

Studies on Bunnett & Bunnett –Olsen parameters of oxidation of L-aspartic acid, L-valine & L-leucine by SeO_2



Chemistry

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ABSTRACT

Bunnett & Bunnett –Olsen data for the oxidation of L-aspartic acid, L-valine & L-leucine by SeO_2 have been determined at different concentrations of Sulphuric acid. The rates were found to be increased with increase in acid concentration. Bunnett plots were drawn between $\log K_1 + H_0$ and $\log aH_2O$. The observations indicate no significant information as the plots were not linear but curved. Further, Bunnett - Olsen plots were drawn between $\log CH^+ + H_0$ & $\log K_1 + H_0$. The slope values of Bunnett-Olsen plots were found to be 1.2, 1.0, & 1.0 respectively. These values of slopes indicate participation of water as a proton transferring agent during the course of reactions.

Introduction:

Bunnett¹ and co-workers² provided a relationship of acidity functions^{3,4} in aqueous solutions for acid catalyzed reactions. This gives significant information about the dependence of the reaction rate on water activity and participation of water molecule in the course of reaction.

In the present paper the oxidation of L-aspartic acid, 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 and the solution of SeO_2 was prepared by dissolving an accurately weighed amount of SeO_2 in distilled water⁵. The solution was protected from light & heat. The solution was standardized at equal intervals iodimetrically. Kinetic studies were carried out in a thermostat at different temperatures ($\pm 0.5^\circ\text{C}$). Flask containing substrate (amino acid and other reagents) was kept in a thermostat together with a flask containing oxidant solution. When the two flasks attained the temperature of thermostat a required volume of oxidant was withdrawn out and poured into reaction flask. The reaction flask was shaken vigorously and immediately 2mls of aliquot were withdrawn at suitable time intervals into an ice cooled flask containing 5 ml of 2% starch solution and 2 ml of 1:1 HCL . 10 ml KI (10%) were then added and liberated Iodine was titrated against standardized Sodium thio sulphate solution. Rate constants were determined by first order equation.

Results & Discussion:

Bunnett suggested that from the slopes of the plots drawn between $\log K_1 + H_0$ and $\log aH_2O$ different reaction mechanisms can be classified on the basis of different nature of water involvement.

Bunnett suggested that the difference in hydration of activated complex and substrate changes the activity of water. Different type of involvement of water as suggested by Bunnett is summarized as:

1. A slope (w) value between -2.5 to 0 indicate the non participation of water molecule.
2. For a positive value of " w " participation of water molecule can be visualized. A " w " value ranging from 1.2 to 3.3, indicates that water molecule acts as a nucleophile; while a value of " w " > 3.3 indicates that water acts as a proton transferring agent.

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 (\emptyset) are called Bunnett-Olsen parameters. The magnitudes of (\emptyset) values indicate as follows:

- i. Water not involved in rate limiting step if $\emptyset < 0$

- ii. Water involved as a nucleophile in rate limiting step if $\emptyset = 0.22$ to 0.56
- iii. Water involved as a proton transferring agent in rate limiting step if $\emptyset > 0.58$

Bunnett & Bunnett –Olsen data for the oxidation of L-aspartic acid, L-valine and L-leucine at different concentrations of acid and other reactants are given in table 1-3. The rates were found to vary with change in acid concentration. Bunnett plots drawn between $\log k_1 + H_0$ and $\log aH_2O$ are shown in Fig.1. In this fig. plots A, B, & C represent oxidation of L-aspartic acid, L-valine & L-leucine respectively. The plots were found to be curved so no significant information about role of water molecule could be derived from these plots because linear plots were suggested by Bunnett. Such dependence of rates on water activity were studied by other workers, also.⁶

Bunnett-Olsen plots for the oxidation of these amino acids are given in Fig.2. In the oxidation of L-aspartic acid, L-valine & L-leucine the slope values of Bunnett-Olsen plots were found to be 1.2, 1.0 & 1.0 respectively (nearly unity) which suggest that during these oxidations, water participates as proton transferring agent. Such type of observations have been studied by other workers also on oxidation of amino acids⁷⁻¹⁸.

Table-1

Bunnett & Bunnett-Olsen plot data.

Oxidation of L-aspartic acid by SeO_2

L-aspartic acid = 1.0×10^{-2} M $\text{SeO}_2 = 1.0 \times 10^{-3}$ M

Ionic strength [μ] = 7.01 M Temperature = 70°C

$[\text{H}_2\text{SO}_4]$	$-H_0^*$	$2+\log CH^+ + H_0$	$K_1 \times 10^5 \text{sec}^{-1}$	$8+\log K_1$	$8+\log K_1 + H_0$	$-\log aH_2O^{**}$
1.0	0.26	1.74	0.807	2.90	2.64	0.02
2.0	0.84	1.46	0.907	2.95	2.11	0.04
3.0	1.38	1.09	1.118	3.04	1.66	0.08
4.0	1.85	0.75	1.433	3.15	1.30	0.14
5.0	2.28	0.41	1.555	3.19	0.91	0.21
6.0	2.76	0.01	1.766	3.24	0.48	0.32
7.0	3.32	-0.48	1.915	3.28	-0.04	0.43

* 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"

Table-2

Bunnett & Bunnett-Olsen plot data.

Oxidation of L-valine by SeO_2 L-valine = 2.0×10^{-2} M $\text{SeO}_2 = 1.0 \times 10^{-3}$ MIonic strength $[\mu] = 3.01$ M Temperature = 70°C

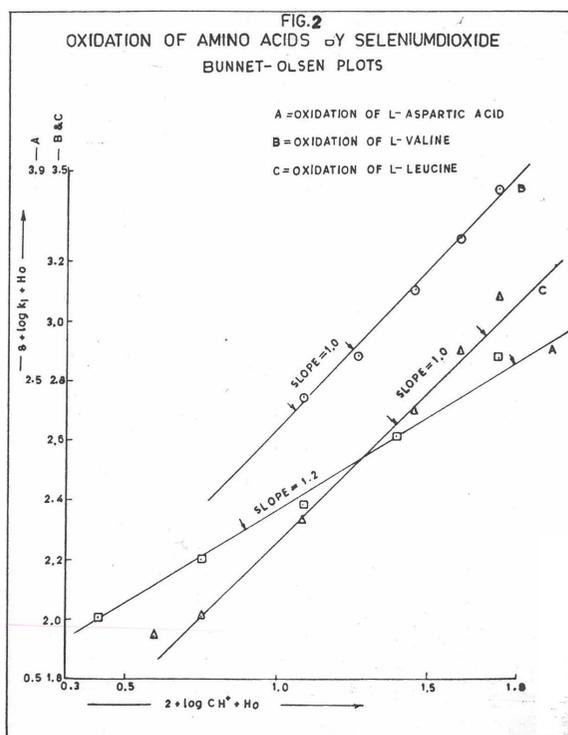
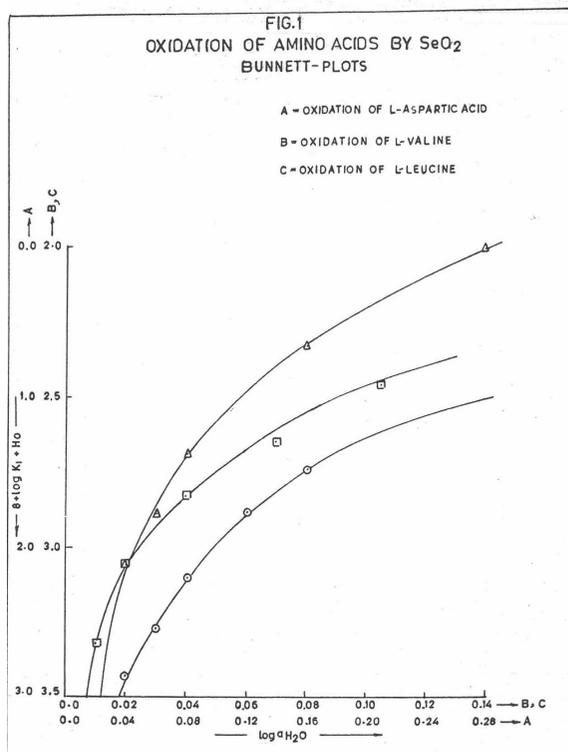
$[\text{H}_2\text{SO}_4]$	$-\text{H}_0^*$	$2 + \log \text{CH}^+ + \text{H}_0$	$K_1 \times 10^5 \text{sec}^{-1}$	$8 + \log K_1$	$8 + \log K_1 + \text{H}_0$	$-\log a \text{H}_2\text{O}^{**}$
1.0	0.26	1.74	4.925	3.69	3.43	0.02
1.5	0.56	1.61	6.848	3.83	3.27	0.03
2.0	0.84	1.46	8.844	3.94	3.10	0.04
2.5	1.12	1.27	10.135	4.00	2.88	0.06
3.0	1.38	1.09	13.216	4.12	2.74	0.08

Table-3

Bunnett & Bunnett-Olsen plot data.

Oxidation of L-leucine by SeO_2 L-leucine = 1.0×10^{-2} M $\text{SeO}_2 = 1.0 \times 10^{-3}$ MIonic strength $[\mu] = 4.51$ M Temperature = 70°C

$[\text{H}_2\text{SO}_4]$	$-\text{H}_0^*$	$2 + \log \text{CH}^+ + \text{H}_0$	$K_1 \times 10^5 \text{sec}^{-1}$	$8 + \log K_1$	$8 + \log K_1 + \text{H}_0$	$-\log a \text{H}_2\text{O}^{**}$
1.0	0.26	1.74	2.156	3.33	3.07	0.02
1.5	0.56	1.61	2.846	3.45	2.89	0.03
2.0	0.84	1.46	3.464	3.53	2.69	0.04
3.0	1.38	1.09	5.224	3.71	2.33	0.08
4.0	1.85	0.75	7.329	3.86	2.01	0.14
4.5	2.06	0.59	10.023	4.00	1.94	0.17

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