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Mechanism of quinquevalent vanadium oxidation of L-typtophan in sulphuric acid medium

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Abstract

The present paper deals with mechanism of quinquevalent vanadium oxidation of L-typtophan in sulphuric acid medium

Key-Words: Quinquevalent vanadium, Oxidation, Sulphuric acid

Oxidation of L-Tryptophan by vanadium (V) in sulphuric acid medium at constant ionic strength follows first order kinetics in oxidant, L_tryptophan and H^+ . The reaction is acid catalysed. Observed stoichiometry, positive salt and solvent effect suggest a mechanism involving interaction of cationic oxidant with the neutral molecule of the amino acid in rate determining step.

The kinetics of oxidation of amino acids by quinquevalant vanadium in sulphuric acid medium was reported earlier from our laboratory[1-3]. As an extension we report herein the kinetics of oxidation of tryptophan by vanadium (V) in sulphuric acid medium.

Oxidant solution was prepared by dissolving ammonium metavanadate (Reidel) in appropriate concentration of sulphuric acid (B.D.H.A.R.) and was standardized by titrating it against standard Fe(II) using N-phenylanthranilic acid as an indicator. Solution of tryptophan (B.D.H.) was prepared by dissolving it in known concentration of sulphuric acid. All other reagents used were of standard grade.

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The reactqants were equilibrated at the desired temperature in a thermostat ($^+$. 0.1^{o}C). The kinetics were followed by examining aliquot portions of the reaction mixture at definite intervals of time for unreacted vanadium (V) by titrating it against standard Fe(II) solution using N-phenylathranilic acid as an indicator.

Different sets of reaction mixture containing varying rations of oxidant to tryptophan in the presence of 0.3 M H_2SO_4 at 30^{o}C for 48 h showed 2 mols of V(V) were consumed for one mol of tryptophan according to the following stoichiometric equation yielding corresponding aldehyde as the product which was tested by the conventional method i.e. by 2:4 dinitrophenyl hydrazone formation.

$$R\text{-}\ CH_2CH(NH_2)COOH + 2V(V) + H_2O \longrightarrow$$

$$R\ CH_2CHO + CO_2 + NH_3 + 2V\ (IV) + 2H$$

The kinetic results can be summarized as follows –

1. The reaction was first order in [V (V)] as revealed by the linear plots of log [V (V)] versus time.
2. The rate increased with increasing [L-tryptophan]. The linear plot of log k_1 versus log [L-tryptophan] gave straight line with slope 1.0 establishing first order dependence in tryptophan.
3. At constant ionic strength an increase in acid concentration from 0.1 to 0.45 mol dm^{-3}, increases the pseudo first order rate constant

linearly (from 19.73 to 89.26 x 10^{-3} min^{-1} in sulphuric ac id and from 18.61 to 84.15 x 10^{-3} min^{-1} in perchloric acid). The plot of log k_1 against $[H^+]$ is linear with slope 0.94 confirming first order dependence on hydrogen ion concentration.

4. There is marginal increase in oxidation rate with increase in ionic strength. For example under the condition [V (V)] = 1.0x10^{-3} mol dm^{-3} , [L-tryptophan]= 1.0 x 10^{-2} mol dm^{-3} , $[H^+]$=0.18 mol dm^{-3} and 30ºC, 10^3 k_1 min^{-1} changed from 35.46 to 35.80 when I was varied from 0.01 to 0.30 mol dm^{-3}. similarly an increase in acetic acid content of the reaction medium from 10 to 50 % (V/V) changed the rate constant from 38.16 to 59.16 x 10^{-3} min^{-1} for the oxidation of tryptophan at 30ºC. Hence the reaction has positive solvent effect.
5. An increase in $[NaHSO_4]$ (0.15 to 0.35 mol dm^{-3}) changed the rate constant from 36.74 to 83.28 x-10^{-3} min^{-1} at 30ºC. The unit slope of the plot log k_1 versus log $[HSO_4]$ HSO_4 suggests the involvement of HSO_4 with V (V) species in the formation of complex.
6. Rate study measurements were carried-out at four different temperatures (25.40ºC) and activation parameters were calculated. The value of E_a, A and $\Delta S^{\ddagger}$ were found to be 59.91 ± 0.2 k J mol^{-1} , 12.6 ± 0.6x10^6 sec^{-1} and 32.59 ± 0.5 J K^{-1} mol^{-1} respectively.

Under the experimental conditions, it is assumed that V (V) exists as V $(OH)_3^{2+}$ and $V(OH)_3HSO_4^+$ (ref 4-7). The increase in oxidizing power of V (V) with increase in [acid] is mainly due to the increase in the oxidation potential of V (V) species. The formation of active oxidizing species may be represented as:

$VO_2^+ + H_2O + H^+ \rightarrow V(OH)_{32}^+$ (K1)

$VO_2^+ + H_2O + H^+ + HSO_4^- \rightarrow V(OH)_3 HSO_4^+$ (K1)

In perchloric acid no such complex formation is possible since sodium pechlorate when added causes no effect, Hence $V(OH)_3^{2+}$ is considered as the active species in perchloric acid whereas increases in rate with increase in concentration of bisulphate ion suggests $V(OH)_3$ HSO_4^+ to be the active species in sulphuric acid.

In acid medium amino acid molecules are in equilibrium with its monoprotonated form. The results of medium effect studies suggest the involvement of neutral molecule and ion in the rate limiting step. Hence the attack of cationic V (V) on unprotonated amino acid looks more plausible.

No kinetic evidence for complex formation was indicated from the reciprocal plot of k_1 versus [tryptophan] as it passes through origin. Such evidence was also obtained by spectrophotometric studies where no shift in the maxima was seen.

The amino acid suffers electrophilic attack by the oxidant yielding an intermediate free radical. The formation of free radicals was confirmed by adding acrylonitrile to the reaction mixture when a thick semisolid due to polymerization was obtained. In subsequent fast steps the free radical suffers attack by the other equivalent of vanadium (V) and yields corresponding aldehyde by decarboxylation followed by deamination which is also supported by the negative test of keto acid as an intermediate.

The following mechanism may thus be schematically represented below:

It is established by wells and kuritsyn[8] that the equilibrium constant for the formation of $V(OH)_3^{2+}$ is very much less than one and so k_2 may also be assumed to be less than one, the above mechanism leads to the rate law as –

Rate = k_1 K_2 [tryptophan] $[VO_2^+]$ $[H^+]$ $[HSO_4^-]$ and in $HClO_4$

Rate = k_1 K_2 [tryptophan] $[VO_2^+]$ $[H^+]$

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