CHAPTER XIII

DISCUSSION AND INTERPRETATION OF KINETIC FEATURES.
13. **DISCUSSION AND INTERPRETATION OF KINETIC FEATURES.**

The study of a chemical reaction is of fundamental concern to a chemist from two aspects. Firstly for ascertaining the fastness or slowness of the reaction and secondly for investigating the effect of different factors – concentration, pressure, temperature, catalyst, on the rate of reaction and thereby workout the optimum conditions for carrying out a process. For the fundamental chemist, these studies enable him to get an insight into the different steps through which the reaction proceeds and work out a reaction mechanism for the process. An important milestone in the understanding of chemical kinetics was the concept of molecular activation as a prerequisite to a chemical reaction first postulated by Arrhenius\(^1\). The concept of molecular activation is now universally accepted and forms the basis of all subsequent theories of chemical reactions.

Evans and Polanyi\(^2\) and Eyring\(^3\) put forth the idea of formation of activated complex as a result of molecular collision between energized molecules and established that the chemical reaction involves first the formation of activated complex in a reversible process which then decomposes irreversibly to give the products of the reaction. This according to Eyring for any chemical reaction to occur, it is necessary for the reacting atoms or molecules to approach each other and
then to pass over a free energy barrier. The molecular species corresponding to the top of such a free energy barrier are referred to as activated complex and the rate of reaction is controlled by the rate by which these complexes travel over the top of the barrier.

Amis (4), in his book "Solvent effects on reaction rate and mechanism" has explained the role of the nature of the solvent on rates of reactions occurring in solution. From the viewpoint of solvent effect, the reaction may be broadly classified into many categories like ion—ion reactions, ion dipolar molecule reaction, electron exchange reaction etc.

In the previous chapters 3 to 12, an attempt has been made to collect the kinetic informations in the oxidation of ethylene glycol, glycerol, erythritol, dulcitol, cyclopentanone and cyclohexanone by potassium bromate in the presence of Ru(III) chloride as a catalyst in acidic medium. These kinetic data have been utilized here to propose the reaction routes of the reactions investigated.

Before the mechanism of the reaction is proposed, it is worthwhile to discuss first the reactive species of various reactants involved in the present investigation. In the present investigation Ru(III) chloride used as a catalyst in the acidic medium, potassium bromate used as an oxidant, the role of mercuric acetate involved is also additionally discussed, thereafter these reactive species along with the various other
kinetic information have been discussed and interpreted to elucidate final reaction mechanism which can explain all the observed kinetic results.

In the following sections, a summary of kinetic features observed, rationalization of reactive species of different reactants and more kinetic information are presented.
13.1. **Kinetic features observed in potassium bromate oxidation of ethylene glycol, glycerol, erythritol, dulcitol catalysed by Ru(III) chloride in perchloric acid medium.**

The title reactions show the following kinetic results:

(i) The reactions were first order with respect to KBrO$_3$ in the initial lower concentration range but first order tended to zero order on increasing the concentration of potassium bromate.

(ii) The reactions were zero order in substrates (ethylene glycol, glycerol, erythritol and dulcitol) in their initial lower concentration range as well as higher concentration of substrate.

(iii) First order kinetics in Ru(III) chloride was observed for the substrates i.e. ethylene glycol, glycerol, erythritol and dulcitol.

(iv) A zero order kinetics in [H$^+$] i.e. negligible effect of [H$^+$] was observed for ethylene glycol, glycerol, erythritol and dulcitol.

(v) A positive effect of chloride ion was also observed on the rate of reaction.
(vi) Negligible effect of addition of acetic acid is seen on varying the concentration of acetic acid.

(vii) Negligible effect of ionic strength of the medium was observed on the velocity of the reactions.

(viii) Insignificant effect of addition of mercuric acetate was observed on the reaction velocity constant.

(ix) Addition of D₂O to the reaction mixture showed negligible effect on the reaction velocity constant.

(x) Significant effect of increase in temperature was observed in the reactions undertaken here.
13.2. A brief outline of kinetic results obtained in Ru(III) catalysed oxidation of some cyclic ketones (cyclopentanone and cyclohexanone) by KBrO$_3$ in acidic medium.

Following kinetic results have been collected for the above title reactions:

(i) In the lower concentration range as well as in the higher concentration range, the reaction follows zero order kinetics with respect to oxidant KBrO$_3$.

(ii) First order dependence of the rate on each substrate (cyclopentanone and cyclohexanone) was seen.

(iii) The title reaction follows first order kinetics in Ru(III) chloride concentration.

(iv) Positive effect of $[\text{H}^+]$ on the rate was observed for the above title reaction.

(v) Negligible effect on the rate was found by the variation of concentration of mercuric acetate.

(vi) Positive effect of chloride ion was also observed for the above mentioned reaction.

(vii) Negligible effect of change in ionic strength of the medium was observed.
(viii) Increase in temperature markedly increases the reaction velocity.
(ix) Negligible effect of addition of acetic acid on varying the concentration of acetic acid was detected.
(x) Addition of $\text{D}_2\text{O}$ to the reaction mixture showed negligible effect on reaction velocity.
13.3. Ascertaining the reactive species of potassium bromate in perchloric acid in present investigation.

It has already been discussed that $[\text{RuCl}_6]^{3-}$ is reactive species of ruthenium(III) chloride in acidic medium and HBrO$_3$ is possible reactive species of KBrO$_3$ and other kinetic features with respect to [Substrate], [H$^+$], [Hg(II)], [Cl$^-$] and ionic strength of the medium.

It has been reported that potassium bromate acts as an oxidant in many reactions in acidic medium and its active species have been reported by earlier workers.

It is clear from the above mechanistic steps that potassium bromate can act as such or HBrO$_3$, BrO$_3^-$, Br$^+$ etc. may be oxidizing species, but these reactive species require negative effect on reaction. So KBrO$_3$ as such is supposed to be reactive species under given conditions of experiments and on the basis of kinetic features observed.
13.4. Ascertaining the reactive species of Ru(III) chloride in perchloric acid medium in present investigation.

Ruthenium (Ru) metal are well known for their capacity to form complexes. Ru(III) chloride is quite soluble in hydrochloric acid and exists as [RuCl₆]³⁻. In aqueous solution [RuCl₆]³⁻ is rather unstable⁹ and it is in equilibrium with [RuCl₅(H₂O)]²⁻ as given below⁹⁻¹²).

\[
[RuCl₆]³⁻ + H₂O \longrightarrow [RuCl₅(H₂O)]²⁻ + Cl⁻
\]

It seems from above equilibria that Ru(III) chloride is catalyzing the reaction either through involvement of its species [RuCl₆]³⁻ or [RuCl₅(H₂O)]²⁻.

In acidic medium the above equation in the right direction would be highly favoured, suggesting [RuCl₅(H₂O)]²⁻ species¹³⁻¹⁴) of Ru(III) chloride as the active species.

In our case, the observed positive effect of Cl⁻ ion clearly indicates that the Cl⁻ ions are used in a pre-equilibrium prior to rate determining step. This confirms that the above equation exist towards the left direction¹¹ and support the assumption that dissociation of Cl⁻ ions does not occur. Therefore under the present experimental condition [RuCl₆]³⁻ can safely be assumed as real reactive species of Ru(III) chloride in our investigation.
13.5. Reactivity of mercuric acetate in the present investigation.

The reactivity of mercuric acetate as oxidant, catalyst and Br⁻ ions scavenger\(^{(5-7)}\) is well known. When the present investigation was carried out with Hg(OAc)\(_2\) but without addition of oxidant potassium bromate, the reaction did not proceed. This rules out the possibility of mercuric acetate acting as oxidant under present condition of experiments. When experiments with potassium bromate were carried out, reaction proceeded, but with comparatively changed behaviour. The colour of the mixture turned yellow and thereafter rate unexpectedly increased while when the same experiments were repeated with initial addition of mercuric acetate in reaction mixture, the reaction proceeded without any sudden drift in the velocity of reaction and without showing any development of colour in the reaction mixture. This shows that in presence of mercuric acetate the appearance of yellow colour is stopped due to trapping of Br⁻ ion (formed in the reaction) by mercuric ions and thus Br\(_2\) (likely to be formed and responsible for yellow colour) formation is totally eliminated.

Variation of concentration of Hg(II) acetate did not influence the reaction velocity constant and thus it did not act as a catalyst. Therefore, mercuric acetate is involved in the present investigation as scavenger for Br⁻ ion which is produced in the reaction and thus Br\(_2\) formation is avoided which complicates the reaction. The presence of mercuric acetate assures pure potassium bromate oxidation of compounds used here.
13.6. Mechanism of Ru(III) catalysed oxidation of Ethylene glycol, Glycerol, Erythritol and Dulcitol by potassium bromate in acidic medium.

It has already been discussed that $[\text{RuCl}_6]^{3-}$ is reactive species of ruthenium (III) chloride in acidic medium and $\text{HBrO}_3$ is possible reactive species of potassium bromate. In view of reactive species of Ru(III) chloride and $\text{KBrO}_3$ and other kinetic features with respect to $[\text{substrate}]$, $[\text{H}^+]$, $[\text{Hg(II)}]$, $[\text{Cl}]$ and ionic strength of the medium following mechanistic steps are proposed.

In acidic solution of $\text{KBrO}_3$ quick formation of $\text{HBrO}_3$ has been reported. Positive effect with respect to chloride ions suggests that the following equilibrium is shifted to right (ii) in acidic ruthenium(III) chloride solution.

Estimation of unconsumed $\text{KBrO}_3$ revealed that one mole of substrate consumed two moles of bromate.

$$\text{BrO}_3^- + \text{RCH}_2\text{OH} \rightarrow \text{RCOOH} + 2\text{BrO}_2^- + \text{H}_2\text{O}$$

(substrate)
The following reaction scheme is suggested where R stands for remaining group.

\[ \text{H}^+ + \text{BrO}_3^- \rightleftharpoons \text{HBrO}_3 \quad \ldots \ldots (i) \]

\[ [\text{RuCl}_3 \text{H}_2\text{O}]^{2-} + \text{Cl}^- \xrightleftharpoons[k_1]{k_{-1}} [\text{RuCl}_6]^{3-} + \text{H}_2\text{O} \quad \ldots \ldots (ii) \]

\( (C_1) \quad (C_2) \)

\[ [\text{RuCl}_6]^{3-} + \text{HBrO}_3 \xrightarrow[k_2]{k_{-2}} \]

(Intermediate \( C_3 \))

\[ \ldots \ldots (iii) \]
In steps (iv) and (vi)

\[ R = -\text{CH}_2\text{OH} \quad \text{for ethylene glycol} \]
\[ R = -\text{CHOH-CH}_2\text{OH} \quad \text{for glycerol} \]
\[ R = -(\text{CHOH})_2\text{CH}_2\text{OH} \quad \text{for erythritol} \]
\[ R = -(\text{CHOH})_4\text{-CH}_2\text{OH} \quad \text{for dulcitol} \]
In step (iv) the formation of carbonium ion and hydride ion transfer theory is well known.\(^{16-17}\)

Considering the above proposed reaction steps, the rate of oxidation of substrates (Ethylene glycol, Glycerol, Erythritol and Dulcitol) by KBrO\(_3\) may be expressed as the rate of loss of concentration of KBrO\(_3\) as given below:

From equation (iii)

\[
\frac{-d [BrO_3^-]}{dt} = k_2 [RuCl_6]^{3-} [HBrO_3] \quad \ldots \quad (vii)
\]

or

\[
\frac{-d [BrO_3^-]}{dt} = k_2 [C_2] [HBrO_3] \quad \ldots \quad (viii)
\]

Now from the above equations:

\[
[ Ru(III) ]_T = [C_1] + [C_2] + [C_3] \quad \ldots \quad (ix)
\]

From equation (ii):

\[
\frac{-d[C_1]}{dt} = k_{-1} [C_2] - k_1 [C_1] [Cl^-]
\]
\[ [C_1] = k_{-1} [C_2] / k_1 [Cl^-] \] ...........(x)

We know that \((-d[C_1]/dt) = 0\), on applying steady state approximation:

\[
\frac{-d[C_3]}{dt} = k_2 [C_2] [HBrO_3] - k_{-2} [C_3]
\]

\[
[C_3] = \frac{k_2 [C_2] [HBrO_3]}{k_{-2}} \] ...........(xi)

Now from equation (ix), (x) and (xi) we get

\[
[Ru(III)]_T = \frac{k_{-1} [C_2]}{k_1 [Cl^-]} + [C_2] + \frac{k_2 [C_2] [HBrO_3]}{k_{-2}}
\]

\[
[Ru(III)]_T = \frac{k_{-1} [C_2]}{k_1 [Cl^-]} + [C_2] + K_2 [C_2] [HBrO_3]
\]

\[
[Ru(III)]_T = \frac{[C_2] k_{-1} + 1 + K_2 k_{-1} [Cl^-] [HBrO_3]}{k_1 [Cl^-]}
\]
From equation (viii)

\[
[C_2] = \frac{[\text{Ru(III)}]_T k_1 [\text{Cl}^-]}{k_{-1} + 1 + K_2 k_{-1} [\text{Cl}^-] [\text{HBrO}_3^-]}
\]

\[\frac{-d [\text{BrO}_3^-]}{dt} = \frac{k_2 k_1 [\text{Ru(III)}]_T [\text{Cl}^-] [\text{HBrO}_3^-]}{k_{-1} + 1 + K_2 k_1 [\text{Cl}^-] [\text{HBrO}_3^-]} \quad ......(xii)
\]

upon rearranging the above equation (xii) we get

\[
\frac{-d [\text{BrO}_3^-]}{dt} = \frac{k_1 k_2 [\text{Ru(III)}]_T [\text{Cl}^-] [\text{HBrO}_3^-]}{k_{-1} + k_2 [\text{HBrO}_3^-] + k_1 [\text{Cl}^-]} \quad ......(xiii)
\]

The rate law (xiii) derived, clearly shows first order at lower concentration of KBrO₃ tending towards zero order kinetics at its higher concentration. The first order dependence on [RuCl₃] and zero order dependence of [H⁺] is also depicted. The rate law (xiii) also shows positive effect of [Cl⁻].
There is negligible effect of Hg(II), acetic acid, addition of D₂O and ionic strength. These are obvious in rate law (xiii).

The rate law (xiii) clearly explains all the experimental results and hence reaction mechanism suggested above, seems to be valid.

Equation (xiii) can be written as:

\[
\frac{1}{1} = \frac{k_{-1}}{k_{1}k_{2}[\text{Ru(III)}][\text{Cl}^{-}][\text{HBrO}_3]} + \frac{k_{2}[\text{HBrO}_3]}{k_{1}k_{2}[\text{Ru(III)}][\text{Cl}^{-}][\text{HBrO}_3]}
\]

\[
- \frac{d[[\text{BrO}_3^{-}]/dt}{k_{1}k_{2}[\text{Ru(III)}][\text{Cl}^{-}][\text{HBrO}_3]}
\]

OR

\[
\frac{1}{1} = \frac{1}{\text{rate}} = \frac{k_{-1}}{k_{1}k_{2}[\text{Ru(III)}][\text{Cl}^{-}][\text{HBrO}_3]}
\]

\[
+ \frac{1}{k_{1}[\text{Ru(III)}][\text{Cl}^{-}]} + \frac{1}{k_{2}[\text{Ru(III)}][\text{HBrO}_3]}
\]

\ldots(xiv)
According to equation (xiv) if a plot is made between \((1 / \text{rate})\) and \((1 / [\text{KBrO}_3])\) a straight line with a positive intercept on the Y-axis is obtained which will also give a value of \((1 / k_1)\) on substituting other concentrations. (Fig. 13A, 13B, 13C, 13D).

Similarly a plot of \((1/\text{rate})\) vs. \((1 / [\text{Cl}^-])\) again, a straight line having positive intercept on the Y-axis (Fig. 13E, 13F) is obtained which will also give value of \((1 / k_2)\).
Plot of \( \frac{1}{(-dc/dt)} \) vs. \( \frac{1}{[\text{KBrO}_3]} \) at 35°C

\[
\begin{align*}
\text{[Hg(OAc)$_2$]} &= 1.25 \times 10^{-3} \text{ M} \\
\text{[Ru(III)]} &= 9.60 \times 10^{-6} \text{ M} \\
\text{[HClO$_4$]} &= 1.00 \times 10^{-3} \text{ M} \\
\text{[KCl]} &= 1.00 \times 10^{-3} \text{ M} \\
\text{[Ethylene glycol]} &= 0.67 \times 10^{-2} \text{ M}
\end{align*}
\]
Plot of \( \{1/(-dc/dt)\} \) vs. \( (1/\text{[KBrO}_3\text{]}\) at 35°C

\[
\begin{align*}
\text{[Hg(OAc)]}_2 &= 1.25 \times 10^{-3} \text{ M} \\
\text{[Ru(III)]} &= 9.60 \times 10^{-6} \text{ M} \\
\text{[HClO}_4\text{]} &= 1.00 \times 10^{-3} \text{ M} \\
\text{[KCl]} &= 1.00 \times 10^{-3} \text{ M} \\
\text{[Glycerol]} &= 2.00 \times 10^{-2} \text{ M}
\end{align*}
\]
Plot of \( \{1/(-dc/dt)\} \) vs. \((1/[\text{KBrO}_3])\) at 35°C

\[
\text{[Hg(OAc)$_2$]} = 1.25 \times 10^{-3} \text{M} \quad \text{[Ru(III)]} = 9.60 \times 10^{-6} \text{M} \\
\text{[HClO$_4$]} = 1.00 \times 10^{-3} \text{M} \quad \text{[KCl]} = 1.00 \times 10^{-3} \text{M} \\
\text{[Erythritol]} = 2.00 \times 10^{-2} \text{M}
\]
Plot of \{ 1 / (-dc/dt) \} vs. \{ 1 / [KBrO_3] \) at 35°C

\[
\begin{align*}
[Hg(OAc)_2] &= 1.25 \times 10^{-3} \text{M} & [\text{Ru(III)}] &= 9.60 \times 10^{-6} \text{M} \\
[HClO_4] &= 1.00 \times 10^{-3} \text{M} & [\text{KCl}] &= 1.00 \times 10^{-3} \text{M} \\
[\text{Dulcitol}] &= 2.00 \times 10^{-2} \text{M}
\end{align*}
\]
Plot of \( \frac{1}{(-dc/dt)} \) vs. \( \frac{1}{[KCl]} \) at 35°C

\[
\begin{align*}
[KBrO_3] &= 1.00 \times 10^{-3} \text{ M} \\
[Hg(OAc)_2] &= 1.25 \times 10^{-3} \text{ M} \\
[Ru(III)] &= 9.60 \times 10^{-6} \text{ M} \\
[HClO_4] &= 1.00 \times 10^{-3} \text{ M} \\
[\text{Ethylene glycol}] &= 0.67 \times 10^{-2} \text{ M (A)} \\
[\text{Glycerol}] &= 2.00 \times 10^{-2} \text{ M (B)}
\end{align*}
\]
Plot of \{ 1 / (-dc/dt) \} vs. \( 1 / [\text{KCl}] \) at 35°C

- \([\text{KBrO}_3]\) = 1.00 \times 10^{-3} \text{ M}
- \([\text{Hg(OAc)}_2]\) = 1.25 \times 10^{-3} \text{ M}
- \([\text{Ru(III)}]\) = 9.60 \times 10^{-6} \text{ M}
- \([\text{HCIO}_4]\) = 1.00 \times 10^{-3} \text{ M}
- \([\text{Erythritol}]\) = 2.00 \times 10^{-2} \text{ M (A)}
- \([\text{Dulcitol}]\) = 2.00 \times 10^{-2} \text{ M (B)}
13.61. Evaluation of constant in Ru(III) catalysed oxidation of some polyhydric alcohols by KBrO₃ in acidic media.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Substrate</th>
<th>1/rate versus 1/[Cl⁻]</th>
<th>Value of intercept</th>
<th>Value of k₂</th>
<th>1/rate versus 1/[KBrO₃]</th>
<th>Value of intercept</th>
<th>Value of k₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylene glycol</td>
<td>0.20 x 10⁷</td>
<td>5.20 x 10⁸</td>
<td>0.125 x 10⁷</td>
<td>8.33 x 10⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Glycerol</td>
<td>0.225 x 10⁷</td>
<td>4.62 x 10⁸</td>
<td>0.15 x 10⁷</td>
<td>6.94 x 10⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Erythritol</td>
<td>0.19 x 10⁷</td>
<td>5.48 x 10⁸</td>
<td>0.12 x 10⁷</td>
<td>8.68 x 10⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Dulcitol</td>
<td>0.25 x 10⁷</td>
<td>4.16 x 10⁸</td>
<td>0.16 x 10⁷</td>
<td>6.61 x 10⁸</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Almost constant values of k₁ and k₂ obtained from the plots of (1 / rate) vs. (1 / [KCl]) and (1 / rate) vs. (1 / [KBrO₃]) for different polyhydric alcohols confirms the rate law (xiii), hence the validity of proposed mechanism.
13.7. Mechanism of Ru(III) catalysed oxidation of cyclopentanone and cyclohexanone by potassium bromate in acidic medium.

Considering HBrO₃ and [RuCl₆]³⁻ as oxidizing and catalyzing species of KBrO₃ and Ruthenium chloride, the acidic solution of reactive species results change into the product. The positive effect of chloride ion suggests that the following equilibrium is shifted to right (eq. iii) in acidic ruthenium(III) chloride solution. Estimation of unconsumed KBrO₃ revealed that two moles of bromate are consumed by one mole of substrate.

\[
(CH_2)_n\overline{CO} + 2 BrO_3^- \rightarrow (CH_2)_n\overline{CO} + 2 BrO_2^- + H_2O
\]

The following reaction scheme is suggested, where n suggested the number of remaining CH₂ group

For cyclopentanone n = 1
For cyclohexanone n = 2
\[(\text{CH}_2)_n\text{--CH}_2 \quad \xrightarrow{k_1} \quad (\text{CH}_2)_n\text{--CH}_2\quad \text{[S}_1]\]
\[\text{CH}_2\text{--CH}_2  \quad \xrightarrow{k_{-1}} \quad \text{CH}_2\text{--CH}_2\quad \text{[S}_2]\]

\[\text{(CH}_2)_n\text{--CH}_2 \quad \xrightarrow{k_2} \quad \text{CH}_2\text{--CH}_2\quad \text{[S}_3]\]
\[\text{CH}_2\text{--CH}_2 \quad \xrightarrow{k_{-2}} \quad \text{CH}_2\text{--CH}_2\quad \text{[S}_2]\]

\[\text{[RuCl}_5\text{H}_2\text{O]}^{2-} + \text{Cl}^- \quad \xrightarrow{k_3} \quad [\text{RuCl}_6]^{3-} + \text{H}_2\text{O}\quad \text{[C}_1]\]
\[\text{[RuCl}_6]^{3-} + \text{H}_2\text{O} \quad \xrightarrow{k_{-3}} \quad \text{[RuCl}_5\text{H}_2\text{O]}^{2-} + \text{Cl}^-\quad \text{[C}_2]\]

\[\text{[S}_3]\]
\[\text{[C}_2]\]

\[\text{[S}_3]\]
\[\text{[C}_2]\]

\[\text{[S}_3]\]
\[\text{[C}_2]\]

\[\xrightarrow{k_4 \quad \text{slow}} \quad \text{[C}_2]\]
\[
\begin{align*}
\text{H} & \quad \text{RuCl}_6 \\
(CH_2)_n & \quad C \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]
\[\text{fast}\]

\[
\begin{align*}
\text{H} & \quad \text{OH} \\
(CH_2)_n & \quad C \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

\[\text{[RuCl}_6\text{H}^+] + \quad \text{[RuCl}_6\text{]}^{2+} + \quad \text{HBrO}_2 + \quad \text{H}_2\text{O}
\]

\[
\begin{align*}
\text{H} & \quad \text{OH} \\
(CH_2)_n & \quad C \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]
\[\text{fast}\]

\[
\begin{align*}
\text{HBrO}_2 & + \quad \text{BrO}_3^- \\
(CH_2)_n & \quad C \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]
Considering the above proposed reaction steps, the rate of oxidation of substrate (cyclopentanone and cyclohexanone) by KBrO$_3$ may be expressed as follows:

On the basis of step (iv) of above scheme which is the slow and rate determining step:

$$\text{Rate} = k_4 [S_3] [C_2]$$

Where $S = S_1 + S_2 + S_3$ (total concentration of substrate)

On applying steady state approximation to $[S_2]$ we have

$$\frac{d[S_2]}{dt} = 0 = k_{-2}[S_3] - k_2[S_2] + k_1[S_1][H^+] - k_{-1}[S_2]$$

......(1)
or

\[ k_2 [S_2] + k_{-1}[S_2] = k_{-2}[S_3] + k_1 [S_1] [H^+] \]

or

\[ [S_2] (k_{-1} + k_2) = k_{-2}[S_3] + k_1 [S_1] [H^+] \]

or

\[ [S_2] = \frac{k_{-2}[S_3] + k_1 [S_1] [H^+]}{k_{-1} + k_2} \]  \hspace{1cm} \text{......(2)}

Again applying steady state approximation to \([S_1]\) :

\[ \frac{d [S_1]}{dt} = 0 = -k_1 [H^+] + k_{-1}[S_2] \]

or

\[ k_1 [S_1] [H^+] = k_{-1}[S_2] \]

or

\[ [S_1] = \frac{k_{-1}[S_2]}{k_{-1}[H^+]} \]  \hspace{1cm} \text{......(3)}
On substituting the value of \([S_1]\) from equation (3) to equation (2)

Then

\[
[S_2] = \frac{k_2[S_3] + \frac{k_1}{k_1} [H^+] [S_2]}{k_1 [H^+]}
\]

or

\[
[S_2] = \frac{k_2[S_3] + k_1 [S_2]}{k_1 + k_2}
\]

or

\[
[S_2] - \frac{k_1 [S_2]}{k_1 + k_2} = \frac{k_2[S_3]}{k_1 + k_2}
\]

or

\[
[S_2] \left[ 1 - \frac{k_1}{k_1 + k_2} \right] = \frac{k_2[S_3]}{k_1 + k_2}
\]
The total concentration of substrate (5) is represented as

\[ [S] = [S_1] + [S_2] + [S_3] \]

from equation (3) and (4) we have

\[ S = \frac{k_{-1}[S_2]}{k_1[H^+]} + \frac{k_{-2}[S_3]}{k_2} + [S_3] \]  

.....(5)

by putting the value of \([S_2]\) in equation (5) from equation (4) we get

\[ [S] = \frac{k_{-1}k_{-2}[S_2]}{k_1k_2[H^+]} + \frac{k_{2}[S_3]}{k_2} + [S_3] \]
or

$$[S] = S_3 \left[ \frac{k_{-1} k_{-2}}{k_2 k_1 [H^+]} + \frac{k_{-2}}{k_2} + 1 \right]$$

or

$$[S] = S_3 \left[ \frac{k_{-1} k_{-2} + k_1 k_2 [H^+] + k_1 k_2 [H^+]}{k_1 k_2 [H^+]} \right]$$

or

$$S_3 = \frac{k_1 k_2 [H^+][S]}{k_{-1} k_{-2} + k_1 k_2 [H^+] + k_1 k_2 [H^+]}$$

Further on applying steady state approximation to $C_1$

$$(-dc_1/dt) = 0 = -k_3 C_1 [CI] + k_{-3} C_2$$

or

$$k_{-3} C_2 = k_3 C_1 [CI]$$

$$C_2 = \frac{k_3 C_1 [CI]}{k_{-3}}$$
The total concentration of Ru(III) chloride i.e. $[\text{Ru}]^{3+}$ may be written as

$$[	ext{Ru(III)}]_T = C_1 + C_2$$

from equation (7)

$$[	ext{Ru(III)}]_T = \frac{k_{-3} C_2}{k_3 [\text{Cl}]} + C_2$$

or

$$[	ext{Ru(III)}]_T = C_2 \left[ \frac{k_{-3}}{k_3 [\text{Cl}]} + 1 \right]$$

or

$$C_2 = \frac{k_3 [\text{Cl}][\text{Ru(III)}]_T}{k_{-3} + k_3 [\text{Cl}]} \quad ....(8)$$

From equation (6) and (8), we know from the above fundamental rate equation

$$\text{Rate} = k_4 C_2 [S_3]$$
\[
\text{Rate} = k_4 \times \frac{k_3 [\text{Cl}^-] [\text{Ru(III)}]_{T} k_1 k_2 [H^+][S] \quad (k_3 + k_3 [\text{Cl}^-]) (k_{-1} k_{-2} + k_{-2} k_1 [H^+] + k_1 k_2 [H^+])}
\]

or

\[
\text{Rate} = \frac{k_1 k_2 k_3 k_4 [\text{Cl}^-] [\text{Ru(III)}]_{T} [H^+][S] \quad (k_3 + k_3 [\text{Cl}^-]) (k_{-1} k_{-2} + k_1 k_2 [H^+] + k_1 k_2 [H^+])}
\]

\[
\text{Rate} = \frac{K_S [\text{Cl}^-] [\text{Ru(III)}]_{T} [H^+][S] \quad (k_3 + k_3 [\text{Cl}^-]) (k_{-1} k_{-2} + k_1 k_2 [H^+] + k_1 k_2 [H^+])}
\]

where \(K_S = k_1 k_2 k_3 k_4\)

The rate law (10) derived, clearly shows zero order at lower concentration of KBrO\(_3\) as well as in higher concentration. The first order dependence on each of [RuCl\(_3\)] and [Substrate] which are cyclopentanone and cyclohexanone is also depicted in the rate law.
The rate law (10) also shows positive effects of both [Cl] and [H⁺] on the reaction rate. Negligible effect of ionic strength of medium is obvious as it does not exist in rate law (10).

Equation (10) can also be written as:–

\[
\frac{1}{\text{rate}} = \frac{k_{-1} k_2 k_3}{K_s [\text{Cl}][\text{Ru(III)}]_T [H^+] [S]} + \frac{k_1 k_2 k_{-3} [H^+]}{K_s [\text{Cl}][\text{Ru(III)}]_T [H^+] [S]}
\]

\[
+ \frac{k_1 k_2 k_3 [H^+]}{K_s [\text{Cl}][\text{Ru(III)}]_T [H^+] [S]} + \frac{k_{-1} k_2 k_3}{K_s [\text{Ru(III)}]_T [H^+] [S]} + \frac{k_1 k_2 k_3}{K_s [\text{Ru(III)}]_T [S]}
\]

\[
+ \frac{k_1 k_2 k_3}{K_s [\text{Ru(III)}]_T [S]}
\]

OR

\[
\frac{1}{\text{rate}} = \frac{k_{-1} k_2 k_3}{K_s [\text{Cl}][\text{Ru(III)}]_T [H^+] [S]} + \frac{k_1 k_2 k_{-3}}{K_s [\text{Cl}][\text{Ru(III)}]_T [S]}
\]

\[
+ \frac{k_1 k_2 k_3}{K_s [\text{Cl}][\text{Ru(III)}]_T [S]} + \frac{k_{-1} k_2 k_3}{K_s [\text{Ru(III)}]_T [H^+] [S]} + \frac{k_1 k_2 k_3}{K_s [\text{Ru(III)}]_T [S]}
\]

\[
+ \frac{k_1 k_2 k_3}{K_s [\text{Ru(III)}]_T [S]}
\]
Or

\[
\frac{1}{\text{rate}} = \frac{k_a}{K_S [\text{Cl}][\text{Ru(III)}][H^+][S]} + \frac{k_b}{K_S [\text{Cl}][\text{Ru(III)}][S]}
\]

\[
+ \frac{k_c}{K_S [\text{Cl}][\text{Ru(III)}][S]} + \frac{k_a}{K_S [\text{Ru(III)}][H^+][S]} + \frac{k_b}{K_S [\text{Ru(III)}][S]}
\]

\[
+ \frac{1}{k_4 [\text{Ru(III)}][S]}
\]

\[
\ldots\ldots \text{(11)}
\]

where \( k_a = k_{-1} k_{-2} k_{-3} \)

\( k_b = k_1 k_{-2} k_3 \)

\( k_c = k_1 k_2 k_{-3} \)

\( K_S = k_1 k_2 k_3 k_4 \)

According to equation (11) if a plot is made between \((1 / \text{rate})\) and \((1 / [\text{Cl}])\) a positive intercept on the y-axis is obtained which gives the value of constant (Fig. 13-G).

Similarly a plot of \((1 / \text{rate})\) vs. \((1 / [H^+])\) again gives a straight line having positive intercept on the y-axis which gives the value of other constant (Fig. 13-H).
On substituting the values of [S], [Ru(III)] and others, the value of constants have been calculated for both the substrate which have been presented in the following table:

### 13.71. Evaluation of constants in Ru(III) catalysed oxidation of cyclic ketones by KBrO₃ in acidic medium.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Substrate</th>
<th>Value of intercept</th>
<th>Value of $\frac{k_a}{K_S \times 10^{-3}} + \frac{k_b}{K_S} + \frac{1}{k_4}$</th>
<th>Value of intercept</th>
<th>Value of $\frac{k_b+k_c}{K_S \times 10^{-3}} + \frac{k_b}{K_S} + \frac{1}{k_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclopentanone</td>
<td>$0.215 \times 10^7$</td>
<td>1.238</td>
<td>$0.176 \times 10^7$</td>
<td>1.01</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexanone</td>
<td>$0.255 \times 10^7$</td>
<td>1.469</td>
<td>$0.265 \times 10^7$</td>
<td>1.53</td>
</tr>
</tbody>
</table>
Figure 13G

Plot of $\frac{1}{(-\frac{dc}{dt})}$ vs. $\frac{1}{[KCl]}$ at 35°C

$[\text{KBrO}_3] = 1.00 \times 10^{-3} \text{ M}$  
$[\text{Hg(II)}] = 1.25 \times 10^{-3} \text{ M}$  
$[\text{Ru(III)}] = 14.40 \times 10^{-6} \text{ M}$  
$[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$  
$[\text{Cyclopentanone}] = 4.00 \times 10^{-2} \text{ M}$ (A)  
$[\text{Cyclohexanone}] = 4.00 \times 10^{-2} \text{ M}$ (B)
Plot of $1 / (-dc/dt)$ vs. $(1/[\text{HClO}_4])$ at 35°C

$[\text{KBrO}_3] = 1.00 \times 10^{-3}$ M
$[\text{Hg(OAc)}_2] = 1.25 \times 10^{-3}$ M
$[\text{Ru(III)}] = 14.40 \times 10^{-6}$ M
$[\text{KCl}] = 1.00 \times 10^{-3}$ M

$[\text{Cyclopentanone}] = 4.00 \times 10^{-2}$ M (A)
$[\text{Cyclohexanone}] = 4.00 \times 10^{-2}$ M (B)
13.8. Calculation of different activation parameters (thermodynamic).

In this chapter an attempt has been made to calculate different activation parameters (thermodynamic) such as specific rate constant ($k_r$), entropy of activation ($\Delta S^*$), enthalpy of activation ($\Delta H^*$), free energy of activation ($\Delta G^*$) and Arrhenius factor ($A$).

Transition state theory gives the equation for specific rate constant ($k_r$) (i.e. rate constant of reaction when concentration of each of the reactants is unity at a given temperature) as:

$$k_r = \frac{kT}{h} \times K^* \quad \ldots \ldots (i)$$

where ($kT / h$) is known as the universal frequency factor and its value depends on temperature, while it is independent of the nature of reactant and type of reaction. $K^*$ is the equilibrium constant for the process of formation of an activated complex which is regarded as a normal molecule.

The equilibrium constant $K^*$ is related to the free energy change ($\Delta G^*$) of the formation of activated complex by the following thermodynamic expression:

$$\Delta G^* = -RT \ln K^* \quad \ldots \ldots (ii)$$
But \[ \Delta G^* = \Delta H^* - T\Delta S^* \]  \hspace{1cm} \text{(Gibbs Helmholtz equation)} \hspace{1cm} \ldots ..(iii)

Thus \[ \Delta H^* - T\Delta S^* = -RT \ln K^* \]

Or \[ \ln K^* = -\left( \frac{\Delta H^*}{RT} \right) + \left( \frac{T\Delta S^*}{RT} \right) \quad \ldots ..(iv) \]

Or \[ K^* = e^{-\left( \frac{\Delta H^*}{RT} \right)} e^{\left( \frac{T\Delta S^*}{R} \right)} \quad \ldots ..(v) \]

From equation (i) and (v)

\[ k_r = \frac{kT}{h} e^{-\left( \frac{\Delta H^*}{RT} \right)} e^{\left( \frac{T\Delta S^*}{R} \right)} \quad \ldots ..(vi) \]

According to van’t Hoff equation

\[ \frac{d \ln K^*}{dt} = \frac{\Delta E^*}{RT^2} \quad \ldots ..(vii) \]

Taking logarithm of equation (i) :-

\[ \ln k_r = \ln \left( \frac{k}{h} \right) + \ln T + \ln K^* \]

Differentiating above equation with respect to temperature, we get :-
\[
\frac{d \ln k_r}{dt} = \frac{1}{T} + \frac{d \ln K^*}{dt} \quad \text{........(viii)}
\]

By putting the value of \(d \ln K^*/dt\) from equation (vii) to equation (viii) we get

\[
\frac{d \ln k_r}{dt} = \frac{1}{T} + \frac{\Delta E^*}{RT^2}
\]

\[
\frac{d \ln k_r}{dt} = \frac{RT + \Delta E^*}{RT^2} \quad \text{........(ix)}
\]

From Arrhenius equation

\[
\ln k_r = \ln A - \frac{E_a}{RT} \quad \text{........(x)}
\]

Differentiating above equation

\[
\frac{d \ln k_r}{dt} = \frac{E_a}{RT^2} \quad \text{........(xi)}
\]

by equation (ix) and (xi)

\[
\frac{RT + \Delta E^*}{RT^2} = \frac{E_a}{RT^2} \quad \text{........(xi)}
\]
Or \( \Delta E^* = E_a - RT \) 

...........(xii)

In terms of \( \Delta H^* \)

\[ \Delta H^* = (E_a - RT) + P \Delta V^* \] 

...........(xiii)

Since for solutions \( \Delta V^* = 0 \)

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

...........(xiv)

Substituting \( \Delta H^* \) value in equation (vi)

\[ k_r = \frac{kT}{h} \cdot e^{-\frac{E_a}{RT}} e^{\frac{\Delta S^*}{R}} \]

By taking logarithm and solving

\[ \frac{\Delta S^*}{4.576} = \log k_r - 10.573 - \log T + \frac{E_a}{4.576} \]

all values are in calories.

From above equation \( \Delta S^* \) can be calculated. It has unit Cal deg\(^{-1}\) mol\(^{-1}\).
And others

(i) $\Delta H^* = E_a - RT$
(ii) $\Delta G = \Delta H - T\Delta S$

(iii) $k_r = \left(-\frac{dc}{dt}\right) / [KBrO_3]^{n_1} [S]^{n_2} [\text{Ru(III)}]^{n_3} [H^+]^{n_4}$

(iv) $\log A = \log k_r + \left(\frac{E_a}{2.303RT}\right)$
13.81. Activation parameters of Ru(III) catalysed oxidation of Polyhydric alcohols and Cyclic ketones by potassium bromate in acidic media.

<table>
<thead>
<tr>
<th>S.No</th>
<th>SUBSTRATE</th>
<th>$\Delta E^*$ k J mol$^{-1}$</th>
<th>Temperature Coeff.</th>
<th>$\Delta S^*$ JK mol$^{-1}$</th>
<th>$\Delta H^*$ k J mol$^{-1}$</th>
<th>$\Delta G^*$ k J mol$^{-1}$</th>
<th>log A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ethylene glycol</td>
<td>57.46</td>
<td>2.03</td>
<td>1.16</td>
<td>56.32</td>
<td>55.96</td>
<td>13.25</td>
</tr>
<tr>
<td>2.</td>
<td>Glycerol</td>
<td>57.45</td>
<td>2.06</td>
<td>0.50</td>
<td>56.94</td>
<td>56.81</td>
<td>10.19</td>
</tr>
<tr>
<td>3.</td>
<td>Erythritol</td>
<td>58.05</td>
<td>2.01</td>
<td>1.07</td>
<td>56.48</td>
<td>57.00</td>
<td>11.34</td>
</tr>
<tr>
<td>4.</td>
<td>Dulcitol</td>
<td>58.80</td>
<td>2.02</td>
<td>1.52</td>
<td>57.29</td>
<td>56.83</td>
<td>12.58</td>
</tr>
<tr>
<td>5.</td>
<td>Cyclopentanone</td>
<td>55.92</td>
<td>1.99</td>
<td>0.87</td>
<td>60.07</td>
<td>58.63</td>
<td>13.06</td>
</tr>
<tr>
<td>6.</td>
<td>Cyclohexanone</td>
<td>56.05</td>
<td>2.01</td>
<td>1.03</td>
<td>58.35</td>
<td>57.50</td>
<td>12.88</td>
</tr>
</tbody>
</table>
The entropy of activation plays an important role in case of reactions between ions or neutral molecules forming ions. When reaction takes place between two oppositely charged ions, there is generally an entropy decrease (i.e. less disorder and $\Delta S^* = -ve$, so frequency of collision will also increase resulting in rapid reaction) going from reactants to activated complex but on the other hand, when it take place between two similar charged ions, there is an entropy increase (i.e. more disorder and $\Delta S^* = +ve$, so the frequency of collision will decrease, resulting in a slow reaction.)

But when reaction between ions or neutral molecules forming ions, occur in solution, then in terms of solvation of ions, the entropy for different reactions can be explained as follows. It is well known that solvation of an ion in general increase with decrease in size (smaller ions are highly solvated) and increase charge on the ion. In case of reaction between two ions of opposite charge, their union forms a neutral molecule which results in a lowering of net charge and due to this, some frozen solvent (such as water molecules frozen around the incipient ions) molecules will be released with an increase in entropy. But on the other hand, when reaction takes place between two similar charged ions, then transition state will be a more highly charged ion, which will be expected to be strongly solvated, so that more solvent molecules will be required than for the separate ions which would lead to decrease in entropy. This is due to desolvation of activated state rather than the reactants.
Hence for the reaction in solution entropy of activation changes with the solvent and it becomes less negative (i.e. increases) while free energy change of activation decreases, as the polarity of solvent increases.

A perusal of table 13.60 shows that high positive value of free energy change of activation ($\Delta G^*$) indicate that the transition state is highly solvated while negative value of entropy of activation ($\Delta S^*$) suggest the formation of an activated complex with a reduction in degree of freedom (i.e. disorderliness decreases) of reactant molecules / ions.
13.9. **Oxidation products in Ru(III) catalysed oxidation of some compounds (polyhydric alcohols and cyclic ketones) by KBrO₃ in acidic medium.**

A. Oxidation products in Ru(III) catalysed oxidation of ethylene glycol, glycerol, erythritol, dulcitol by KBrO₃ in acidic medium.

When various sets of reactions were performed with different [KBrO₃] : [polyhydric alcohol] ratios under different conditions, estimation of unconsumed [KBrO₃] indicated that two moles of KBrO₃ were required to oxidize one mole of each of the substrate in presence of Ru(III) chloride catalyst in acidic medium.

On the basis of equivalence recorded, the stoichiometric equations formulated for the oxidation of polyhydric alcohols may be written as:

(i) For **ethylene glycol** (C₂H₆O₂)

\[
\begin{align*}
CH₂OH & \quad + \quad 2 \ BrO₃^- \quad \xrightarrow{RuCl₃} \quad COOH \\
CH₂OH & \quad [H^+] \quad \xrightarrow{[H^+]} \quad 2 \ BrO₂^- + H₂O
\end{align*}
\]

(ethylene glycol) \hspace{2cm} (glycollic acid)
(ii) For glycerol \((C_3H_8O_3)\)

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{COOH} \\
\text{CHOH} + 2\text{BrO}_3^- & \quad \text{CHOH} + 2\text{BrO}_2^- + \text{H}_2\text{O} \\
\text{CH}_2\text{OH} & \quad \text{CHOH} \\
\end{align*}
\]

\((\text{glycerol})\) \quad \text{(glyceric acid)}

(iii) For erythritol \((C_4H_{10}O_4)\)

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{COOH} \\
\text{CHOH} + 2\text{BrO}_3^- & \quad \text{CHOH} + 2\text{BrO}_2^- + \text{H}_2\text{O} \\
\text{CH}_2\text{OH} & \quad \text{CHOH} \\
\end{align*}
\]

\((\text{erythritol})\) \quad \text{(erythronic acid)}
(iv) For dulcitol \((C_6 H_{14} O_6)\)

\[
\text{CH}_2\text{OH} \quad \text{COOH} \\
\text{CHOH}_4 + 2 \text{BrO}_3^- \quad \text{RuCl}_3 \quad \text{H}^+ \\
\text{CH}_2\text{OH} \quad \text{BrO}_2^- + \text{H}_2\text{O}
\]

(dulcitol) (galactonic acid)

The corresponding mono carboxylic acids were detected by conventional methods.\(^{(18)}\)
13.9. Oxidation products in Ru(III) catalysed oxidation of cyclopentanone and cyclohexanone in acidic media.

Further various sets of experiments were carried out with different KBrO$_3$ and substrate ratio under different conditions. Determination of unconsumed KBrO$_3$ indicated that one mole of KBrO$_3$ was consumed to oxidize one mole of each cyclopentanone and cyclohexanone catalysed by acidic solution of Ru(III) chloride and accordingly (i.e. on the basis of number of equivalents) following stoichiometric equations could be formulated for oxidation of above mentioned substrates.

(i) For cyclopentanone ($C_5H_8O$)

\[
\begin{align*}
\text{(cyclopentanone)} & \quad \text{RuCl}_3 + 2\text{BrO}_3^- + \text{H}^+ \rightarrow \text{(cyclopentane 1, 2 dione)} \\
\end{align*}
\]
(ii) For cyclohexanone (C₆H₁₀O)

\[
\begin{array}{c}
\begin{array}{c}
C \end{array} \\
\begin{array}{c}
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\end{array}
\end{array}
\begin{array}{c}
\text{+ 2 BrO}_3^- \\
[\text{H}^+] \\
\rightarrow \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\end{array}
\begin{array}{c}
\begin{array}{c}
C = O \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{+ 2 BrO}_2^- + \text{H}_2\text{O} \\
\end{array}
\end{array}
\end{array}
\]

(cyclohexanone) \rightarrow \text{ cyclohexane 1, 2 dione)

The end products (the corresponding diketones) were identified by TLC followed by conventional spot test analysis\(^{(18)}\) and also through their ninitrophenylhydrazine (DNP) derivative.\(^{(19)}\)