Chapter-IV

PROBABLE REACTION
MECHANISM AND RATE LAW
MECHANISM OF OXIDATION OF ALCOHOLS IN ABSENCE OF Ru(III)

The oxidation of alcohols by TCICA proceeds smoothly to yield the corresponding carbonyl compounds as a product. The reactions are not complicated by any product oxidation or chlorination. However, it was observed that the reaction provides smooth kinetics only in the presence of chloride ions. Under these conditions, the most important details needed for the postulation of a probable mechanism for the oxidation are as under.

1. The rate of oxidation exhibits a first order dependence on the concentration of the substrate oxidized and the oxidant TCI.

2. Unlike in the reactions with ketones, $\alpha$ phenols the reactions are largely unaffected by added acid.

3. The reaction in addition to exhibiting smooth kinetics in presence of $\text{Cl}^-$ exhibits to fractional order of dependence on $[\text{Cl}^-]$.

4. The reactions in both series are profoundly affected by the presence of polar substituents in the benzene ring-electron-releasing substituents retarding it considerably.

5. A decrease in solvent dielectric constant decreases the rate.

6. The oxidation of benzhydrol exhibit an isotope of fact $k_H/k_D$, 2.28 at 30°C.

\[
\text{rate} = k[\text{TCI}] [R_2\text{CHOH}] [\text{Cl}^-] 0.5 \text{ to } 0.
\]

In view of the solubility considerations of the oxidant and the substrates, the use of 80% HOAc as solvent has been considered. Under these conditions the TCI exists in the following equilibrium.

\[
\text{N} - \text{Cl} + H^+ \rightleftharpoons \text{N}^+ \text{Cl} \] ........................ (2)
Probable Reaction Mechanism and Rate Law

For the purpose of convenience TCI has been represented as \( \text{N} - \text{Cl} \) as there are three such groups in every molecule. Both the unprotonated as well as the protonated forms can serve as the oxidants but at different rates. This kinetics is in the conditions when no Cl\(^{-}\) was added.

In the presence of added Cl\(^{-}\), the following reaction sets in

\[
\text{N}^+\text{Cl}^+ + \text{Cl}^{-} \xrightarrow{k_1} \text{[complex]} \xrightarrow{k_{-1}} \text{N}^+\text{Cl}^+\text{Cl}^{-}
\] ........................ (3)

The complex thus generated is the effective oxidizing agent in a molecular pathway. The following mechanism can be proposed for the oxidation form which the rate law can be derived.

\[
\text{R} + \text{CHOH} \xrightarrow{\text{slow}} \text{C} = 0 + 2\text{HCl} + \text{TCA}
\] ........................ (5)

\[
\text{Rate} = k_2 [\text{complex}]
\] ........................ (6)

On the assumption that all the TCI is reacting as TCIH\(^{+}\),

\[
[\text{complex}] = k \cdot [\text{TCIH}^+] \cdot \text{eq} \cdot [\text{Cl}^-]
\] ........................ (7)

\[
[\text{TCIH}^+] \cdot \text{equation} = [\text{TCIH}^+]\text{total} - [\text{complex}]
\] ........................ (8)

\[
[\text{Complex}] \cdot \{1 + K[\text{Cl}^-]_{\text{eq}}\} = k \cdot [\text{TCIH}^+]\text{total} \cdot [\text{Cl}^-]_{\text{eq}}
\] ........................ (9)

\[
[\text{Complex}] = K \cdot \{ [\text{TCIH}^+]\text{total} - \text{complex} \} \cdot [\text{Cl}^-]_{\text{eq}}
\] ........................ (10)
Probable Reaction Mechanism and Rate Law

Chapter-IV

\[
[\text{complex}] = \frac{k \left[ \text{TCIH}^+ \right]_{\text{total}} [\text{Cl}']_{\text{eq}}}{1 + k[\text{Cl}']_{\text{eq}}} \]

…………………. (11)

Assuming \([\text{Cl}']_{\text{eq}} = [\text{Cl}'] - [\text{complex}] \approx [\text{Cl}']\)

…………………. (12)

\[
[\text{complex}] = \frac{k \left[ \text{TCIH}^+ \right]_{\text{total}} [\text{Cl}']}{1 + k[\text{Cl}']} \]

…………………. (13)

Rate \(= k_2[R_2\text{CHOH}] [\text{complex}] \)

…………………. (06)

\[
= \frac{k_2 [R_2\text{CHOH}] k \left[ \text{TCIH}^+ \right]_{\text{total}} [\text{Cl}']}{1 + k[\text{Cl}']} \]

…………………. (14)

An alternative and simpler explanation to account for the observed kinetics is the following mechanism.

Scheme - II

\[
\begin{align*}
\text{N}^+ - \text{Cl} + \text{H}_3\text{O}^+ &\rightarrow \text{N}^+ - \text{Cl} + \text{H}_2\text{O} \\
\text{N}^+ - \text{Cl} + \text{Cl}^- &\xrightleftharpoons[k_1]{k_-1} \text{SH} + \text{Cl}_2 \quad (\text{SH} = \text{ICA})
\end{align*}
\]

…………………….. (15)

\[
\begin{align*}
\text{ROH} + \text{Cl}_2 &\rightarrow \text{products} \\
\end{align*}
\]

…………………….. (17)

For which the rate expression will be of the form –

\[
\frac{d [\text{products}]}{dt} = \frac{k_1 k_2[R\text{OH}][\text{Cl}'][\text{TCI}]}{k_1[\text{Cl}'] + K_{-1}[\text{TCA}] + k_2[R\text{OH}]} \]

…………………. (18)

This rate law demands a fractional dependence on [ROH] at least in certain concentration ranges which has not been observed over a wide range. Thus, this scheme is in accord with the observed retardation with added TCA.
The mechanism proposed above (Scheme-I) is consistent with all the experimental data obtained in the present investigations. The two most important points that justify this conclusion are.

1. The isotope effect in the oxidation of benzhydrol.

2. The substituent effects on the oxidation rate. The former, although giving a low discrimination ratio of $\approx 2$, shows clearly that $\alpha$-CH bond is being broken in the rate determining step. It is interesting to compare the isotope effect observed in similar oxidations with molecular halogens. Swain et al., while studying the oxidation of propan-2-ol by $\text{Br}_2$ obtained a $k_\text{H}/k_\text{D} \sim 2.0$ and on the basis of an analysis of the substituent effect on the kinetic isotope effect concluded that $\alpha$ C-H bond was being broken with the hydrogen being lost as a hydride ion.

**MECHANISM OF OXIDATION OF ALCOHOLS IN PRESENCE OF Ru(III)**

Under the conditions $[\text{alcohol}] \gg [\text{TCICA}]$ the reaction is zero order in $[\text{TCICA}]$ as revealed by the linear plots of $[\text{TCICA}]$ vs. time. This was further confirmed by repeating it at different initial $[\text{TCICA}]$. The plots in all these cases were linear and parallel to each other. The zero order rate constants ($k_{\text{obs}}$) were calculated from the slopes of such plots. The rate increased considerably with an increase in $[\text{alcohol}]$ and the order with respect to $[\text{alcohol}]$ was found to be fractional. (Fig. 3,4,9,10,15,16,21,22,27,28).

The Michaelis-Menten type of plot of $1/k_{\text{obs}}$ vs $1/[\text{substrate}]$ was linear with an intercept indicating the formation of a stable complex involving the substrate. (Fig. 5,6,11,12,17,18,23,24,29,30) The rate increased considerably in the presence of trace amounts of Ru(III) and the order with respect to [Ru(III)] was found to be unity.

The rate constants at different $[\text{H}^+]$ indicate that $[\text{H}^+]$ has no effect on the rate of the reaction. For example under the conditions of $[\text{TCICA}] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{EtOH}] = 0.400 \text{ mol dm}^{-3}$, $[\text{Ru(III)}] = 1.50 \times 10^{-6} \text{ mol dm}^{-3}$ [HOAc] = 20 vol. % at 308 K, the rate constants ($k_{\text{obs}}$ in $\text{mol dm}^{-3} \text{ s}^{-1}$) were found to be 1.20, 1.23, 1.24 and 1.21 for the $[\text{H}^+]$ of 0.100, 0.200, 0.300 and 0.400 mol dm$^{-3}$ respectively.
The reactions were carried out at various solvent compositions and the rate constants decreased with increasing percentage of acetic acid in the reaction mixture. A plot of log $k_{obs}$ vs. $1/D$ was linear with a negative slope indicating the involvement of a dipole and negative ion in the rate-determining step. (Fig. 73, 74, 79, 80, 85, 86, 91, 92, 97, 98).

No polymerization was observed when acrylonitrile was added to the reaction system indicating the absence of free radicals. The rate of the reaction is not affected by the addition of $[\text{Cl}^-]$ ion to the system. The rates ($k_{obs}$ = 107 mol dm$^{-3}$ s$^{-1}$) observed in the case of ethanol are 1.32, 1.33, 1.31, 1.33 at 0.005, 0.100, 0.15, 0.20 mol dm$^{-3}$ of $[\text{KCl}]$, respectively.

4.1 CONCLUSION

The observed zero order in TCICA shows that it is not involved in the rate determining step. The fractional order in substrate indicates that probably it is known to form complexes with the organic substrates. Even though there is no direct evidence for the formation of alcohol-[Ru(III)] complex, the kinetic evidence for such a complex is obtained by the $1/k_{obs}$ vs. $1/[\text{alcohol}]$ plot. It is therefore, not unreasonable to assume the formation of a complex between Ru(III) and alcohol, before it decomposes to products in the rate-determining step. The results are in acceptance with the observed results by some authors$^{110,194}$.

TCICA generally undergoes hydrolysis in aqueous acidic medium producing various types of species such as dichloroisocyanuric acid (DCICA), monochloroisocyanuric acid (MCICA), isocyanuric acid (ICA), HOCI, $\text{H}_2\text{OCl}$, etc. As TCICA is involved in a fast step its speciation will not affect the rate of the reaction. Therefore, it is not important which one of the above species act as reactive ones. However, from the values of the hydrolysis constant of TCICA, it is seen that the predominant species is HOCI which may enter into protonation equilibria giving $\text{H}_2\text{OCl}^+$. The reactive species may therefore be assumed to be HOCI and $\text{H}_2\text{OCl}^+$.

Based on the above experimental observations the following mechanism is proposed.
The probable reaction mechanism and rate law for the reaction are as follows:

\[
\begin{align*}
\text{Cl}_2\text{N-} & \text{N} - \text{Cl} \quad + \quad \text{OH}_2 \quad \xrightarrow{K_{h1}} \quad \text{Cl}_2\text{N=OCl} \\
\text{(TCICA)} & \quad \text{fast} \quad \quad \quad \quad \quad \quad \quad \quad \text{fast} \quad \quad \quad \quad \quad \quad \quad \quad \text{(DCICA)}
\end{align*}
\]

The reaction mechanism is as follows:

1. \( R - \text{CH}_2\text{OH} + \text{Ru(III)} \rightarrow [\text{Ru(III)}\text{-alcohol}] \text{ complex} \) (fast)
2. \([\text{Ru(III)}\text{-alcohol}] \text{ complex} \rightarrow R - \text{C}^+\text{H-OH} + [\text{Ru(III)}\text{H}^2+] \) (slow)
3. \( R - \text{C}^+\text{H-OH} \rightarrow R - \text{CHO} + \text{H}^+ \) (fast)
4. \([\text{Ru(III)}\text{H}^2+] + \text{HOCI} \rightarrow \text{Ru (III)} + \text{Cl}^- + \text{H}_2\text{O} \) (fast)

From the above mechanism, the following rate law can be derived:

\[
-\frac{d[\text{TCICA}]}{dt} = \frac{K_2k_3[\text{alcohol}][\text{Ru(III)}]}{1+K_2[\text{alcohol}] + K_3[\text{Ru(III)}]} = k_o k_s 
\]

Since \([\text{RuCl}_3]\) is very small (10^{-6} \text{ mol dm}^3) compared to \([\text{alcohol}] \) (10^{-1} \text{ mol dm}^3), it could be neglected in the denominator.

Thus

\[
-\frac{d[\text{TCICA}]}{dt} = \frac{K_2k_3[\text{alcohol}][\text{Ru(III)}]}{1+K_2[\text{alcohol}]} = k_o k_s 
\]

Equation 3 explains all the experimental results. The reciprocal of eq. 3 gives

\[
\frac{1}{k_o} = \frac{1}{K_2k_3[\text{alcohol}][\text{Ru(III)}]} + \frac{1}{k_3[\text{Ru(III)}]} 
\]

From eq. 4, a straight line is expected upon plotting 1/k_o Vs. 1/[alcohol] at constant [Ru(III)]. From the slope and the intercept of such plots, the disproportionation rate constant \(k_3\) and the formation constant \(K_2\) of the complex were calculated.
For ethanol $k_3$ and $K_2$ were found to be $0.222 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ and $3.00 \text{ dm}^3 \text{ mol}^{-1}$, respectively.

The isokinetic temperature ($\beta$) calculated from the plot of $\Delta H^*$ vs. $\Delta S^*$ is found to be $286.60 \text{ K} \ (r = 0.930)$ which is well below the experimental temperature range (308-323K) used in the present study, suggesting that the reactions are entropy controlled. This value of $\beta$ was also tested and found genuine by applying Exner's criterion. The isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and changes in both $\Delta H^*$ and $\Delta S^*$ values. The constancy in the $\Delta G^*$ values for all the alcohols studied indicate that probably a similar mechanism is operative in all the cases. The negative $\Delta S^*$ values indicate that the activated complex is more rigid compared to the reactants. The similar type of results has been observed.$^{95,96,111}$