SUMMARY

N-bromosuccinimide [1-9] and potassium iodate [10-14] have been earlier used as oxidants in number of reactions but, so far, literature on kinetics of oxidation of 1,2-propanediol (Propylene glycol), and crotonic acid (CA) by N-bromosuccinimide (NBS), and potassium iodate using Ir(III), Ru(III) and Osmium(VIII) as catalyst has not been reported. Therefore in the present thesis, an attempt has been made to study the kinetics and mechanism of Ir(III) and Ru(III) catalysed oxidation of propylene glycol by NBS in acidic and alkaline medium as well as Os(VIII) promoted potassium iodate oxidation of CA in alkaline solution. The thesis has been presented in seven chapters.

Chapter–I deals with the fundamental definitions and classification of the chemical kinetics. A brief account of redox systems have been given along with survey of literature.

Chapter–II contains the details of materials used, method of investigation and stoichiometry of the reaction and product analysis.

The thesis comprises of two parts: Part – A and Part - B

Part – A includes chapter-III and chapter–IV

Chapter–III contains Mechanistic studies of aquachloroiridium(III) catalysis in the oxidation of 1,2-propanediol by N-bromosuccinimide in acidic medium

Chapter–IV contains Mechanistic studies of Ruthenium(III) catalysed oxidation of 1,2-propanediol by acidic solution of N-bromosuccinimide.

Part – B contains three chapters, viz., chapter-V, chapter VI and chapter-VII
Chapter–V includes Mechanistic study of Osmium(VIII) promoted oxidation of crotonic acid by aqueous alkaline solution of potassium iodate.

Chapter–VI deals with the Kinetic and mechanistic study of Iridium(III) catalysed oxidation of 1,2-propanediol by N-bromosuccinimide in alkaline medium.

Chapter–VI deals with the Kinetic and mechanistic study of oxidation of 1,2-propanediol by aqueous alkaline solution of N-bromosuccinimide in the presence of aquachloro-complex of Ruthenium (III) used as homogeneous catalyst.

1. Kinetic results observed in Ir(III) catalysed N-bromosuccinimide oxidation of 1, 2-propanediol in aqueous acidic medium

Following are kinetic observations made in the title reaction.

1. The title reaction shows zero-order kinetics with respect to N-bromosuccinimide used as oxidant.
2. First order tending to zero order kinetics with respect to 1,2-propanediol has been observed.
3. In case of Iridium (III) chloride used as catalyst first-order kinetics at lower [Ir(III)] tends to zero-order at its higher concentrations.
4. Negative effect of [HClO₄] variation on the rate was observed.
5. Successive addition of each of mercuric acetate and succinimide (NHS) showed negligible effect on the rate of reaction.
6. Negative effect of added KCl on the rate was observed.
7. Negligible effect of ionic strength of medium on the rate was observed.
8. Marked effect of rise in temperature on the rate was observed.
Elucidation of reaction mechanism and rate law

Considering NBS as such and [IrCl₅(H₂O)]²⁻ as oxidizing and potential catalytic species respectively along with other observed kinetic results the following reaction scheme for the Ir(III) catalysed oxidation of 1,2-propanediol by acidic NBS is suggested.

**Scheme-1**

\[
\begin{align*}
[\text{IrCl}_6]^{3-} + \text{H}_2\text{O} & \xrightleftharpoons{K_1} [\text{IrCl}_5(\text{H}_2\text{O})]^2- + \text{Cl}^- \quad \text{(i)} \\
\text{C}_2 + \text{OH}^-\text{CH} \xrightarrow{K_2} [\text{Cl}_5\text{Ir} - \text{O} - \text{CH}]^{2-} + \text{H}_2\text{O} \quad \text{(ii)} \\
[\text{Cl}_5\text{Ir} - \text{O} - \text{CH}]^{2-} & \xrightarrow{K_3} [\text{Cl}_5\text{Ir} - \text{O} - \text{CH}]^{3-} + \text{H}^+ \quad \text{(iii)} \\
\text{C}_4 + \text{H}_2\text{O} & \xrightarrow{\text{kd}} \text{Cl}_4\text{Ir} \left(\text{O} - \text{CH} \right) \text{H}_2\text{O} + \text{Cl}^- \quad \text{(iv)}
\end{align*}
\]

\[
\begin{align*}
[\text{CH}_2 - \text{O} - \text{H}]^{2-} + \text{Br}^- \xrightarrow{\text{Ir} - \text{N}} [\text{CH}_2\text{OH}]^{2-} + \text{Br}^- \quad \text{(V)}
\end{align*}
\]
Considering the above reaction steps the rate of the reaction may be written in terms of rate of loss of concentration of NBS as
\[ -\frac{d \text{[NBS]}}{dt} = \frac{k_d K_1 K_2 K_3 [\text{Ir (III)}]_T [S]_T}{[H^+]} \left( K_1 + [Cl^-] \right) + K_1 K_2 \left( K_3 [S] + [H^+] [\text{Ir (III)}]_T \right) \]

The rate law fully explains all the observed kinetic results. Zero effect of variation of ionic strength of the medium is in agreement with slow and rate determining step (iv) which involves interaction between negatively charged species and a dipole.

2. **Kinetic results observed in Ru(III) catalysed N-bromosuccinimide oxidation of 1, 2-propanediol in aqueous acidic medium**

Following are kinetic observations made in the title reaction.

1. The title reaction shows first-order kinetics with respect to N-bromosuccinimide used as oxidant.
2. Zero order kinetics with respect to 1, 2-propanediol has been observed.
3. In case of Ruthenium (III) chloride used as catalyst first-order kinetics at lower [Ru(III)] tends to zero-order at its higher concentrations.

4. Positive effect of [HClO₄] variation on the rate was observed.

5. Successive addition of each of mercuric acetate and succinimide (NHS) showed negligible effect on the rate of reaction.

6. Positive effect of added KCl on the rate was observed.

7. Negative effect of ionic strength of medium on the rate was observed.

8. Marked effect of rise in temperature on the rate was observed.

**Elucidation of reaction mechanism and derivation of rate law**

In view of positive effect of chloride ion and hydrogen ion on the rate of Ru (III) chloride catalysed oxidation of 1,2-propanediol by acidic solution of N-Bromosuccinimide (NBS or >NBr) and other kinetic results, the following reaction steps are suggested:

```
| RuCl₃(H₂O)(C₁) | RuCl₆(C₂) |
-----------------|-----------|
| 2+ + Cl⁻       | 3+ + H₂O  |

NBr + H⁺ → NBr⁺

RuCl₆(C₃) + H⁺ → RuCl₅(H₂O)²⁻ + Cl⁻
```

**Summary**
Considering the above reaction steps, the rate of the reaction may be written in term of rate of loss of [NBS]:

\[
\frac{-d[NBS]}{dt} = \frac{3 k K_1 k_2 [NBS]_T [Ru(III)]_T [H]^+ [Cl^-]}{1 + K_2 [H^+] \{k_{-2}(1 + K_1 [Cl^-]) + k K_1 [Ru(III)]_T [Cl^-]\}}
\]

The rate law shows all the observed kinetics with respect to all the reactants. It also shows zero order in 1,2-propanediol and zero effect of addition of each of succinimide (the reduction product of NBS) and mercuric acetate (used as bromide ion scavenger). The negative effect of variation of ionic strength of the medium is also in agreement with the slow and rate determining step (iii) which involves interaction between oppositely charged reactive species.

3. **Kinetic results observed in Os(VIII) promoted oxidation of crotonic acid by Potassium iodate in aqueous alkaline medium**

Following are kinetic observations made in the title reaction.

1. The title reaction shows zero-order kinetics with respect to Potassium iodate (KIO₃) used as oxidant.
2. In case of crotonic acid (CA) used as reducing agent first-order kinetics at lower [CA] tends to zero-order at higher concentrations.
3. First-order kinetics with respect to catalyst osmium tetroxide has been observed.
4. Accelerating effect of [OH ] variation on rate of the reaction was observed.
5. Zero effect of ionic strength of medium on the rate was observed.
6. Marked effect of rise in temperature on the rate was observed.
**Elucidation of reaction mechanism and derivation of rate law**

The following reaction steps in the scheme 1 are suggested on the basis of reactive species of Os(VIII) and KIO₃ in alkaline medium and other kinetic results obtained in the oxidation of crotonic acid by alkaline potassium iodate.

\[
\begin{align*}
[\text{OsO}_3(\text{OH})_3]^1^- + \text{OH}^- & \quad \overset{K_1}{\rightleftharpoons} \quad [\text{OsO}_4(\text{OH})_2]^2^- + \text{H}_2\text{O} \quad \text{..........................................................(I)} \\
[\text{OsO}_4(\text{OH})_2]^2^- + \text{CA} & \quad \overset{K_2}{\rightleftharpoons} \quad [\text{OsO}_4(\text{OH})_2.\text{CA}] \quad \text{..........................................................(II)} \\
[\text{OsO}_4(\text{OH})_2]^2^- + \text{IO}_3^- & \quad \overset{K_3}{\rightleftharpoons} \quad [\text{OsO}_4(\text{OH})_2.\text{IO}_3]^{1-} \quad \text{..........................................................(III)} \\
[\text{OsO}_4(\text{OH})_2.\text{CA}] + 2\text{H}_2\text{O} & \quad \overset{\text{kd slow}}{\underset{\text{H}}{\rightarrow}} \quad [\text{OsO}_2(\text{OH})_4]^2^- + \text{H}_3\text{C-C-C-COOH} \quad \text{..........................................................(IV)} \\
\text{H}_3\text{C-C-C-COOH} + \text{IO}_3^- & \quad \overset{\text{fast}}{\rightarrow} \quad \text{CH}_3\text{CHO} + \text{CHO} + \text{IO}_2^- + \text{H}_2\text{O} \quad \text{..........................................................(V)} \\
[\text{OsO}_2(\text{OH})_4]^2^- + \text{IO}_2^- & \quad \overset{\text{fast}}{\rightarrow} \quad [\text{OsO}_4(\text{OH})_2]^2^- + \text{IO}^- + \text{H}_2\text{O} \quad \text{..........................................................(VI)} \\
\text{CH}_3\text{CHO} + \text{IO}^- & \quad \overset{\text{fast}}{\rightarrow} \quad \text{CH}_3\text{COOH} + \text{I}^- \quad \text{..........................................................(VII)} \\
\end{align*}
\]

By considering the above mechanistic steps final rate law can be written as:

\[
\text{Rate} = \frac{-d[\text{KIO}_3]}{dt} = \frac{\text{kd} K_1 K_2 [\text{CA}][\text{OH}^-][\text{Os(VIII)}]_T}{1 + K_1 K_2 [\text{CA}][\text{OH}^-]}
\]

The rate law clearly explains the observed kinetics with respect of [CA], [OH⁻]. Absence of [KIO₃] on the right side of equation clearly indicates zero order with respect to potassium iodate. The observed decrease in rate at higher [Os(VIII)] is due to slight formation of the complex,
[Os(VIII).IO$_3^-$ (Step III) which seems to be involved either in the fast step or inactive. The slow step (IV) involves a dipole (H$_2$O) indicating negligible effect of ionic strength of the medium on the rate of the reaction. Hence the proposed mechanism seems to be valid.

4. Summary of kinetic results observed in Ir(III) catalysed oxidation of 1,2-propanediol by alkaline solution of N-bromosuccinimide.

The following kinetic results were observed.

1. First-order kinetics with respect to N-bromosuccinimide was observed in oxidation of 1,2-propanediol.
2. Zero-order kinetics with respect to 1,2-propanediol was observed.
3. First order kinetics with respect to Ir(III) chloride was observed.
4. Variation of [NaOH] shows positive effect on the rate of reaction.
5. Addition of sodium perchlorate was found to have zero effect on the rate of reaction.
6. Addition of various concentrations of potassium chloride decreases rate of reaction significantly, showing thus negative effect of chloride ions on rate of reaction.
7. Successive addition of mercuric acetate, and succinimide (NHS) did not bring about significant change in the rate of the reaction.
8. Rate of the reaction increased markedly with rise of temperature.

Elucidation of reaction mechanism and derivation of rate law

In the light of reactive species of N-bromosuccinimide and Ir(III) chloride in alkaline solution as NBS itself and [IrCl$_2$(OH)(H$_2$O)$_3$] respectively, statement regarding the role of Hg(OAc)$_2$ in the reaction and on the basis
of all other observed kinetic results the following reaction scheme-1 is suggested.

\[
\begin{align*}
\text{[IrCl}_3\text{(H}_2\text{O)}_3\text{]} + \text{OH}^- & \xrightleftharpoons[k_1]{K_1} \text{[IrCl}_2\text{(OH)}(\text{H}_2\text{O)}_2\text{]} + \text{Cl}^- \quad \text{(I)} \\
\text{NBr} + \text{C}_2 & \xrightarrow[k{\text{slow}}]{\text{slow}} \text{[Cl}_2\text{Ir(OH)}(\text{H}_2\text{O)}_2\text{]} + \text{H}_2\text{O} \quad \text{(II)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH} + \text{CHOH} + \text{[Cl}_2\text{Ir(OH)}(\text{H}_2\text{O)}_2\text{]} & \xrightarrow{\text{slow}} \text{[Cl}_2\text{Ir(OH)}(\text{H}_2\text{O)}_2\text{]} + \text{H}_2\text{O} \quad \text{(III)}
\end{align*}
\]

\[
\begin{align*}
\text{HO} + \text{H}_2\text{O} & \xrightarrow{\text{slow}} \text{[Cl}_2\text{Ir(OH)}(\text{H}_2\text{O)}_2\text{]} + \text{H}_2\text{O} \quad \text{(IV)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{CHO} + \text{HCHO} + \text{HBr} & \xrightarrow{\text{slow}} \text{[Cl}_2\text{Ir(OH)}(\text{H}_2\text{O)}_2\text{]} + \text{H}_2\text{O} \quad \text{(V)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CHO} & \xrightarrow{\text{NBS /Ir(III) /OH}^-} \text{CH}_3\text{COOH} + \text{NH} + \text{HBr} \quad \text{(VI)}
\end{align*}
\]

\[
\begin{align*}
\text{HCHO} & \xrightarrow{\text{NBS /Ir(III) /OH}^-} \text{HCOOH} + \text{NH} + \text{HBr} \quad \text{(VII)}
\end{align*}
\]

The rate of the reaction may be written in terms of rate of loss of [NBS] in the light of aforesaid reaction scheme.

\[
\frac{-d[\text{NBS}]}{dt} = \frac{k_1 k [\text{NBS}][\text{OH}^-][\text{Ir (III)}]_T}{k_{-1} [\text{Cl}^-] + k_1 [\text{OH}^-]}
\]

The rate law agrees well with all the observed kinetic results. It also explains zero effect of ionic strength of the medium indicating dipole – dipole interaction which is evident from the slow step (II).
5. Summary of kinetic results observed in Ru(III) catalysed N-bromosuccinimide oxidation of 1, 2-propanediol in aqueous alkaline medium

Following are kinetic observations made in the title reaction.

1. The title reaction exhibits first-order kinetics at lower [NBS] tending to zero order at its higher concentrations.

2. First order kinetics with respect to reducing agent 1, 2-propanediol has been observed.

3. In case of Ruthenium (III) chloride used as catalyst first-order kinetics was observed.

4. Positive effect of [OH\textsuperscript{-}] variation on the rate was observed in its concentration range from $0.50 \times 10^{-2}$ to $1.33 \times 10^{-2}$ mol dm\textsuperscript{-3} and after reaching a maximum constant effect was observed from $2.00 \times 10^{-2}$ to $5.00 \times 10^{-2}$ mol dm\textsuperscript{-3} [OH\textsuperscript{-}] ions.

5. Successive addition of each of mercuric acetate and succinimide (NHS) showed negligible effect on the rate of reaction.

6. Positive effect of added KCl on the rate was observed.

7. Negligible effect of ionic strength of medium on the rate was observed.

8. Marked effect of rise in temperature on the rate was observed.

**Elucidation of reaction mechanism and derivation of rate law**

In view of positive effect of chloride ion and first tending to zero effect of hydroxide ion (OH\textsuperscript{-}) on the rate of Ru (III) chloride catalysed oxidation of 1,2-propanediol by alkaline solution of N-bromosucccinimide (NBS or >NBr) and other kinetic results, the following reaction steps are suggested:
\[
\begin{align*}
\text{RuCl}_2(H_2O)_2OH + OH^- & \rightleftharpoons K_1 \text{RuCl}_2(H_2O)(OH)_2^- + H_2O \quad \text{(i)} \\
\text{RuCl}_2(H_2O)(OH)_2^- + Cl^- & \rightleftharpoons k_2 \text{RuCl}_3(H_2O) Cl^- + OH^- \quad \text{(ii)} \\
\text{RuCl}_3(H_2O) Cl^- + >\text{NBr} & \rightleftharpoons K_3 \left[ \text{OH}(H_2O) Cl\text{Ru} - \text{N} \right] + H_2O \quad \text{(iii)}
\end{align*}
\]

Where >NBr is N-bromosuccinimide (NBS)

\[
\begin{align*}
\left[ \text{OH}(H_2O) Cl\text{Ru} - \text{N} \right]^+ + \text{CH}_2\text{OH} & \xrightarrow{kd \text{ slow}} \left[ \text{OH}(H_2O) Cl\text{Ru} - \text{N} \right]^+ + \text{Cl}^- \quad \text{(iv)} \\
\left[ \text{OH}(H_2O) Cl\text{Ru} - \text{N} \right]^+ & \xrightarrow{+ \text{H}_2\text{O}} \left[ \text{OH}(H_2O) Cl\text{Ru} - \text{O} \right] + \text{NH} \quad \text{(v)} \\
\left[ \text{OH}(H_2O) Cl\text{Ru} - \text{O} \right] & \xrightarrow{+ \text{H}_2\text{O}} \left[ \text{OH}(H_2O) Cl\text{Ru} - \text{OH} \right] + \text{HCl} \quad \text{(vi)} \\
\text{H}_2\text{C} - \text{OH} & \xrightarrow{\text{HCl} - \text{O} - \text{Br}} \text{H}_2\text{C} - \text{CHO} + \text{HCHO} + \text{HBr} \quad \text{(vii)} \\
\text{CH}_3\text{CHO} & \xrightarrow{\text{Ru}(III)/NBS OH} \text{CH}_3\text{COOH} \quad \text{(viii)} \\
\text{HCHO} & \xrightarrow{\text{Ru}(III)/NBS OH} \text{HCOOH} \quad \text{(ix)}
\end{align*}
\]
By considering the above mechanistic steps, final rate law can be written as:

\[
\frac{-d [\text{NBS}]}{dt} = \text{rate} = \frac{3 \ kd \ k_2 \ K_1 \ K_3 [\text{NBS}][\text{Ru(III)}][\text{Cl}^-][\text{OH}^-][1,2 - \text{propanediol}]}{k_3 [\text{NBS}] + k_2 K_1 [\text{OH}^-][\text{Cl}^-]}
\]

The rate law shows all the observed kinetics with respect to all the reactants. It also shows first order in NBS and Ru(III), positive effect of chloride ions, positive effect of hydroxide ion and zero effect of addition of each of succinimide (the reduction product of NBS) and mercuric acetate (used as bromide ion scavenger).
REFERENCES


