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LIST OF ABSTRACT AND PAPERS
PUBLISHED AND COMMUNICATED

ABSTRACT

1. KINETIC STUDIES ON THE OXIDATION OF LEUCINE BY QUINQUEVALENT VANADIUM IN PRESENCE OF MICELLE FORMING SURFACTANT

Neelu Bhargava, Archna Pandey* and Madhvi Choubey, Proc. of 33rd convention of chemists, CDRM - 27, P.No. 6-5, 1996

2. MECHANISTIC OXIDATION OF GLYCINE BY VANADIUM(V) IN MICELLAR SYSTEM.


3. KINETICS OF OXIDATION OF MONOAMINOMONOCARBOXYLIC BY VANADIUM (V) IN MICELLAR SYSTEM.


4. MICELLAR CATALYSED OXIDATION OF PROLINE BY VANADIUM (V) IN SULPHURIC ACID MEDIUM : A KINETIC AND MECHANISTIC APPORACH.


5. KINETIC OXIDATIVE DEAMINATION DECARBOXYLATION- DL-ALANINE BY QUINQUEVALENT VANADIUM IN MICELLAR SYSTEM,

PAPERS

1. KINETICS OF OXIDATION OF GLYCINE BY VANADIUM (V) IN MICELLAR SYSTEM.
   Madhvi Choubey, Archana Pandey*, Oxi Comm., 1999, 22, 233

2. KINETICS OF OXIDATION OF PROLINE BY VANADIUM (V) IN MICELLAR SYSTEM.

3. KINETIC OXIDATION DEAMINATION DECARBOXYLATION OF GLYCINE BY QUINQUEVALENT VANADIUM IN MICELLAR SYSTEM.

4. Kinetic oxidation Decorboxylation deamination of valine by vanadium (v) in Micellar system.
   Madhvi Choubey, Archana Pandey*, Madhya Bharti (accepted).

5. KINETIC STUDIES ON THE OXIDATION OF VALINE BY QUINQUEVALENT VANADIUM IN PRESENCE OF MICELLE FORMING SURFACTANT.
   Madhvi Choubey, 14th Young Scientist Conference, 1999 to be held at Bhopal (M.P.)

6. KINETIC OXIDATION DECARBOXYLATION DEAMINATION OF MONOAMINO MONO CARBOXYLIC ACID IN MICELLAR SYSTEM.

7. KINETIC OXIDATION DEAMINATION DECARBOXYLATION OF DL-ALANINE BY QUINQUEVALENT VANADIUM IN MICELLAR SYSTEM.

8. KINETICS AND MECHANISTIC OXIDATION OF \(\alpha\)-AMINO ACID BY QUINQUEVALENT VANADIUM IN MICELLAR SYSTEM.
   Madhvi Choubey, Archana Pandey*, Ind. Journal of Chemistry Pub; 3/4 (Sec A 7063)/98. (Communicated).
KINETICS OF OXIDATION OF GLYCINE BY VANADIUM (V) IN MICELLAR SYSTEM

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ABSTRACT

A kinetic study of oxidation of glycine by vanadium (V) in the absence and in the presence of cationic surfactant in sulphuric acid medium has been carried out. The reactions exhibit first order dependence in oxidant and substrate and in the absence and in the presence of surfactant. The reactions are micellar catalyzed. The activation parameters have also been computed. A probable mechanism has been proposed on the basis of experimental results.

Keywords: mechanism, oxidation, micellar medium, glycine.

AIMS AND BACKGROUND

The kinetics of oxidation of ε-amino acid has been studied with many oxidants such as chloramine-T (Ref. 1), peroxomonophosphoric acid², N-bromoacetamide³, hexacyanoferrate⁴, and many metal oxidants⁵–⁶. Earlier we have reported oxidation kinetics of glycine by vanadium (V). The survey of current literature shows that very few electron transfer processes have been studied in the presence of surfactant. Hence in the present communication we report the micellar catalyzed oxidation of glycine by vanadium (V) in sulphuric acid.

EXPERIMENTAL

A stock solution of vanadium (V) was prepared by dissolving ammonium meta vanadate (Lobachemie) in sulphuric acid and was standardized by the usual method. The concentration of H⁺ was also estimated. A solution of glycine (Loba) was prepared by dissolving it in desired concentration of sulphuric acid (BDH). A solution of CTAB was prepared in doubly distilled water. All other chemicals used were of standard grade.

The reactants were kept in a thermostat to attain the desired temperature before the final mixing. The kinetics was followed by estimating the un consumed oxidant by titrating against standard ferrous ammonium sulphate solution using N-phenyl anthranilic acid as an indicator.

The final products of oxidation of glycine by vanadium (V) were found to be aldehyde, ammonia and carbondioxide. The aldehyde was examined by preparing 2,4-dinitro phenyl-1-hydrazine derivative. In a portion of reaction mixture the
solution of sodium hydroxide was added and heated. The smell of ammonia confirmed its formation during the oxidation.

RESULTS

The order in vanadium (V) was found to be one as revealed by the linear plot of 

\[ \log (a-x) \text{ versus time for different initial concentration of oxidant.} \]

The order in [glycine] was found to be unity from the slope values of the linear plot of \( k_{\text{obs}} \) versus [glycine] (Fig. 1).

The reactions are acid catalyzed and the order with respect to [\( H^+ \)] is two. The second order rate constants were determined at different hydrogen ion concentration. The plot of \( k_1 \) versus \([H^+]^2\) was a straight line passing through origin, suggesting that the reactions involved only acid catalyzed independent path. The Zucker-Hammert and Bunett calculations were applied. The plots of \( \log k_1 \) versus \(-H_o\) and \( \log k_1 + H_o \) versus \( a_{H_2O} \) were found to be linear with slope values 3.1 and 1.5, respectively (Figs 2 and 3). A 'W' value of +1.5 suggested the

![Fig. 1. Plot of \( 1/k_{\text{obs}} \) versus \( 1/[\text{glycine}] \)]

![Fig. 2. Plot of \( \log k_1 \) versus \(-H_o\)]

![Fig. 3. Plot of \( \log k_1 + H_o \) versus \( a_{H_2O} \)]
Table 1. Thermodynamic parameters of glycine - V(V) system in the absence and in the presence of surfactant.

<table>
<thead>
<tr>
<th></th>
<th>$E^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^*$ (JK$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta S^*$ (JK$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs. - 24.0</td>
<td>24.7</td>
<td>99.9</td>
<td>398.4</td>
<td></td>
</tr>
<tr>
<td>Pre. - 29.2</td>
<td>24.7</td>
<td>92.8</td>
<td>305.0</td>
<td></td>
</tr>
</tbody>
</table>

participation of a water molecule as proton abstracting agent in the rate determining step.

Kinetics runs have been carried out at different temperatures (25 - 40°C). The values of various thermodynamic parameters have been obtained from the Verheusen plot (Table 1).

DISCUSSION

The initial species of V(V) in acid medium exists as VO$_2^+$ (Ref. 8) and at concentration higher than 4.5 as VO(OH)$_2^+$ (Ref. 9). In sulphuric acid the species VO(OH)$_2$HSO$_4^-$ is known to exist. The nitrogen atom of the amino acid coordinates with V(V) species yielding an unstable complex which in the rate determining step suffers nucleophilic attack by water leading to the formation of intermediate free radical (X) which finally gives the products via deamination and decarboxylation steps.

In the absence of the surfactant: The whole mechanism and rate law has already been studied$^{10}$.

In the presence of the surfactant:

1. $\text{NH}_2\text{CH}_2\text{COOH} \rightarrow \text{NH}_2\text{CH}_2\text{COO}$
2. $\text{NH}_2\text{CH}_2\text{COO}^- + \text{H} \rightarrow \text{NH}_2\text{CH}_2\text{COOH}$
3. $\text{VO}_2^- + \text{2H} \rightarrow \text{VO}$OH$_2^-$
4. $\text{VO(OH)}_2^- + \text{HSO}_4^- \rightarrow \text{VO}$OH$^- + \text{HSO}_4^-$
5. $\text{ND} \leftrightarrow \text{Dn}$ (molecular surfactant)
6. $\text{Dn} + \text{NH}_2\text{CH}_2\text{COOH} \rightarrow \text{Dn} + \text{NH}_2\text{CH}_2\text{COOH}$
7. $\text{Dn} + \text{NH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O} + \text{VO(OH)}_2$HSO$_4^-$ \rightarrow $\text{Dn} + \text{NH}_2\text{CH}_2\text{COOH}$
\[
\text{Dn} \ldots \hat{\text{NH}}_2\text{CH}_2\text{COO}^- + \text{H}_2\text{O}^- + \text{V(IV)} \quad (\text{rate determining step})
\]

\[
\text{Dn} \ldots \hat{\text{NH}}_2\text{CH}_2\text{COO}^- \underset{\text{decarboxylation}}{\longrightarrow} \text{Dn} \ldots \hat{\text{NH}}_2\text{CH}_2^- + \text{CO}_2
\]

\[
\text{Dn} \ldots \hat{\text{NH}}_2\text{CH}_2^- + \text{V(IV)} + \text{H}_2\text{O} \underset{\text{deamination}}{\longrightarrow} \text{Dn} + \text{HCHO} + \text{NH}_3 + 2\text{H}^+ + \text{V(IV)}
\]

From equation (7) it follows

\[
\frac{d[V(V)]}{dt} = k_1[Dn \ldots \hat{\text{NH}}_2\text{CH}_2\text{COOH}][\text{H}_2\text{O}][\text{V(OH)}_2\text{HSO}_4]^2^+ \quad (10)
\]

By applying the law of mass action in equations (4) and (5)

\[
K_s = \frac{[\text{V(OH)}_2\text{HSO}_4]^2^+}{[\text{V(OH)}_2^3^+] [\text{HSO}_4^-]}
\]

\[
K_s = \frac{[\text{Dn} \ldots \hat{\text{NH}}_2\text{CH}_2\text{COOH}]}{[\text{Dn}] [\hat{\text{NH}}_2\text{CH}_2\text{COOH}]}
\]

\[
K_s = \frac{[\text{Dn} \ldots \hat{\text{NH}}_2\text{CH}_2\text{COOH}][\text{H}_2\text{O}][\text{V(OH)}_2^3^+] [\text{HSO}_4^-]}
\]

By the application the law of mass action, the values of \([\text{Dn}] [\hat{\text{NH}}_2\text{CH}_2\text{COOH}][\text{V(OH)}_2^3^+] [\text{HSO}_4^-] \) can be obtained. Thus surfactant catalyzed reaction corresponds to the rate law.

\[
\frac{d[V(V)]}{dt} = k [\hat{\text{NH}}_2\text{CH}_2\text{COOH}][\text{V(OH)}_2^3^+]
\]

The above rate law is in accordance with the experimental findings.
CONCLUSION

In continuation to our earlier studies it has been found out that the reaction is catalyzed both by acid and micelles. The higher values of free energy change in the presence of surfactant indicated the strong binding of substrate with micellas.

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Kinetics of Oxidation of Proline by Vanadium (V) in Micellar System

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Kinetic oxidation of proline by vanadium (V) has been studied in presence and in absence of micelles. The reaction is first order with respect to [vanadium] and [proline]. The reactions are micellar catalysed. The reaction exhibits Hammett's relationship. The Bunnett's plot indicates water acting as a nucleophile. The thermodynamic parameters have been computed and a suitable mechanism has been proposed.

The rate of chemical reaction may be modified by presence of micellar aggregates in the system under study. The investigation of micellar catalysis has provoked a great interest since the study might provide a basic model for the interpretation of some aspects of enzymatic catalysis. Both catalytic micelles and enzymes bind substrate in a non-covalent manner and the kinetics and micellar catalysis resemble that of enzymatic catalysis in that the micelles may be saturated by the substrate. The oxidation of proline by vanadium(v) in moderately concentrated acidic medium has been discussed here.

Introduction

Micellar systems exhibit wide unusual properties such as high interfacial area, low viscosity, high solubilizing capacity etc., which offer good potential for numerous applications like catalysis, detergency, biotechnology etc. Although the analogy between micelle catalysed reactions and enzyme catalysed reactions is far from perfect, there are important similarities that both micelles and enzymes are similar in that they have hydrophobic cores with polar groups on their surface.

Micellar catalysis of a large number of reactions have been the area of current research because of the similar behaviour of macro-molecules and enzymes. The survey of current literature shows that very few electron transfer processes have been studied in the presence of surfactant. We for the first time have undertaken the systematic study of the oxidation of different amino acids by vanadium(v) to explore the effect of surfactant on the kinetic parameters.

Materials and Methods

A stock solution of vanadium(v) (0.16 M) was prepared by dissolving ammonium meta vanadate (Loba chemie) in sulphuric acid (7.0 M) and was standardised by the usual method. The concentration of H⁺ (7.0 M) was also estimated. A solution of proline (2.0 M) (Loba chemie) was prepared by dissolving it in desired concentration of sulphuric acid (BDH, AR). A solution of cetyltrimethylammoniumbromide (Lobe chemie) (0.1 M) was prepared in doubly distilled water. The structure of CTAB is very similar to the lipid bilayers of biological membrane. Thus, when CTAB dispersed in water, produces spontaneously a bilayer structure which form lamellae and vesicles. The aggregation tendency of CTAB is greater, because modified ammonium group is used as hydrophilic moiety.

The reactants were kept in a thermostat to attain the desired temperature before the final mixing. The kinetics was followed by estimating the unconsumed oxidant by titrating against standard ferrous ammonium sulphate solution using N-phenyl anthranilic acid as an indicator.

The final product of oxidation of proline by vanadium(v) were found to be aldehyde which was examined by preparing 2 : 4 dinitro phenyl hydrazine derivative. In a portion of reaction mixture the solution of sodium hydroxide was added and heated. The smell of ammonia confirmed its formation during the oxidation.

Results and Discussion

The order in vanadium(v) was found to be one as revealed by the linear plot of log (a - x) versus time for different initial concentration of
oxidant (Fig. 1). The order in [proline] was found to be unity from the slope value of the linear plot of $k_{obs}$ versus [proline] (Fig. 2). The reactions are acid catalyzed and the order with respect to $[H]^+$ in two. The plot of $k_1$ versus $[H^+]^2$ was a straight line passing through the origin suggesting that the reaction involved only acid catalysed independent path. (Fig. 3). Zucker-Hamnett and Bunnett's application were applied. The plots of log $k_1$ versus $-H_0$ and log $k_1 + H_0$ versus $a_{H_2O}$ were found to linear (Fig. 4).
Effect of Surfactant

The reaction was studied at different concentration of the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) in the range $2 \times 10^{-3}$ mol dm$^{-3}$ to $10 \times 10^{-3}$ mol dm$^{-3}$. The plot of $k_m$ versus [surfactant] was found that the rate of reaction increases up to maximum and then decreases with the increasing concentration of CTAB (Fig. 5), however, above the optimum concentration (broadly the cmc) of the surfactant the oxidation rate decreases.

![Graph showing the relationship between $k_m$ and surfactant concentration.]

**Table 1:** [Vanadium(V)] - $4 \times 10^{-3}$ M, [Proline] - 2.0 M, [H$_2$SO$_4$] - 7.0 M, temp. -35°C

<table>
<thead>
<tr>
<th>S. No.</th>
<th>CTAB $\times 10^{-3}$ mol dm$^{-3}$</th>
<th>$k_1 \times 10^{-3}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2.0</td>
<td>4.3</td>
</tr>
<tr>
<td>2.</td>
<td>4.0</td>
<td>6.3</td>
</tr>
<tr>
<td>3.</td>
<td>5.0</td>
<td>7.0</td>
</tr>
<tr>
<td>4.</td>
<td>6.0</td>
<td>7.5</td>
</tr>
<tr>
<td>5.</td>
<td>7.0</td>
<td>6.0</td>
</tr>
<tr>
<td>6.</td>
<td>8.0</td>
<td>5.0</td>
</tr>
<tr>
<td>7.</td>
<td>10.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Micelles speed reaction of proline and vanadium(V) in accordance with expectation. The pseudo first order rate constant $k_0$ and $k_m$ for the uncatalyzed and micellar reactions respectively have been evaluated at different [proline] and it is found to be in the order $k_m$ is greater than $k_0$.

The double reciprocal plot of $k_0^{-1}$ or $k_m^{-1}$ versus [proline]$^{-1}$ have been found to be linear with intercept on one ordinate indicating that both the uncatalyzed and micellar catalyzed oxidations proceed via complex formation obeying Michaelis-Menten Kinetics (Fig. 6).

![Graph showing the double reciprocal plot.]

The rate law is therefore of the form

$$\frac{1}{k_0} \quad \text{or} \quad \frac{1}{k_m} = \frac{1}{k_t} + \frac{1}{k_t k \text{[Proline]}}$$

A linear relationship between log $(k_v - k_0)/(k_m - k_v)$ versus log [D] was obtained with positive co-operativity, implying stimulation of the interaction of additional substrate molecule by the interaction of first molecule with micelle (Fig. 7).

![Graph showing the linear relationship.]

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The above rate expression is in accordance with the observed facts. This observation in the highly concentrated acidic medium in the presence of surfactant leads to the mechanistic criterion regarding cationic species of molecule V(OH)\(_2\)\(^{3+}\) and micelle absorbed charged species in the rate determining steps. The linear Zucker Hammett plot shows that the reaction is acid catalyzed. The Bunnett’s plot indicate that water acts as nucleophile in rate determining step (Fig. 8).

**Dependence of the rate on the temperature**

The reaction between proline and vanadium[\(\text{v}\)] was studied at four different temperatures in the range 30-40°C and the activation parameters were calculated (Table-2) from the usual relationships.

**Table 2.** Thermodynamic parameters.

<table>
<thead>
<tr>
<th>Condition</th>
<th>(\Delta E) (KJ mol(^{-1}))</th>
<th>(\Delta H^*) (KJ mol(^{-1}))</th>
<th>(\Delta G^*) (JK mol(^{-1}))</th>
<th>(\Delta S^*) (KJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>In absence of surfactant</td>
<td>45.5812</td>
<td>24.2984</td>
<td>30.98175</td>
<td>-95.8118</td>
</tr>
<tr>
<td>In presence of surfactant</td>
<td>56.1477</td>
<td>24.3772</td>
<td>31.39859</td>
<td>-113.544</td>
</tr>
</tbody>
</table>

**Acknowledgement**

The authors are thankful to Prof. S.P. Banerjee, Head, Department of Chemistry, Dr. H. S. Gour Vishwavidyalaya, Sagar for facilities.

**References**

Dear Madhvi Choubey,

Your communication entitled "KINETIC OXIDATIVE DECARBOXYLATION, DEAMINATION OF VALINE BY VANADIUM(V) IN MICELLAR SYSTEM", has been accepted for publication in Madhya Bharati Journal of Dr. H. S. Gour Vishwavidyalaya, Sagar (M.P.). The paper will appear in the coming issue of the Journal.

To,
Ku. Madhvi Choubey
&
Dr. Archana Pandey
Deptt. of Chemistry,
Dr. H. S. Gour University,
SAGAR

/Yours sincerely/

( K. C. Pitre )
EDITOR

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