Research Paper

Volume : 2 | Issue : 3 | Mar 2013 • ISSN No 2277 - 8179

Studies on Bunnett & Bunnett –Olsen parameters of oxidation of some amino acids by V(V)

Chemistry

KEYWORDS : Amino acids, Kinetics of oxidation, Bunnett & Bunnett – Olsen Parameters.

A. K. Mishra Dept. of Chemistry,UIT,RGPV,Bhopal,M.P., 462033,India

S. D. Sharma Professor of Chemistry (Retired), HNo. 925/13, Civil lines, Jhansi, U.P.,284001, India

ABSTRACT

Bunnett & Bunnett –Olsen data for the oxidation of L-aspartic acid, L-cysteine, L-valine & L-leucine by V(V) have been determined at different concentrations of sulphuric acid . The rates were found to be increased with increase in acid concentration. Bunnett plots between log K1 + H0 and log aH2O have been determined. The observations indicate dependence of reactions on water activity. The slope values of Bunnett plots were found to be 6.6, 4.1, 3.3 and 3.1 respectively. Further, Bunnett - Olsen plots between log CH+ + H0 & log K1 + H0 have been determined. The slope values of Bunnett-Olsen plots were found to be 1.0, 0.5, 0.88 & 0.83 respectively.

Introduction:
Bunnett[1] and co-workers[2] suggested a detailed treatment of dependence of acidity functions[3,4] in aqueous solutions. For acid catalyzed reactions in acidic media, the difference in hydration of activated complex and substrate changes the activity of water. This gives significant information about the dependence of the reaction rate on water activity and participation of water molecule in the course of reaction.

Bunnett found that a plot between log of rate constant and log aH_2O gives a straight with slope more than unity in case the reaction is bimolecular. 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:
Solutions of amino acids were prepared by dissolving them in distilled water[5] and the solution of V(V) was prepared in distilled water along with 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 Aliquots (2 ml) were withdrawn at suitable time interval and poured in a chilling flask containing standard Ferrous Ammonium Sulphate. The concentration of unreacted Ferrous Ammonium Sulphate was then determined by titrating with intermediate V(V) solution. Rate constants were determined by first order equation.

Results & Discussion:
Bunnett & Bunnett –Olsen data for the oxidation of L-aspartic acid, L-cysteine, L-valine and L-leucine at different concentrations of acid and other reactants are given in table 1-4. The rates were found to vary with change in acid concentration. Bunnett plots between log $k_1 + H_0$ and log aH_2O are shown in fig.1. In this fig. plots A, B, C & D represent oxidation of L-aspartic acid, L-cysteine, L-valine & L-leucine respectively. The slope values for the oxidation of L- aspartic acid, L-cysteine, L-valine and L-leucine were found to be 6.6, 4.1, 3.3 & 3.1 respectively. These values show that reactions are bimolecular with dependence of rates on water activity as slope values are more than unity in all the cases. Such magnitudes of slopes and dependence of rates on water activity were obtained by other workers, also.[6,7] This suggest involvement of water molecule as a proton transferring agent in these reactions. Bunnett & Olsen further suggested that linear free energy relationship exist between log $K + H_0$ & log $CH^+ + H_0$. The correlation obtained are better for understanding the nature of water molecule. The slopes values (Ø) are called Bunnett-Olsen parameters. This characterize the response of the reaction with change in mineral acid concentration. The magnitudes of (Ø) values indicate as follows:

i. Water not involved in rate limiting step if Ø < 0
ii. Water involved as a nucleophile in rate limiting step if Ø = 0.22 to 0.56
iii. Water involved as a proton transferring agent in rate limiting step if Ø > 0.58

Bunnett-Olsen plots for the oxidation of these amino acids are given in fig.2.

In the cases of oxidation of L-aspartic acid, L-valine & L-leucine the slope values of Bunnett-Olsen plots were found to be 1.0, 0.88 & 0.83 respectively which suggest that during these oxidations water participates as proton transferring agent while in the oxidation of L-cysteine the slope value was found to be 0.50 which suggests that water is involved as a nucleophile in this reaction. This shows that oxidation of L-cysteine follows some different path. Other workers have also carried out studies on oxidation of amino acids[8-20].

Table-1
Bunnett & Bunnett-Olsen plot 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

$[H_2SO_4]$	$-H_0^*$	$2+\log CH^+ + H_0$	$K_1 x10^5 sec^{-1}$	$8+\log K_1$	$8+\log K_1 + H_0$	$-\log aH_2O^{**}$
1.0	0.26	1.74	3.236	3.51	3.25	0.02
2.0	0.84	1.46	5.708	3.75	2.91	0.04
3.0	1.38	1.09	8.543	3.93	2.55	0.08
3.5	1.62	0.92	10.670	4.02	2.40	0.11
4.0	1.85	0.75	11.740	4.06	2.21	0.14
5.0	2.28	0.41	17.621	4.24	1.96	0.21
6.0	2.76	0.01	25.634	4.40	1.64	0.33

* Values taken from M.A. Paul and F.A . Long, Chem.Revs. 57, 1 (1957)
**Values taken from Herbert S., Harned & Bunton Bowen," Physical Chemistry of Electrolytic Solution", p-574

Table- 2
Bunnett & Bunnett-Olsen plot 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

$[H_2SO_4]$	$-H_0^*$	$2+\log CH^+ + H_0$	$K_1 x10^4 sec^{-1}$	$7+\log K_1$	$7+\log K_1 + H_0$	$-\log aH_2O^{**}$
1.0	0.26	1.74	2.567	3.40	3.14	0.02
1.5	0.56	1.61	4.924	3.69	3.13	0.03
2.0	0.84	1.46	8.294	3.91	3.07	0.04
2.5	1.12	1.27	12.798	4.10	2.98	0.06
3.0	1.38	1.09	18.332	4.26	2.88	0.08

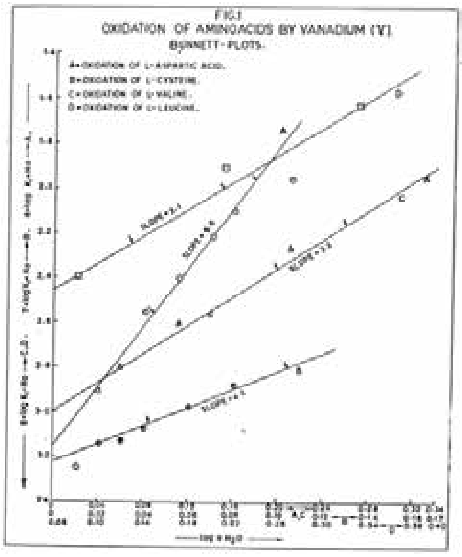
Table- 3
Bunnett & Bunnett-Olsen plot data.
Oxidation of L-valine by V(V)
L-valine =1.0 x 10^{-2} M Vanadium (V) = 1.0 x 10^{-3} M

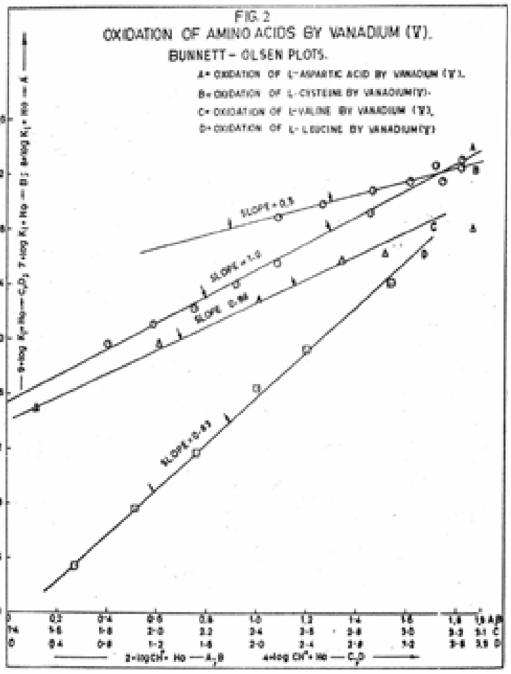
Ionic strength [μ] = 7.01 M Temperature = 80°C

$[H_2SO_4]$	$-H_0^*$	$4+\log CH^++H_0$	$K_1 x10^5 sec^{-1}$	$9+\log K_1$	$9+\log K_1+H_0$	$-\log aH_2O^{**}$
2.5	1.12	3.27	0.85	3.92	2.80	0.06
3.5	1.62	2.92	1.73	4.23	2.61	0.11
4.0	1.85	2.75	2.59	4.41	2.56	0.14
5.0	2.28	2.41	3.60	4.55	2.27	0.21
6.0	2.76	2.01	5.21	4.71	1.95	0.32
7.0	3.32	1.52	6.60	4.81	1.49	0.43

Table-4
Bunnett & Bunnett-Olsen plot 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

$[H_2SO_4]$	$-H_0^*$	$4+\log CH^++H_0$	$K_1 x10^5 sec^{-1}$	$9+\log K_1$	$9+\log K_1+H_0$	$-\log aH_2O^{**}$
3.0	1.38	3.09	0.61	3.78	2.40	0.08
5.0	2.28	2.41	1.56	4.19	1.91	0.21
6.0	2.76	2.01	2.52	4.40	1.64	0.32
7.0	3.32	1.52	2.98	4.47	1.15	0.43
8.0	3.87	1.03	4.17	4.62	0.75	0.58





REFERENCE

1. Bunnett, J.F., J.Am.Chem.Soc.,1961, 83, 4956-78. | 2. Bunnett, J.F. & Olsen, F.P. Can. J. Chem.,1966, 44, 1917-31. | 3. Zucker, L. and Hammett, L.P., J. Am. Chem. Soc., 1939,61,2791. | 4. Hammett, L.P., Physical Organic Chemistry, Mc Graw Hill Co., 1940. | 5. Prakash, S., Ph.D.,Thesis , Jiwaji University.,1975,82. | 6. Bunton, C. A., Fendler, E. J. & Fendler, F. H., J. Am. Chem. Soc., 1967,89,1221. | 7. Bhatwadekar, S. S., Ph.D Thesis, Jiwaji University., 1972. | 8. Taft, R.W., Deno, N.C. & Skell, P.S., Ann.Rev.Phys.,Chem.,1958,9,303. | 9. Littler, J.S.,& Waters, W.A., J.Chem.Soc.,1959,4046. | 10. Venkata Subramaniam, N. J. Sci. & Ind. Res., 1961, 20B, 541. | 11. Shankar,R. & Bakore,G.V., Current Science,India,1962,31,376. | 12. Schaefer, J. J.Am.Chem.Soc.,1962, 84, 713-717. | 13. Mishra, H. C. & Simons, M.C.R., J. Chem. Soc., 1962, 4411. | 14. Bakore, G.V. & Narayan, S., J.Chem.Soc., 1963,3419. | 15. Yadav, R.L., & Bhagwat, W.V., J.Ind.Chem.Soc., 1964,41,427. | 16. Bakore, G.V., & Shankar, R., Ind. J. Chem., 1968, 6, 6901. | 17. Dixit, R.S. & Shrivastav , S.N., Bul.Insti.Polyech.,1977,23, 29-33. | 18. Usha, A.V., Sethuram, B. & Rao,T.N., Ind.J.Chem.,1977,15A, 6, 528-30. | 19. Singh, K. J., & Anand, S.N., J. Ind. Chem. Soc.,1979, Vol.LVI, 364. | 20. Fadnis, A.G. & Kulshrestha, S.K., J. Ind. Chem.,1981, 8, 763.