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An analysis of Zucker-Hammett & Hammett acidity function parameters of oxidation of some amino acids by V(V)

Chemistry

KEYWORDS : Amino acids, Kinetics of oxidation, Zucker-Hammett & Hammett, acidity functions, Dependence of rate on [H$^+$] & [H$^+$]^2

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ABSTRACT

The oxidation of amino acids viz; L-aspartic acid, L-cysteine, L-valine & L-leucine by V(V) have been found to be acid catalyzed. Zucker -Hammett data for the oxidation of these amino acids have been calculated at different concentrations of acid. Zucker-Hammett plots between log K1 & log CH+, and Hammett acidity function plots between log K1 & H0 have been determined. The observations indicate dependence of rate on Hammett acidity function H0. Zucker -Hammett data indicate participation of water molecule in the course of reactions & bimolecular nature of the reactions.

Introduction:

Zucker-Hammett[1] & Hammett acidity functions[2] have been found to be significant in deciding the molecularity of acid catalyzed reactions. Hammett acidity function H_0 is a useful measure of the protonating ability of a given acid containing medium and acidity functions are useful in developing an understanding of the nature of acid catalysis.

Zucker & Hammett have found that a plot between log of rate constant and log of CH$^+$ at different concentrations of acid can give an idea about the participation of water molecule in the course of reaction. The slope values of the plots indicate the role of water molecule and also the molecularity of the reaction. In the present paper the oxidation of L-aspartic acid, L-cysteine, L-valine & L-leucine have been studied at different concentrations of acid and observed data have been analyzed.

Method:

Amino acids were dissolved in distilled water and solutions of desired concentrations were prepared[3]. The solution of V(V) was prepared in distilled water and known volume of H_2SO_4 . Kinetic studies were carried out in a thermostat at different temperatures (±0.5° C). Aliquots (2 ml) were withdrawn at suitable time interval and poured in a chilling flask containing standard ferrous ammonium sulphate ; unreacted ferrous ammonium sulphate was then titrated with intermediate V(V) solution. Rate constants were determined by first order equation.

Results & Discussion:

Zucker –Hammett data for the oxidation of L-aspartic acid, L-cysteine, L-valinee and L-leucine at different concentrations of acid and other reactants are given in table 1-4. The rates have been found to vary with change in acid concentration. The plots between log k_1 and log CH$^+$ have been shown in fig.1. In this fig. plots A & B represent oxidation of L-aspartic acid and L-cysteine. At lower acidities the values of slope were found to be 2.0 and at higher acidities the values of slope were found to be 4.0. The probable reason is dependence of rate on [H+] at lower acidities & on [H+]2 at higher acidities. In the same figure plots C & D represent oxidation of L-valine & L-leucine. In both the cases the slope values were 2.0 and the straight lines observed resemble each other, which indicate similar type of oxidation mechanisms in these reactions.

Hammett acidity plots for the oxidation of these amino acids are given in fig.2. Which indicates dependence of rates on Hammett acidity functions. Straight lines with slopes less than unity indicate bimolecular nature of the reactions.

Table-1
Zucker-Hammett & Hammett acidity function data.
Oxidation of L-aspartic acid by V(V)
L-aspartic acid =1.0 x 10^{-3} M Vanadium (V) = 1.0 x 10^{-4} M
Ionic strength [μ] = 6.01 M Temperature = 70°C

[H_2SO_4]	2 + log CH$^+$	-H_0^*	K_1x10^5 sec^{-1}	8+ log K_1
0.5	1.69	0.13	1.480	3.17
1.0	2.00	0.26	3.236	3.51
2.0	2.30	0.84	5.708	3.75
3.0	2.47	1.38	8.543	3.93
3.5	2.54	1.62	10.670	4.02
4.0	2.60	1.85	11.740	4.06
4.5	2.65	2.06	14.547	4.16
5.0	2.69	2.28	17.621	4.24
6.0	2.77	2.76	25.634	4.40

Table- 2
Zucker-Hammett & Hammett acidity function data.
Oxidation of L-cysteine by V(V)
L-cysteine =1.0 x 10^{-2} M Vanadium (V) = 1.0 x 10^{-3} M
Ionic strength [μ] = 3.01 M Temperature = 30°C

[H_2SO_4]	2 + log CH$^+$	-H_0^*	K_1x10^4 sec^{-1}	7+ log K_1
0.5	1.69	0.13	1.326	3.12
1.0	2.00	0.26	2.567	3.40
1.5	2.17	0.56	4.924	3.69
2.0	2.30	0.84	8.294	3.91
2.5	2.39	1.12	12.798	4.10
3.0	2.47	1.38	18.332	4.26

Table- 3
Zucker-Hammett & Hammett acidity function data.
Oxidation of L-valine by V(V)
L-valine =1.0 x 10^{-2} M Vanadium (V) = 1.0 x 10^{-3} M
Ionic strength [μ] = 7.01 M Temperature = 80°C

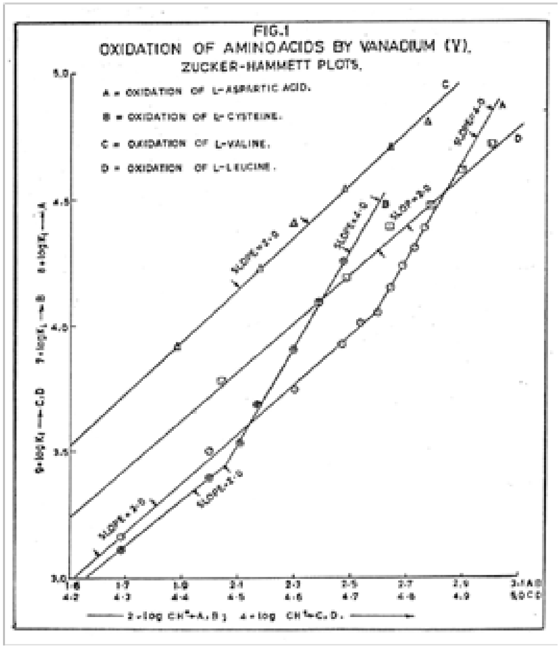
[H_2SO_4]	4+ log CH$^+$	-H_0^*	K_1x10^5 sec^{-1}	9+ log K_1
2.5	4.39	1.12	0.85	3.92
3.5	4.54	1.62	1.73	4.23
4.0	4.60	1.85	2.59	4.41
5.0	4.69	2.28	3.60	4.55
6.0	4.77	2.76	5.21	4.71
7.0	4.84	3.32	6.60	4.81

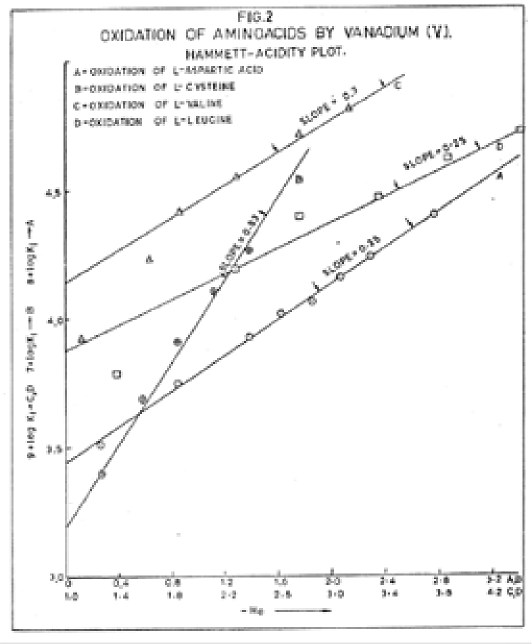
Table-4
Zucker-Hammett & Hammett acidity function data.
Oxidation of L-leucine by V(V)
L-leucine =1.0 x 10^{-2} M Vanadium (V) = 1.0 x 10^{-3} M
Ionic strength [μ] = 9.01 M Temperature = 70°C

[H_2SO_4]	4 + log CH$^+$	-H_0^*	K_1x10^5 sec^{-1}	9+ log K_1
3.0	4.47	1.38	0.61	3.78
5.0	4.69	2.28	1.56	4.19
6.0	4.77	2.76	2.52	4.40
7.0	4.84	3.32	2.98	4.47
8.0	4.90	3.87	4.17	4.62
9.0	4.95	4.40	5.28	4.72

* Values taken from M.A. Paul and F.A . Long, Chem.Revs. 57, 1 (1957)

Thus, it can be concluded from the Zucker-Hammett data that all the four oxidation reactions follow similar type of mechanisms as the slopes obtained were more than unity. Hammett acidity data indicate bimolecular nature of the reactions. Which have been supported by other workers,also.[4-17]





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