Discussion
In this chapter, the kinetic results of the oxidation of amino acids i.e. glycine, alanine, valine, proline by vanadium (v) in the absence as well as presence of micelle with vanadium (iv) in moderately concentrated sulphuric acid medium under study are summarised and their behaviours towards oxidation is discussed.

General Behaviour of Reaction

The oxidation of α-amino acid in the absence and in presence of cationic micelles i.e. cetyltrimethyl ammonium bromide (CTAB) with vanadium (v) in aqueous sulphuric acid medium is measurable. The reaction follow first order kinetics with respect to oxidant and substrate while second order dependent to $[H^+]^2$.

Order of Reaction

Dependence of Rate on Initial Concentration of Oxidant

Vanadium(v) oxidation of all the four amino acids was examined at different initial concentration of oxidant and at constant concentration of other reactants in the absence and in the presence of micelles. Under each condition it was observed that reactions follow first order kinetics at each concentration of oxidant.

In the presence of CTAB, the value of rate constant increases with increase in the concentration of oxidantant. The values of pseudo-first order rate constant obtained from the integrated rate equation are nearly constant. Concentration-time plot showed the linear relation in each concentration of oxidant for each amino acid in absence as well as presence of micelles.

Dependence of Rate on Concentration of α-Amino Acids.

The effect of variation of the initial concentration of amino acid was studied and it was observed that the reaction obey first order, rate equations at all the
concentration of amino acids. In the absence as well as presence of micelle, the pseudo-first order rate constant increases with increase in the concentration of substrate. The values of $k_2$ (second order rate constant) obtained by $k_0$ and $k_m$ versus [amino acid] were found to be reasonably constant. A linear plot between log $k_0$ and log $k_m$ versus log [amino acid] with nearly unit slope values was obtained for each amino acid. The double reciprocal plot between $k_0$ and $k_m$ versus [amino acid] shows, linearity slightly positive intercept. From the above findings following conclusion was made -

1. For each amino acid, in absence and in presence of micelles, the order with respect to substrate is one.

2. The small positive intercept of double reciprocal plot may be attributed to the formation of highly unstable complex. However, if any complex is formed between substrate and vanadium (V); its formation constant is extremely small.

Dependence of Rate on Sulphuric Acid Concentration

The effect of variation in the concentration of sulphuric acid on the reaction rate was examined at different initial concentrations of acid and at constant ionic strength. It was found that without sufficient concentration of the acid the oxidation of amino acid is very slow, therefore, oxidation was carried out at acid concentration $\gg 5.0$ M. The plot of $k_0$ and $k_m$ versus [H$_2$SO$_4$]$^2$ for each amino acid is linear passing through origin. The slope value of these plots are nearly two suggest that order with respect to acid is two. The Zucker-Hammett plots (log $k_0$ and $k_m$ versus - H$_0$) (Fig. 3.08, 4.08, 5.08 and 6.08) and log $k_0$ and log $k_m$ versus log [H$^+$] were found linear. This shows that the reaction was acid catalysed even in the presence of another catalyst, the surfactant. The linear plots were obtained between log $k_0$ + H$_0$ and log $k_\text{A}^+$ H$_0$ against log a$_{H_2O}$, log $k_0$ - log [Acid]
and log \( k_m - \log [\text{Acid}] \) versus \( \log a_{H_2O} \) and \{log \( k_0 - \log [H^+] \) and log \( k_m - \log [H^+] \) - \( H_0 \) versus \( a_{H_2O} \)\} with slope values of 1.89 and respectively. Thus as the plots were found linear and looking to the respective slope values, according to Bunnett’s hypothesis the water molecule should act as proton abstracting agent in the rate determining stage, the values of order of reaction with respect to different reactant in absence and in presence of micelles are recorded in (Table - 8.01).

<table>
<thead>
<tr>
<th>Reactants</th>
<th>o.w.r. to [V(v)]</th>
<th>o.w.r to [Substrate]</th>
<th>o.w.r. to [H+]</th>
<th>Total order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine + V(v)</td>
<td>1 1</td>
<td>1 1</td>
<td>2 2</td>
<td>4 4</td>
</tr>
<tr>
<td>Alanine + V(v)</td>
<td>1 1</td>
<td>1 1</td>
<td>2 2</td>
<td>4 4</td>
</tr>
<tr>
<td>Valine + V(v)</td>
<td>1 1</td>
<td>1 1</td>
<td>2 2</td>
<td>4 4</td>
</tr>
<tr>
<td>Proline + V(v)</td>
<td>1 1</td>
<td>1 1</td>
<td>2 2</td>
<td>4 4</td>
</tr>
</tbody>
</table>

From the Table 8.01 it is obvious that the order of reaction with oxidant and substrate is one while the order with respect to the acid is two, thus the rate expression should be of the following from:

\[
\text{Rate} = k_1 [V(v)] \cdot [\text{Substrate}] \cdot [H^+]^2
\] ——— (1)

When substrate is taken in excess equation (1) reduces to;

\[
\text{Rate} = k_2 [V(v)] [H^+]^2
\] ——— (2)

where \( k_2 = \frac{k_1}{[\text{Substrate}]} \)

Similarly when substrate and acid are much large in comparision to the oxidant concentration eq (2) can be written as

\[
\text{Rate} = k_3 [V(v)]
\]
Where \( k_3 = \frac{k_2}{[H^+]^2} \)

The values of \( k_1, k_2 \) and \( k_3 \) are calculated in this manner for glycine, alanine, valine and proline.

**Effect of Acrylonitrile on the Reaction Rate**

Acrylonitrile is well known as a free radical scavenger [294]. The oxidation of the substrate was carried out in the presence of acrylonitrile. The reaction results in the formation of a dense polymer. In control reactions, when the substrate absent, no polymer formation was observed. The induced polymerisation of acrylonitrile indicates the formation of free radicals during the course of the reaction. This is consistent with the one electron oxidation by \( V(\nu) \).

**Dependence of Rate on the Medium**

The effect of variation in dielectric constant of the medium was investigated by using acetic acid - water binary mixture of different compositions. It is observed that reaction rate increase with increase of solvent concentration. This may be due to the possible interaction of an ion and a dipole. The observed solvent effect (Table 3.13, 4.13, 5.13 and 6.13 & Fig. 3.10, 4.10, 5.10 and 6.01) leads to the reported conclusion. This coupled with the effect of \([H^+]\) on the rates, leads to the conclusion that \( V(OH)_2^{3+} \) is the reactive species of \( V(\nu) \).

**Reactive \( V(\nu) \) Species in Sulphuric Acid**

The effect of \([H^+]\) on the rate of reaction is the main factor which decides the reactive \( V(\nu) \) species in sulphuric acid medium.

In the present study the source of oxidant taken is ammonium meta vanadate which in acid solution acts as -

\[
2H^+ + NH_4VO_3 \rightleftharpoons VO_2^+ + NH_4^+ + H_2O
\]
Thus $VO_2^+$ [295] is the initial species of the oxidant present in the nature of the species varies with the concentration of acid used. Many workers have shown that at low acidity, $VO_2^+$ is present in the following equilibria [296, 297].

$$VO_2^+ + H_3O^+ \rightleftharpoons V(OH)_3^{2+}$$

Whereas at higher acidities it exists as [298].

$$VO_2^+ + 2H^+ \rightleftharpoons V(OH)_2^{3+}$$

It has been observed that when the reaction is first power dependence of the hydrogen ion, the active species in the reaction is $V(OH)_3^{2+}$ whereas, the reaction is second power dependence of the $H^+$, $V(OH)_2^{3+}$ is the potent species of vanadium (v). In the present investigation the second power dependence of the $H^+$ has been observed. The species, therefore, regarded as $V(OH)_2^{3+}$. The fact is also confirmed from our kinetic data that amino acid is resistive to the oxidation at low acidity i.e. below 4.0 M.

In fact these species when present in sulphuric acid they form 1:1 or 1:2 complex with bisulphate ion. Littler and Water mentioned various other complexes with sulphate ion. In the oxidation of cyclohexanol with $V$(v) according to them the sulphate ion acts as a chelating ligand, and compared it with that observed in case of Ce (iv) oxidation. Ashok Kumar and Mehrotra [299] have proposed that linear dependence of rate on $HSO_4^-$ results to the species [VO$_2$ HSO$_4$]. Santappa and Saccubai [300] observed a linear dependence of rate on $HSO_4^-$ in the case of propyl alcohol, sorbitol, diglycolic acid and teta hydrofurane and propoed $[V(OH)_3 HSO_4]^+$ to be the reactive species in addition to $V(OH)_3^{2+}$. The second order dependence of rate on [$H^+$] in case of $\alpha$-phenyl ethyl alcohol with $V$(v). Venkatsubramanian [301] has postulated $V(OH)_2^{3+}$ and $[V(OH)_2 HSO_4]^{2+}$ to be
the active oxidising species. In our case rate is first power dependence with $\text{HSO}_4^-$, therefore, the potent oxidising species of vanadium may be considered as $[\text{V(OH)}_2\text{HSO}_4]^2^+$. 

Mehrotra suggested, in the case of oxidation of propane-1,3-diol, butane-1,3-diol and butane-1,4-diol with vanadium (v), a similar oxidising species.

**Reactive Species of Amino Acid in Sulphuric Acid**

It is well known that, depending on the $[\text{H}^+]$ of the solution, amino acid can exist either as cation, zwitter ion or anion [302]

\[
\begin{align*}
\text{NH}_2\text{CHR COOH} & \rightleftharpoons \text{NH}_3\text{CHR COO}^- \\
\text{Zwitter ion} & \\
\text{acidic} \quad \text{NH}_3\text{CHR COO}^- + \text{H}^+ & \rightleftharpoons \text{NH}_3\text{CHR COOH} \\
\text{Cation} & 
\end{align*}
\]

Many workers reported this mechanism [303, 304].
Mechanism for Oxidation of Amino Acids in Absence of Micelle

The above observation leads to the following mechanism.

\[
\begin{align*}
\text{VO}_2^{+} + 2H^+ & \xrightleftharpoons{K_1} \text{V(OH)}_2^{3+} \\
\text{V(OH)}_2^{3+} + \text{HSO}_4^- & \xrightleftharpoons{K_2} \left[\text{V(OH)}_2 \text{HSO}_4^{2+}\right] \\
\left[\text{V(OH)}_2 \text{HSO}_4^{2+}\right] + \text{H}_3\text{N}^+ \cdot \text{CHR} - \text{C} - \text{OH} & \xrightleftharpoons{K_3} \\
\end{align*}
\]

Intermediate (I)

\[
\begin{align*}
\text{I} + \text{H}_2\text{O} & \xrightarrow{k_1, \text{Slow}} \text{H}_3\text{N}^+ - \text{CHR} - \text{C} - \text{O}^- + \text{V(IV)} + \text{H}_3\text{O}^+ \\
\text{free radical formation} \\
\text{H}_3\text{N}^+ - \text{CHR} - \text{C} - \text{O}^- + \text{V(V)} & \xrightarrow{\text{fast, decarboxylation}} \text{CO}_2 + \text{V(IV)} \\
\end{align*}
\]

\[
\begin{align*}
\text{NH} & \xrightarrow{\text{fast, deamination}} \text{HCHO} + \text{NH}_3 \\
\end{align*}
\]

The above consumption of vanadium (v) was also supported by stoichiometric studies.

R = Glycine, Alanine, Valine and Proline.
Rate Expression

On the basis of above proposed mechanism the rate expression may be derived as:

\[ \text{VO}_2^+ + 2H^+ \rightleftharpoons V(OH)_2^{3+} \] \hspace{1cm} (1)

\[ V(OH)_2^{3+} + HSO_4^- \rightleftharpoons [V(OH)_2 HSO_4^{2+}] \] \hspace{1cm} (2)

\[ \text{NH}_3 - \text{CHR COOH} + [V(OH)_2 HSO_4^{2+}] \rightleftharpoons \text{Complex} \] \hspace{1cm} (3)

(Very unstable)

Very unstable complex + H_2O \xrightarrow{k_1} \text{free radical} + V(IV) + H_3O^+ \hspace{1cm} (4)

\(X^+\)

\[ X^+ + V(V) \rightarrow \text{Products} \] \hspace{1cm} (5)

Rate = \(k_1\) [Very unstable complex] \hspace{1cm} (6)

From eq (1) \(K_1 = \frac{[V(OH)_2^{3+}]}{[\text{VO}_2^+][H^+]^2}\) \hspace{1cm} (7)

or \([V(OH)_2^{3+}] = K_1 [\text{VO}_2^+][H^+]^2\) \hspace{1cm} (8)

From equation 2

\[ K_2 = \frac{[V(OH)_2 HSO_4^{2+}]}{[V(OH)_2^{3+}][HSO_4^-]} \]

or \([V(OH)_2 HSO_4^{2+}] = K_2 [V(OH)_2^{3+}][HSO_4^-]\) \hspace{1cm} (9)

Complex] = \(K_3 [\text{AA}] [V(OH)_2 HSO_4^{2+}]\) \hspace{1cm} (10)

Substituting value of \([V(OH)_2 HSO_4^{2+}]\) from (9) to eq. (10) and value of \([V(OH)_2^{3+}]\) from 8 to eq 10.
[Complex] = \( K_2 K_3 [AA] [V(OH)_2^3][HSO_4^-] \)

[Complex] = \( K_1 K_2 K_3 [AA] [VO_2^+][H^+]^2 [HSO_4^-] \)

Rate = \( K_1 K_2 K_3 [AA] [VO_2^+][H^+]^2 [HSO_4^-] \) —— (11)

\[
[V(V)]_T = [VO_2^+] + [V(OH)_2HSO_4^{2+}] + [\text{Complex}]
\]

\[
= [VO_2^+] + K_2 [V(OH)_2^3][HSO_4^-] + K_1 K_2 K_3 [AA] [VO_2^+][H^+]^2 [HSO_4^-]
\]

\[
= [VO_2^+] + K_1 K_2 K_3 [VO_2^+][H^+]^2 [HSO_4^-] + K_1 K_2 K_3 [AA] [VO_2^+][H^+]^2 [HSO_4^-]
\]

\[
= [VO_2^+] \left\{ 1 + K_1 K_2 [HSO_4^-][H^+]^2 + K_1 K_2 K_3 [AA] [H^+]^2 [HSO_4^-] \right\}
\]

\[
[VO_2^+] = \frac{[V(V)]_T}{1 + K_1 K_2 [H^+]^2 [HSO_4^-] + K_1 K_2 K_3 [AA] [H^+]^2 [HSO_4^-]}
\]

Substituting the value of \([VO_2^+]\) in eq (11)

\[
\text{Rate} = \frac{k_1 K_2 K_3 [AA] [H^+]^2 [HSO_4^-] [V(V)]_T}{1 + K_1 K_2 [H^+]^2 [HSO_4^-] + K_1 K_2 K_3 [AA] [H^+]^2 [HSO_4^-]}
\]

\[
\frac{\text{Rate}}{[V(V)]_T} = k_{\text{obs}} = \frac{k_1 K_2 K_3 [AA] [H^+]^2 [HSO_4^-]}{1 + K_2 [HSO_4^-] (K_1 [H^+]^2 + K_1 K_3 [AA] [H^+]^2)}
\]

\[
= \frac{k_1 K_2 K_3 [AA] [H^+]^2 [HSO_4^-]}{1 + K_1 [H^+]^2 + K_1 K_2 K_3 [H^+]^2 [HSO_4^-] [AA]}
\]

\[
\frac{\text{Rate}}{[V(V)]_T} = k_{\text{obs}} = \frac{k_1 K_2 K_3 [AA] [H^+]^2 [HSO_4^-]}{1 + K_1 [H^+]^2 + K_1 K_2 [H^+]^2 [HSO_4^-] (1 + K_3 [AA])} —— (12)
\]

According to Well's and Kuritsyn [305] the equilibrium constant for the formation of \( V(OH)_2^3+ \) is very small and so \( K_2 \) may also be assumed to be less than one. Thus, at constant \([V(V)]_T\) equation (12) becomes,

\[
k_{\text{obs}} = k_1 K_1 K_2 K_3 [AA] [H^+]^2 [HSO_4^-] —— (13)
\]
or,

\[ k_{\text{obs}} = k' [AA][H^+]^2[HSO_4^-] \]  \hspace{1cm} (14)

Where \( k' = K_1 K_2 K_3 \)

The rate law (14) corresponds to all the experimental observations negating significant concentration of an intermediate complex.

**Mechanism for Oxidation of Glycine in Presence of Surfactant.**

\[
\begin{align*}
\text{NH}_2 \text{CH}_2 \text{COOH} & \rightleftharpoons \text{NH}_3 \text{CH}_2 \text{COO}^- \quad \hspace{1cm} (1) \\
\text{NH}_3 \text{CH}_2 \text{COO}^- + H^+ & \rightleftharpoons \text{NH}_3 \text{CH}_2 \text{COOH} \quad \hspace{1cm} (2) \\
\text{VO}_2^+ + 2H^+ & \rightleftharpoons \text{V(OH)}_2^{3+} \quad \hspace{1cm} (3) \\
\text{V(OH)}_2^{3+} + \text{HSO}_4^- & \rightleftharpoons [\text{V(OH)}_2\text{HSO}_4^{2+}] \quad \hspace{1cm} (4) \\
\text{Dn} + \text{NH}_3 \text{CH}_2 \text{COOH} & \rightleftharpoons \text{Dn} \cdots \text{NH}_3 \text{CH}_2 \text{COOH} \quad \hspace{1cm} (6)
\end{align*}
\]

\[
\begin{align*}
\text{Dn} \cdots \text{NH}_3 \text{CH}_2 \text{COOH} + [\text{V(OH)}_2\text{HSO}_4^{2+}] & \rightleftharpoons \text{Dn} \cdots \text{NH}_3 \text{CH}_2 \text{COOH} \quad \hspace{1cm} (7)
\end{align*}
\]
Mechanism for Oxidation of Alanine in Presence of Surfactant.

\[
\begin{align*}
\text{NH}_2 (\text{CH}_3) \text{CH COOH} & \rightleftharpoons \text{NH}_3 (\text{CH}_3) \text{CH COO}^- & (1) \\
\text{NH}_3 (\text{CH}_3) \text{CH COO}^- + H^+ & \rightleftharpoons \text{NH}_3 (\text{CH}_3) \text{CH COOH} & (2) \\
\text{VO}^2+ + 2H^+ & \rightleftharpoons \text{V(OH)}^3_2 & (3) \\
\text{V(OH)}^3_2 + \text{HSO}_4^- & \rightleftharpoons [\text{V(OH)}_2\text{HSO}_4^{2-}] & (4) \\
\text{Dn} & \rightleftharpoons K_5 \text{Dn} & (5)
\end{align*}
\]

\[(\text{no. of detergents}) \quad (\text{aggregation, micells})\]

\[
\begin{align*}
\text{Dn} + \text{NH}_3 (\text{CH}_3) \text{CH COOH} & \rightleftharpoons \text{Dn} \cdots \text{NH}_3 (\text{CH}_3) \text{CH COOH} & (6) \\
\text{Dn} + \text{NH}_3 (\text{CH}_3) \text{CH - C} & \rightleftharpoons \text{Dn} \cdots \text{NH}_3 (\text{CH}_3) \text{CH COO}^- + [\text{V(OH)}_2\text{HSO}_4^{2-}] & (7)
\end{align*}
\]
Mechanism for Oxidation of Valine in Presence of Surfactant.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH} - \text{CH} - \text{COOH} \quad \text{Protonation} \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \quad \text{CH} - \text{CH} - \text{COO}^- + \text{H}^+ \quad \text{Protonation} \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \quad \text{CH} - \text{CH} - \text{COO}^- + \text{H}^+ \quad \text{Protonation} \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \quad \text{CH} - \text{CH} - \text{COOH} \quad \text{Protonation} \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \quad \text{CH} - \text{CH} - \text{COOH} \\
\end{align*}
\]

\[
\begin{align*}
\text{VO}_2^+ + 2\text{H}^+ & \rightleftharpoons \text{V(OH)}^3^+ \quad \text{(3)} \\
\text{V(OH)}^3^+ + \text{HSO}_4^- & \rightleftharpoons \text{[V(OH)}_2\text{HSO}_4^{2+}] \quad \text{(4)} \\
\text{nd} \quad \text{(no. of detergents)} \quad \text{K}_s \quad \text{Dn} \quad \text{(micelles)} \quad \text{(5)} \\
\end{align*}
\]
\[
\text{D}_n + \text{H}_3\text{C} \xrightarrow{K_d} \text{CH} = \text{CH} - \text{COOH} \quad \text{H}_3\text{C} \xrightarrow{K_d} \text{CH} - \text{CH} - \text{COOH} \quad \text{NH}_3
\]

\[
\text{H}_3\text{C} \xrightarrow{K_d} \text{CH} = \text{CH} - \text{COOH} + [\text{V(OH)}_2\text{HSO}_4^{2+}] 
\]

Intermediate

\[
\text{H}_3\text{C} \xrightarrow{k_m} \text{CH} = \text{CH} - \text{C} \xrightarrow{\text{H}_2\text{O}} \text{V}^{2+} - \text{OH} \quad \text{O SO}_2\text{OH}
\]

\[
\text{H}_3\text{C} \xrightarrow{\text{fast decarboxylation and deamination}} \text{CHCHO} + \text{CO}_2 + \text{V (IV)} + \text{NH}_3 + \text{D}_n + 2\text{H}^+
\]
Mechanism for Oxidation of Proline in Presence of Surfactant

\[ \text{HO-N-COOH} \rightleftharpoons \text{HO-N-COOH}^- \]  \( \text{(1)} \)

\[ \text{HO-N-COOH} + \text{H}^+ \rightleftharpoons \text{HO-N-COOH}^+ \]  \( \text{(2)} \)

\[ \text{[VO}_2^+\text{]} + 2\text{H}^+ \rightleftharpoons \text{[V(OH)}_2^{3+}\text{]} \]  \( \text{(3)} \)

\[ \text{[V(OH)}_2^{3+}\text{]} + [\text{HSO}_4^-] \rightleftharpoons \text{[V(OH)}_2\text{HSO}_4^{2+}\text{]} \]  \( \text{(4)} \)

\[ \text{(no. of detergents)} \text{ D}_n \rightleftharpoons \text{D}_n \text{ (micelles)} \]  \( \text{(5)} \)

\[ \text{D}_n + \text{HO-N-COOH} \rightleftharpoons \text{D}_n \text{ HO-N-COOH}^+ \]  \( \text{(6)} \)

\[ \text{D}_n \text{ HO-N-COOH}^+ + [\text{V(OH)}_2\text{HSO}_4^{2+}] \rightleftharpoons \text{D}_n \text{ HO-N-COOH} \]  \( \text{(7)} \)
Rate Expression in Presence of CTAB

On the basis of above proposed mechanism the rate expression may be derived as;

Rate law from eq (8)

\[
\frac{d[V(v)]}{dt} = k_m \text{ [Intermediate stage]} [H_2O]
\]  

(10)

By applying law of mass action to equation (4), (6) and (7) we get,

\[
K_2 [V(OH)_{2+}] [HSO_4] = [V(OH)_{2+} HSO_4]^{2+}
\]  

(11)

and,

\[
K_d = \frac{[D_n . . . . . . . . \text{NH}_3 \text{CHR COOH}]}{[\text{NH}_3 \text{CHR COOH}] [D_n]}
\]

\[
K_d [\text{NH}_3 \text{CHR COOH}] [D_n] = [D_n . . . . . . . . \text{NH}_3 \text{CHR COOH}]
\]  

(12)

\[
K_3 = \frac{[\text{Intermediate}]}{[AA][V(OH)_{2+} HSO_4^{2+}]}
\]

\[
K_3 [AA][V(OH)_{2+} HSO_4^{2+}] = [\text{Intermediate}]
\]  

(13)

By putting equation (11), (12) and (13) in equation (10)
\[
\frac{-d[V(v)]}{dt} = k_m K_2 K_3 K_d [D_n] [NH_3 CHR COOH] [V(OH)_2^{3+}] [HSO_4^-] [H_2O]
\]

(14)

By the application of law of mass action the value of 

\([V(OH)_2^{3+}] [HSO_4^-] [H_2O]\)

can be obtained. Thus the surfactant catalysed reaction corresponds to the law:

\[
\frac{-d[V(v)]}{dt} = k_m K_2 K_d [D_n] [NH_3 CHR COOH] [H^{2+}] [VO_2^+] [V(OH)_2 HSO_4^{2+}] [H_2O]
\]

\[
[VO_2^+] = K_2 \frac{[V(OH)_2^{3+}]}{[H^{2+}]}
\]

\[
= k_m k_2 k_s [D_n] [NH_3 CHR COOH] [H^{2+}] [VO_2^+]
\]

\[
[HSO_4^-] = \frac{[V(OH)_2 HSO_4^{2+}]}{k_3 [V(OH)_2^{3+}]} \]

and also from equation (13) it becomes,

\[
\frac{-d[V(v)]}{dt} = k_m K_2 K_d [D_n] [NH_3 CHR COOH] [H^{2+}] [VO_2^+] [V(OH)_2 HSO_4^{2+}] \]

(15)

according to Well's and Kuritsyn the equilibrium constant \(k_2\) for the formation of \([V(OH)_2 HSO_4^{2+}]\) is small then unity. So that equation (15) becomes,

\[
\frac{-d[V(v)]}{dt} = k [D_n] [NH_3 CHR COOH] [H^{2+}] [VO_2^+]
\]

Where \(k = k_m k_d k_s\)

The above rate law is in accordance with experimental findings.

\[R = \text{Glycine, Alanine, Valine and Proline}\]

**Stoichiometry and Reaction Products**

The results of stoichiometry indicated that two mols of oxidant consumed one mole of substrate in case of all amino acids.
The stoichiometric equation for the different substrate can, therefore, be written as follows.

\[
\text{HCH (NH}_2\text{)}\text{COOH} + 2 \text{V(II)} + \text{H}_2\text{O} \rightarrow \text{HCHO} + \text{NH}_3 + \text{CO}_2 + 2 \text{V(IV)} + 2\text{H}^+ 
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH-CH}_2\text{NH}_2 \\
\text{H}_3\text{C}
\end{array}
\]

\[
\text{COOH}\quad \text{2 V(II)} + \text{H}_2\text{O} \rightarrow \text{HCHO} + \text{NH}_3 + \text{CO}_2 + 2\text{H}^+ + 2\text{V(IV)}
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH-CH} \\
\text{H}_3\text{C}
\end{array}
\]

\[
\text{C=O} + \text{CO}_2 + \text{NH}_3 + 2\text{H}^+ + 2\text{V(IV)}
\]

\[
\begin{array}{c}
\text{NH}_2\text{CH}_3\text{CHCOOH} + 2 \text{V(II)} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + \text{NH}_3 + \text{CH}_3\text{CHO} + 2 \text{V(IV)}
\end{array}
\]

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{H}
\end{array}
\]

\[
+ 2 \text{V(II)} + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_6\text{O} + \text{CO}_2 + \text{NH}_3 + 2\text{V(IV)} + 2\text{H}^+
\]

**Influence of Temperature**

The oxidation of all amino acids and vanadium (V) was studied at four different temperatures and the activation parameters were calculated (Table 3.15, 3.16, 4.15, 4.16, 5.15, 5.16 and 6.15, 6.16) from the usual relationship. The activation energy values are found to increase in presence of surfactant in the case of glycine and proline. This indicates that activated complex is more stable in surfactant medium, similarly the decrease of entropy of activation value with CTAB in case of glycine, proline and alanine suggests that the transition state is less compact than that in the absence of surfactant. The large negative value of entropy of activation suggests a rigid transition state and the formation of free radical [306]. \(\Delta G^\dagger\) values for the oxidation of amino acids in the presence
of surfactant are similar to that in the absence of surfactant suggesting that similar mechanism prevails under both the conditions. On the basis of $E_a$ value the order of reactivity of amino acids is in the absence and in presence of surfactant glycine $>$ alanine $>$ valine $>$ proline. In the absence and in presence of surfactant almost similar trend of order of reactivity support similar mechanism involving a transition state.

The Role of Cationic Surfactant in Oxidation of Amino Acids by Vanadium (V).

Interest in the kinetics and mechanism for organic reactions occurring on the surface of micelles formed from ionic detergents has been sharpened by the relation of a relationship between these processes and those which are enzymatic in nature [307].

Cationic micelle i.e. cetyl trimethyl ammonium bromide has also been found to catalyse many has also been found to catalyse many oxidation and reduction reactions [308].

In attempting to elucidate the mechanisms by which enzymes effect catalysis, chemists have expended a great deal of effort in studying mechanism of simpler, model chemical reactions [309]. Among these model have been reactions catalysed with in micelles [310].

The oxidations in presence of micelles have promoted us to further develop earlier studies of certain reactions by attempting to illuminate the scope of catalysis in terms of variation in substrates and detergent structure and to define the dependence of such catalysis on addition parameters including ionic strenght and temperature, such studies ought to bothshed light on the source of the catalytic activity and more closely define the relationship between those relation which occure on the surface of protein and the surfaces of micelles [311].
The rate constants of micelle catalysed reactions when plotted versus detergent concentration give sigmoid shaped curves (Fig. 3.01, 4.01, 5.01 and 6.01). This behaviour is analogous to positive co-operativity in enzymatic reaction.

The plot of \( k_v \) values against [CTAB] shows (Fig. 3.02, 4.02, 5.02 and 6.02) marginal acceleration of rate till around cmc of CTAB but then decreases. The observation may be attributed to increasing solubilisation of the reactant species with increase in [surfactant] which reaches limiting value of cmc. Hence a rate maximum is obtained at cmc. Further increase in [surfactant] results in increase in [micellar phase] thus exerting a dilution effect on the reactant species resulting in gradual decrease of the rate. Observations of this type have been reported by Reinsborough and Robinson [312] in metal complex formation reactions as well as by Bunton and Cerichelli [313] in the oxidation of n-butyl ferrocence by ferric nitrate in the presence of CTAB.

According to Piszkiewicz model the relationship of rate constants to detergent concentration assumes that the micelle \( D_n \), forms a noncovalent complex with the substrate, \( s \), before catalysis may takes place.

\[
D_n + s \quad \xrightleftharpoons{K_D} \quad D_n s \quad \quad (1)
\]

\[
D_n s + V(v) \xrightarrow{k_m} \text{Product} \quad \quad (2)
\]

\[
S + V(v) \xrightarrow{k_o} \text{Product} \quad \quad (3)
\]

\( K_D \) is the dissociation costant of micelle back to its free components.

\[
k_v = \frac{k_m [D]^n + k_o K_D}{K_D + [D]^n} \quad \quad (4)
\]
on rearrangement and its log taken to give

\[ \log \frac{k_v - k_o}{k_m - k_v} = n \log [D] - \log K_o \quad (5) \]

In analysing the kinetic data \( k_m \) is taken as highest value for catalysed reaction and \( k_o \) is the rate of reaction without surfactant. \( k_v \), the rate with any given amount of surfactant concentration with in the given range and \([D]\) is the surfactant concentration of the rate \( k_v \).

According to equation (5) when \( \log (k_v - k_o) / (k_m - k_v) \) was plotted against \( \log [D] \) for each amino acid \( V(v) \) micelle system a straight line was obtained (Fig 3.02, 4.02, 5.02 and 6.02) which justifies the Piszkiewicz model.

From these plots slope 'n' (co-operativity index) intercept \( \log K_o \) and \( \log [D]_{50} \) were evaluated (Table 3.08, 4.08, 508 and 608). The values of “n” in the present study (for all amino acids) were found > 1. It is analogous to positive co-operativity in enzymatic reactions [314]. The values of \( \log [D]_{50} \) demonstrates the existance of submicellar aggregates involving detergent and substrate molecules of varying stoichiometers. Value of \( \log K_o \) also indicate the existance of significant detergent - substrate interaction for all the amino acids.
SAMPLE ID: (null)

POINT PICK
212.0 0.510
289.0 0.484
PEAK PICK