>Exptl.</th>
<th>Cald. #</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>5.0</td>
<td>2.24</td>
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</tr>
<tr>
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</tr>
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<td></td>
</tr>
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</tr>
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<td></td>
</tr>
<tr>
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<td>9.15</td>
<td></td>
</tr>
<tr>
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<td>11.5</td>
<td>11.2</td>
<td></td>
</tr>
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<td>14</td>
<td>17.4</td>
<td>17.4</td>
<td></td>
</tr>
</tbody>
</table>

# Ini. rates were calculated using K and k of 42±2 dm^3 mol^{-1} and 1.0±100 dm^3 mol^{-1}s^{-1} respectively from fig.IVA(iv), p.225.

Error ± 3%
Fig. IVA(ii): Order in Ce(IV) (-O-) and AA' (--O--) 
Os(VIII) catalysed Ce(IV) oxidation of AA.

(conditions as in table IVA(ii), p.219).
Table IVA(iii)-a: Effect of catalyst, [Os(VIII)], on osmium(VIII) catalysed oxidation of allyl alcohol by cerium(IV) at 27°C.

\[
\begin{array}{cccccc}
[\text{Ce(IV)}] & 1.0 \times 10^{-4} & [\text{AA}] & 5.0 \times 10^{-3} & [\text{H}_2\text{SO}_4] & 0.20, \\
\text{I} & 0.90/\text{mol dm}^{-3} & \\
\hline
[\text{Os(VIII)}] \times 10^7 & 1.0 & 2.0 & 4.0 & 6.0 & 8.0 & 10.0 & 20.0 \\
\text{mol dm}^{-3} & \\
\text{Inl. rate} \times 10^7 (\text{Expt}) & 1.75 & 3.50 & 6.80 & 10.0 & 13.2 & 16.6 & 33.1 \\
\text{mol dm}^{-3} \text{s}^{-1} & \\
\text{Inl. rate} \times 10^7 (\text{Cald}) & 1.72 & 3.45 & 6.90 & 10.2 & 13.8 & 17.0 & 34.0 \\
\text{mol dm}^{-3} \text{s}^{-1} & \\
\end{array}
\]

Table IVA(iii)-b: Effect of product, [Ce(III)], on osmium(VIII) catalysed oxidation of allyl alcohol by cerium(IV) at 27°C.

\[
\begin{array}{cccccc}
[\text{Ce(IV)}] & 1.0 \times 10^{-4}, & [\text{AA}] & 5.0 \times 10^{-3}, & [\text{Os(VIII)}] & 4.0 \times 10^{-7}, \\
[\text{H}_2\text{SO}_4] & 0.20, & \text{I} & 0.90/\text{mol dm}^{-3}. & \\
\hline
[\text{Ce(III)}] \times 10^4 & 0.30 & 0.50 & 0.95 & 1.0 & 1.5 & 2.0 \\
\text{mol dm}^{-3} & \\
\text{Inl. rate} \times 10^7 & 6.80 & 6.75 & 6.80 & 6.68 & 6.70 & 6.75 \\
\text{mol dm}^{-3} \text{s}^{-1} & \\
\text{Error} & \pm 3\%. & \\
\end{array}
\]
Fig. IVA(iii) : Order in Os(VIII) (−o−) and H⁺ (−Δ−):
Os(VIII) catalysed Ce(IV) oxidation of AA.

(conditions as in tables IVA(iii), p.221 and IVA(iv), p.224).
constant reactant concentrations. No significant changes in the initial rates were observed in presence of added product, cerium(III), (Table IV A(iii); p.221). The effect of acrolein on the reaction could not be studied as it was unstable because of its tendency to readily undergo polymerisation, and use of stabilising agents was not thought desirable.

Effect of varying acid concentrations

Hydrogen ions accelerated the rate of the reaction with an order of around 0.80 in \([H^+]\) (Table IVA(iv); p. 224 and fig.IVA(iii) p.222). The effect of acid on the reaction may be ascribed to the changing concentrations of one or more cerium(IV) species, such as \(\text{Ce(OH)}^{3+}\), \(\text{Ce(SO}_4\text{)}^{2+}\), \(\text{Ce(SO}_4\text{)}_2\), \(\text{HCe(SO}_4\text{)}^{-}\) and \(\text{H}_3\text{Ce(SO}_4\text{)}^4\) which are known in aqueous sulphuric acid solutions. The concentrations of such species were calculated as in an earlier study (Chapter IA, p. 55) from a knowledge of the equilibrium constants of such species and the acid-sulphate dissociation constant. The results of such calculations are shown in table IVA(iv) (p.224) and fig. IVA(iv) (p.225). It is seen from such results that, of the different cerium(IV) species, the variation of only \([\text{H}_3\text{Ce(SO}_4\text{)}^4]\) with increasing acidity shows a parallelism with the corresponding variation of rate with acidity.
Table IVA(iv) : Effect of \([H^+]\) on \([\text{Ce(IV)} \text{ species}]\) and rates on osmium (VIII) catalysed Ce(IV)-AA reaction at 27°C.

\[
\begin{align*}
[\text{Ce(IV)}] &= 1.0 \times 10^{-4}, & [\text{AA}] &= 5.0 \times 10^{-3}, & [\text{Os(VIII)}] &= 4.0 \times 10^{-7}, & I &= 0.90/\text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>([H_2SO_4]) x10</th>
<th>([H^+]) x10</th>
<th>([SO_2^-]) x10</th>
<th>([HSO_4^-]) x10</th>
<th>([\text{Ce(IV)}]_{\text{eq}}) x10</th>
<th>([\text{Ce(OH)}^3+]) x10⁵</th>
<th>([\text{Ce(SO}_4^2+]) x10⁴</th>
<th>([\text{H(\text{Ce(SO}_4}_2)^-}) x10⁶</th>
<th>([\text{H(\text{Ce(SO}_4}_2)^3-}) x10⁷</th>
<th>([\text{H(\text{Ce(SO}_4}_2)^4-}) x10⁸</th>
<th>Inl. rate x10⁷ mol dm⁻³ s⁻¹</th>
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</thead>
<tbody>
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</tr>
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<td>0.30</td>
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<td>7.6</td>
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<td>0.17</td>
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<td>1.5</td>
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<td>0.85</td>
<td>1.2</td>
<td>8.7</td>
<td>9.8</td>
</tr>
</tbody>
</table>

# All concentrations are in mol dm⁻³.

Error ± 4%.
Fig. IVA(iv): Effect of acid concentration on the different Ce(IV) species on the initial rates: Os(VIII) catalysed Ce(IV) oxidation of AA.

(condition as in Table IVA(iv), p. 224).
Effect of solvent polarity

The effect of dielectric constant (D) on the reaction was studied by changing the solvent polarity by use of different quantities of acetic acid in the solution keeping the ionic strength constant at 0.90 mol dm$^{-3}$, all other conditions and reactant concentrations being constant. The dielectric constants (D) of the solvent at different volumes of acetic acid in water were calculated as in chapter IA(p.63). The effect of solvent polarity on initial rates are tabulated in the table IVA(v)(p.227). The plot of log (initial rate) versus 1/D was found to be linear with negative slope as shown in fig.IVA(v)(p.228).

Effect of ionic strength and added sulphate

The effect of ionic strength was studied by varying the concentration of sodium perchlorate at constant concentration of reactants, catalyst and acidity. Increase in ionic strength by addition of sodium perchlorate did not show any significant change. The added sodium sulphate concentration was studied under similar conditions. It was found that the reaction rate decreased with increasing sodium sulphate concentration (Table IV A(v), p.228).
Table IVA (v): Effect of polarity of solvent and sulphate ion concentration on the Os(VIII) catalysed oxidation of alcohol by cerium(IV) at 27°C.

\[
[\text{Ce(IV)}] = 1.0 \times 10^4, \quad [\text{Os(VIII)}] = 4.0 \times 10^7, \quad [\text{AA}] = 5.0 \times 10^{-3}
\]

\[
[H_2SO_4] = 0.20/\text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>HAc/water percentage (V/V)</th>
<th>Dielectric constant (D)</th>
<th>rate $\times 10^7$ mol dm$^{-3}$s$^{-1}$</th>
<th>$[SO_4^{2-}]$ rate $\times 10^7$ mol dm$^{-3}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I = 0.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>78.5</td>
<td>6.72 $^*$</td>
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</tr>
<tr>
<td>10</td>
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<td>4.40</td>
<td>0.3</td>
</tr>
<tr>
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<td>0.4</td>
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<tr>
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<td>0.96</td>
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Error $\pm$ 3%.
Fig. IVA(v) : Effects of solvent polarity (-o-) and temperature (-A-) 
Os(VIII) catalysed Ce(IV) oxidation of AA. 
(conditions as in tables IVA(v), p.227 and IVA(v1), p.230).
Test for free radicals

Free radical intervention in the reaction was tested by following the reaction in presence of the scavenger, acrylamide. When the reaction mixture containing acrylamide kept over 24 hours was diluted with methanol, a copious precipitation occurred showing polymerisation.

Effect of temperature

The reaction was studied at 25, 30, 35, 40, 45°C and the data are given in table IV A(vi) (p. 230). From the plot of log (Inl. rate) versus 1/T (Fig. IVA(v), p. 228), the energy of activation, $E_a$, was found to be $58.7 \pm 2$ kJ mol$^{-1}$ and entropy of activation, $AS^\#$ resulted as $-114 \pm 20$ JK$^{-1}$ mol$^{-1}$

DISCUSSION

The cerium(IV) oxidation of allyl alcohol has been studied earlier$^9$ and yields acrylic acid as the main product. A four equivalent reaction is involved. Catalysis of the reaction by chromium(III) also results$^{12}$ in acrylic acid. Moreover, while the uncatalysed reaction involves the formation of cerium(IV)-allyl alcohol complex, the catalysed reaction goes through a chromium(III)-alcohol complex. In the
Table IVA(vi) : Effect of temperature and ionic strength on osmium(VIII) catalysed Cd(IV)-AA reaction.

\[ \text{[Ce(IV)]} = 1.0 \times 10^{-4}, \quad \text{[AA]} = 5.0 \times 10^{-3} \]
\[ \text{[Os(VIII)]} = 1.0 \times 10^{-7}, \quad \text{[H}_2\text{SO}_4] = 0.20 / \text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Rate $\times 10^7$ mol dm$^{-3}$s$^{-1}$</th>
<th>Ionic strength effect</th>
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<tr>
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<td>I = 0.90 mol dm$^{-3}$</td>
<td>Temp. = 25°C</td>
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</tr>
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</table>

\[ \text{Ea} = 58.7 \pm 2 \text{kJ mol}^{-1} \]
\[ \Delta S^\# = -114 \text{JK}^{-1} \text{mol}^{-1} \]

Error $\pm$ 4%.
present case of the osmium(VIII) catalysis also, a similar complex may be expected in view of the order in allyl alcohol being less than unity. Attempts to obtain spectral evidence of such complexes were 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. The rate law of the catalysed reaction can be understood in terms of the mechanism of Scheme 1 where a catalyst-substrate complex

$$\text{Os(VIII)} + \text{CH}_2 = \text{CHCH}_2\text{OH} \xrightleftharpoons{K} \text{Complex, C}$$

$$\text{C} + \text{Ce(IV)} \xrightarrow{k} \text{CH}_2 = \text{CHOH + Ce(II)}$$

$$+ \text{Os(VIII)} + H^+$$

$$\text{CH}_2 = \text{CHOH} + \text{Ce(IV)} \xrightarrow{\text{fast}} \text{CH}_2 = \text{CHO} + \text{Ce(III)} + H^+$$

Scheme 1

formation is followed by its oxidation in succeeding steps. A free radical intervention is also accommodated by Scheme 1. This scheme leads to the rate law of (2).

$$\frac{d[\text{Ce(IV)}]}{dt} = \frac{KK[\text{Ce(IV)}][\text{AA}][\text{Os(VIII)}]}{(1+K[\text{AA}])}$$

(2)

The rate of disappearance of cerium(IV) concentration is
given by (3).

\[- d[Ce(IV)]/dt = k[Ce(IV)][C] \tag{3}\]

The concentration of the complex, C, may be written, from its formation equilibrium (Scheme 1), as in (4) where \([Os(VIII)]_f\) and \([AA]_f\) are the uncomplexed or free osmium(VIII) and allyl alcohol concentrations

\[[C] = K[Os(VIII)]_f[AA]_f \tag{4}\]

respectively. The total concentrations of osmium(VIII) and allyl alcohol, represented as \([Os(VIII)]_T\) and \([AA]_T\), are the sums of the concentrations of the free and the complexed osmium(VIII) and allyl alcohol respectively and they are given by (6) and (7).

\[[Os(VIII)]_T = [Os(VIII)]_f + [C] \tag{5}\]

or

\[[Os(VIII)]_T = [Os(VIII)]_f + K[Os(VIII)]_f[AA]_f \tag{6}\]

\[[AA]_T = [AA]_f + K[AA]_f[Os(VIII)]_f \tag{7}\]

Therefore, the concentrations of free osmium(VIII) and allyl alcohol may be seen to result from (6) and (7) as in (8) and (9) respectively.

\[[Os(VIII)]_f = [Os(VIII)]_T / (1 + K[AA]_T) \tag{8}\]

\[[AA]_f = [AA]_T / (1 + K[Os(VIII)]_T) \tag{9}\]
Use of expressions for [Os(VIII)]\(_f\) and [AA]\(_f\) from (8) and (9) in (4) gives [C] which is used in (3); and, rate law (2) results.

The reaction tended to slow down after about 30% of the reaction. The product isolation had showed the formation of a polymer presumably resulting from acrolein, one of the products. The reaction rate was checked at different stages of the reaction and was found to be still first order with respect to oxidant in presence of excess allyl alcohol. Neither had the catalyst lost its activity as shown by using the same catalyst for a fresh run of the same reaction. Presumably after the earlier stages of the reaction, a part of the oxidant is involved in complexation with acrolein and this latter complex reacts with allyl alcohol with a slower rate or, alternatively, a part of the oxidant is involved in oxidation of the polymeric acrolein. In any case, Scheme 1, is clearly applicable to the initial stages of the reaction.

The effect of increasing acidity on the reaction may be understood in terms of the formation of the protonated cerium(IV) sulphate complexes as stated in the results section. The species \(H_3Ce(SO_4)_4^-\) increases in
concentration with acidity as does the rate of the reaction (Table IV A(iv); p.224). A plot of rate versus $[\text{H}_2\text{SO}_4]$ is linear passing through the origin (Fig.IVA(iv), p.225) indicating that a protonated species is active. A further evidence for such cerium(IV) species comes from runs carried out in the absence of sulphate and sulphuric acid. When perchlorate-perchloric acid media are used for the reaction, it is observed that the rate decreases with an increase in acidity. This result is in agreement with Ce(OH)$^{3+}$ being the active species of cerium(IV) as its concentration may be expected to decrease with increasing acidity thereby causing the resulting decrease in rate. Hence, $\text{H}_3\text{Ce(SO}_4)_4^-$ may be concluded to be the active oxidant species in sulphuric acid-sulphate media.

The catalyst, osmium(VIII), is known to exist in acid medium in the form of undissociated acid, $\text{H}_2\text{OsO}_5$ ($K_a=8.0\times10^{-13}$). While the lack of influence of ionic strength on the reaction may be understood in terms the two neutral species, allyl alcohol and osmium(VIII), being involved in the reaction, the decreasing rate with decreasing dielectric constant shows that an essentially polar transition state stabilised by solvent polarity is presumably involved in the second step of Scheme 1. The
modest activation energy and sizable negative entropy of activation support a complex transition state in the reaction.

As regards the retardation caused by sodium sulphate, it may be attributed to the formation of double salt with ceric sulphate or due to the decrease in the free \( [H^+] \) (due to the acid sulphate equilibrium); reduction in free \( [H^+] \) reduces the \( [H_3Ce(SO_4)_4^-] \).

Finally, the rate law (2) may be verified in the form (10), according to which a plot of left hand side versus \( [AA]^{-1} \) should be linear. This is found to be so as shown

\[
\frac{[Os(VIII)][Ce(IV)]}{\text{rate}} = \frac{1}{kK} \frac{1}{[AA]} + \frac{1}{k}
\]  

(10)

in fig.IVA(vi) (p.236). From the slope and intercept of such a plot, the value of \( K \), the formation constant of the catalyst-substrate complex, and \( k \), the rate constant of step 2 of Scheme 1, are found to be around \( 42 \pm 2 \) \( \text{dm}^3\text{mol}^{-1} \) and \( 1.0 \times 10^5 \pm 100 \) \( \text{dm}^3\text{mol}^{-1} \text{s}^{-1} \) respectively. These values may be used to find rates under different conditions of the reaction. Rates calculated in this way are in good agreement with experimentally measured rates (Tables IVA(ii); p.219 and IVA(iii); p.221).
Fig. IVA(vi) : Verification of rate law (2).

(conditions as in table IVA(ii), p.219).
Findings

The osmium(VIII) catalysed cerium(IV)-allyl alcohol reaction in an aqueous acid medium is understood to occur via formation of a catalyst-alcohol complex and this is followed by a slow step of cerium(IV) oxidation of the complex and other fast steps. The active species of the oxidant in aqueous sulphuric acid medium is found to be $\text{H}_3\text{Ce(SO}_4\text{)}_4$.

Importance of the results of Chapter IVA:

While osmium(VIII) is known to be a powerful catalyst in both acid and alkaline media, in the present reaction, the catalytic activity of osmium(VIII) is high in aqueous sulphuric acid. In perchloric acid medium, the catalyst is not so effective. The product of allyl alcohol-cerium(IV) reaction is found to depend on the catalyst used. While acrylic acid is the usual product, in the present case, acrolein is the main product.
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