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The present studies incorporate a detailed investigations of kinetics and mechanism of oxidation of some organic compounds by hexacyanoferrate(III) in alkaline medium in presence of ruthenium(III) as catalyst.

The whole thesis has been divided in four parts on the basis of kinetics being followed by the substrates used.

(A) In the first part of the thesis, a detailed kinetic study of the ruthenium(III) catalysed oxidation of formaldehyde and acetaldehyde by hexacyanoferrate(III) in alkaline medium have been investigated. The results obtained are summarised as follows.

1. The rate of oxidation followed first order dependence with respect to each oxidant, reducing substrate and catalyst. However, the order of reaction with respect to reducing substrate decreased from unity in case of formaldehyde.

2. In both system studied, the rate of oxidation is independent in alkali concentration. The added hexacyanoferrate(II) and neutral salt (NaClO₄) has no effect on the rate of oxidation.

3. The reactions were also studied at various temperatures and the E_{act} were calculated in each case.

4. On the basis of observed kinetic data, following common mechanism has been suggested,
(1)

\[
R\overset{\text{O}}{\underset{\text{H}}{\text{C}}}{\overset{\text{OH}}{\text{H}}} + [\text{Ru(III)(OH)}]^{2+} \xrightleftharpoons[k_2]{k_2} \text{Complex(C}_2\text{)}^{2+} + \text{H}_2\text{O}
\]

(hydrated form)

\[(\text{C}_2\text{)}^{2+} + \text{Fe(CN)}_6^{3-} \xrightarrow{k_3} \text{RCOOH} + \text{Ru(II)} + \text{Fe(CN)}_6^{4-} + \text{H}^+ \]

\[\text{Ru(II)} + \text{Fe(CN)}_6^{3-} \xrightarrow{\text{fast}} \text{Ru(III)} + \text{Fe(CN)}_6^{4-} \]

where \( R = \text{H} \) and \( \text{CH}_3^- \) for formaldehyde and acetaldehyde respectively.

By applying steady state conditions with respect to intermediate (C₂), the rate law equation was obtained as

\[- \frac{d}{dt} [\text{Fe(CN)}_6^{3-}] = \frac{2K_2 k_3 [F][\text{Ru(III)}]_T [\text{Fe(CN)}_6^{3-}]}{1 + k_2[F]} \]

where \( K_2 = \frac{k_2}{k_2} \)

The above rate equation (4) successfully predicts all the experimental results.

B. In the second part of thesis, the kinetics of ruthenium(III) catalysed oxidation of ethylamine, n-butylamine and isopropylamine by alkaline hexacyanoferrate(III) have been investigated. The results obtained, are summarised briefly as follows.

1. The reactions follow first order dependence in each hexacyanoferrate(III), ruthenium(III) and amines.
2. The effect of \( \text{OH}^- \), added hexacyanoferrate(II), and salt on the rate of oxidation was negligible in each case.
3. The reactions were studied at various temperatures and 
$E_{\text{act}}$ were calculated.

4. On the basis of observed kinetic data, the following 
mechanism has been proposed.

$$
R \xrightarrow[C]{H} + [\text{Ru(III)(OH)}]^{2+} \xrightarrow{\text{Complex (C$_2$)$_2^+$}} (A) \xrightarrow{(C_1)}
$$

$$(C_2)^{2+} + \text{Fe(CN)$_6^3-$} \xrightarrow{k_5} R' \rightarrow C^+ - \text{NH}_2 + \text{Ru(II)} + \text{H}_2\text{O}
+ \text{Fe(CN)$_6^{4-}$} (2)
$$

$$
\text{Ru(II)} + \text{Fe(CN)$_6^3-$} \xrightarrow{k_6 \text{ fast}} \text{Ru(III)} + \text{Fe(CN)$_6^{4-}$} (3)
$$

$$
R \rightarrow C^+ - \text{NH}_2 + \text{OH}^- \xrightarrow{\text{fast}} \text{Product} + \text{NH}_3 (4)
$$

where $R = \text{CH}_3$ and $R' = \text{H}$ for ethylamine

$R = R' = \text{CH}_3$ for isopropylamine and

$R = \text{CH}_3\text{CH}_2\text{CH}_2$ and $R' = \text{H}$ for n-butylamine.

By applying steady state condition with respect to 
intermediate (C$_2$), the rate law equation has been obtained as

$$
- \frac{d}{dt} [\text{Fe(CN)$_6^{3-}$}] = \frac{2k_4 k_5 [A][\text{Ru(III)}]_T [\text{Fe(CN)$_6^{3-}$}]}{k_4 + k_5 [\text{Fe(CN)$_6^{3-}$}]} (5)
$$

At lower $[\text{Fe(CN)$_6^{3-}$}]$ where $k_4 \gg k_5 [\text{Fe(CN)$_6^{3-}$}]$, the 
rate law equation (5) becomes,

$$
- \frac{d}{dt} [\text{Fe(CN)$_6^{3-}$}] = \frac{2 k_4 k_5}{k_4} [A][\text{Ru(III)}]_T [\text{Fe(CN)$_6^{3-}$}] (6)
$$
The above rate law (6) successfully predicts all the experimental facts.

(C) In this part of the study, the kinetics of ruthenium(III) catalysed oxidation of 2- aminoethanol, 3-amino propanol, diethanolamine and triethanolamine by hexacyano ferri rate(III) in alkaline medium have been investigated. The results are summarised briefly in following paragraphs.

1. The reactions followed almost similar kinetics. The order of reaction with respect to oxidant was found to be two while that was unity in both the reducing substrate and alkali.

2. The second order dependence with respect to ruthenium(III) was observed in case of 2-aminoethanol and 3-amino propanol whereas in case of diethanolamine and triethanolamine, the order of reaction with respect to ruthenium(III) was unity.

3. The effects of hexacyanoferrate(II) and ionic strength on reaction rate have been found to be negligible.

4. The reactions were also investigated at various temperatures and $E_{act}$ were calculated in each case.

5. On the basis of observed kinetic data, the following mechanism has been suggested for 2-aminoethanol and 3-amino propanol.

\[\text{(Aminoalcohol)} + 2[\text{Ru(III)(OH)}]^{2+} \xrightarrow{k_3} X + \text{OH}^- \]  

(1)

\[X + \text{Fe(CN)}_6^{3-} \xleftrightarrow{k_3} \text{Y (Complex)} \]

(2)
\[
Y + \text{Fe(CN)}_{6}^{3-} \xrightarrow{k_{5}} \text{Product} + 2\text{Fe(CN)}_{6}^{4-} + 2 \text{Ru(III)}
\]

By applying steady state conditions with respect to intermediates \([X]\) and \([Y]\), the rate law was obtained as,

\[
-\frac{d}{dt} \left[ \text{Fe(CN)}_{6}^{3-} \right] = \frac{2k_{3}k_{4}k_{5}K^{2}[A][\text{OH}^{-}]^{2}[\text{Ru(III)}]^{2}[\text{Fe(CN)}_{6}^{3-}]^{2}}{k_{3}k_{4}[\text{OH}^{-}] + k_{4}k_{5}[\text{Fe(CN)}_{6}^{3-}]^{2}}
\]

(4)

At lower \([\text{Fe(CN)}_{6}^{3-}]\) where \(k_{3}k_{4}[\text{OH}^{-}] \gg k_{4}k_{5}[\text{Fe(CN)}_{6}^{3-}]\), equation (4) reduce to,

\[
-\frac{d}{dt} \left[ \text{Fe(CN)}_{6}^{3-} \right] = 2k_{5}k_{3}K_{4}K^{2}[A][\text{OH}^{-}][\text{Ru(III)}]^{2}[\text{Fe(CN)}_{6}^{3-}]^{2}
\]

(5)

where \(K_{3} = k_{3}/k_{3}\)
\[K_{4} = k_{4}/k_{4}\]

The above rate law equation (5) successfully predicts all the experimental facts.

The mechanism for oxidation of diethanolamine and triethanolamine which follow similar kinetics, may be proposed as

\[
(Aminoalcohol) + [\text{Ru(III)}(\text{OH})]^{2+} \xleftrightarrow{k_{13}} X \xrightarrow{k_{13}} X (\text{Complex})
\]

(6)

\[
X + \text{Fe(CN)}_{6}^{3-} \xleftrightarrow{k_{14}} Y (\text{fast})
\]

(7)

\[
Y + \text{Fe(CN)}_{6}^{3-} \xrightarrow{k_{15}} 2\text{Fe(CN)}_{6}^{4-} + \text{Ru(III)} + \text{Products(Intermediate)}
\]

(8)
By applying steady state conditions with respect to intermediates \([X]\) and \([Y]\), the rate law equation was obtained as

\[
\frac{d}{dt} [\text{Fe(CN)}_{6}^{3-}] = \frac{2K_{13}k_{14}k_{15}[A][OH^-][\text{Ru(III)}][\text{Fe(CN)}_{6}^{3-}]^2}{k_{13}k_{14} + k_{14}k_{15} [\text{Fe(CN)}_{6}^{3-}]^2}
\]  

Further, at lower \([\text{Fe(CN)}_{6}^{3-}]\) where \(k_{13}k_{14} \gg k_{14}k_{15}[\text{Fe(CN)}_{6}^{3-}]^2\) may be taken as suitable approximation, the above equation (9) reduce to

\[
\frac{d}{dt} [\text{Fe(CN)}_{6}^{3-}] = 2K_{13}k_{14}k_{15}[A][OH^-][\text{Ru(III)}][\text{Fe(CN)}_{6}^{3-}]^2
\]  

where \(K_{13} = k_{13}/k_{14}\)
\(K_{14} = k_{14}/k_{13}\)

D. In the last part of study, the kinetics of ruthenium(III) catalysed oxidation of 2-aminoethanol, 3-aminopropanol, diethanolamine and triethanolamine by cerium(IV) in sulphuric acid medium have been investigated. The kinetic results are briefly summarised as follows.

1. The rate of oxidation was independent to cerium(IV) concentrations while that was directly proportional to [ruthenium(III)] and [substrate].

2. The order of reaction with respect to acid was unity in case of 2-aminoethanol and 3-aminopropanol while in case of diethanolamine and triethanolamine, the effect of acid concentration on the rate of oxidation was negligible.
3. Addition of a salt (NaClO₄) showed a slight positive effect in case of 2-aminoethanol, and 3-aminopropanol while a negligible effect has been observed in case of diethanolamine and triethanolamine.

4. Added cerium(III) had no effect on the reaction rate in each case.

5. The reactions were also investigated at various temperatures and $E_{act}$ and $\Delta S^\neq$ were obtained in each case.

6. It has been observed that ruthenium(III) converted to ruthenium(VIII) rapidly and quantitatively, therefore, on the basis of this fact and experimental results, the mechanism for oxidation of 2-aminoethanol and 3-aminopropanol has been proposed as follows.

$$S + H^+ \overset{\text{fast}}{\rightleftharpoons} SH^+$$ (1)

$$SH^+ + \text{Ru(VIII)} \overset{k_3}{\rightleftharpoons} \text{Intermediate} + H^+ \text{ (rds)}$$ (2)

$$\text{Intermediate} \overset{\text{fast}}{\longrightarrow} F^+ + NH_3 + H^+ + \text{Ru(VII)}$$ (3)

$$F^+ + \text{Ce(IV)} \overset{\text{fast}}{\longrightarrow} \text{Products} + H^+ + \text{Ce(III)}$$ (4)

$$\text{Ru(VII)} + \text{Ce(IV)} \overset{\text{fast}}{\longrightarrow} \text{Ru(VIII)} + \text{Ce(III)}$$ (5)

where $S = \text{aminoalcohol}$ and $F^+ = \text{free radical}$.

On the basis of above mechanism, the following rate law equation has been obtained,

$$-\frac{d}{dt} [\text{Ce(IV)}] = 2 k_3 K_2 [H^+] [S] [\text{Ru(III)}]$$ (6)

where $k_4 >> k_3[H^+]$ has been taken as suitable approximation.

The rate law equation (6) is in agreement with the experimental results.
The mechanism for oxidation of diethanolamine may, therefore, be proposed as

\[ S + Ru(\text{VIII}) \xrightleftharpoons{\text{fast}} \overset{(rds)}{\rightarrow} \text{Intermediate} \]  
(7)

\[ \text{Intermediate} \overset{\text{fast}}{\rightarrow} 2F^- + NH_3 + 2H^+ + Ru(\text{VI}) \]  
(8)

\[ F^- + Ce(\text{IV}) \xrightarrow{\text{fast}_{\text{HOH}}} \text{Product} + H^+ + Ce(\text{III}) \]  
(9)

\[ Ru(\text{VI}) + Ce(\text{IV}) \xrightarrow{\text{fast}} Ru(\text{VII}) + Ce(\text{III}) \]  
(10)

\[ Ru(\text{VII}) + Ce(\text{IV}) \xrightarrow{\text{fast}} Ru(\text{VIII}) + Ce(\text{III}) \]  
(11)

In case of triethanolamine, the step (8) can be replaced by step (12)

\[ \text{Intermediate} \overset{\text{fast}}{\rightarrow} 3F^- + NH_3 + 2H^+ + Ru(V) \]  
(12)

Ruthenium(V) formed in step (12) converted back to ruthenium(VIII) with cerium(IV) via formation of ruthenium(VI) and ruthenium(VII) in the fast steps.

The rate law equation for oxidation of diethanolamine and triethanolamine in general was obtained as

\[ -\frac{d}{dt} [Ce(\text{IV})] = k[S][Ru(\text{III})] \]  
(13)

The above rate law equation (13) successfully predicts the experimental results.