



Kinetics and Mechanism of Oxidation of Glutamic Acid with Bi(V) Phosphato Complex

AVINASH KUMAR, MUKESH KUMAR JHA and ASHOK KUMAR JHA*

Department of Chemistry, L.N.M.U. Darbhanga (India).

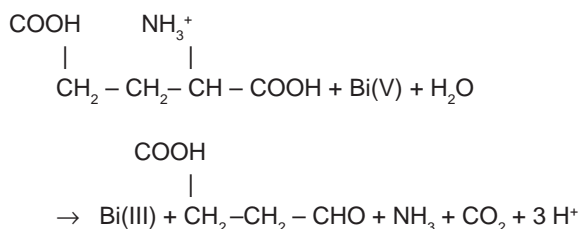
*C.M. Science College, Darbhanga (India).

*Corresponding author: E-mail : bauaaji2009@gmail.com

(Received: February 20, 2012; Accepted: March 25, 2012)

ABSTRACT

Kinetics of oxidation of Glutamic acid with Bi(V) in aqueous phosphoric acid medium has been studied. The reaction is first order with respect to the oxidant and it is complex one with respect to substrate. The mode of electron transfer is through an intermediate to be formed in two equivalent step taking decarboxylation of α - carboxylic group. The stoichiometry of the oxidant of glutamic acid by Bi(V) corresponds to the reaction represented by the equation



The observed kinetic rate law is given by the equation

$$\frac{-d[\text{Bi(V)}]}{dt} = \frac{k K [\text{Bi(V)}] [\text{GA}]}{1 + K [\text{GA}]} \cdot \frac{1}{1 + k_p [\text{H}^+]}$$

A plausible reaction mechanism corresponding to the rate law² has been proposed.

INTRODUCTION

Our aim is to undertake study of the reaction of Glutamic acid with Bi(V) was basically to determining the pattern of reactivity of Glutamic acid towards Bi(V) in Phosphoric acid medium.

MATERIAL AND METHODS

Bi(V) solution : There is only one known method¹ that utilizes a mixture of HClO_4 and HF for digesting sodium bismuthate to obtain Bi(V) in the solution. Such solution in HClO_4 – HF mixture are

not stable at ambient temperature. Moreover, the speciation of Fluorobismuth(V) species in such solution is yet to be resolved. Further the method of standardization of this solution requires critical conditions. However, these problems are not encountered for Bi(V) solution in phosphoric acid medium. Recently, kinetics of oxidation of various compounds by Bi(V) in HClO_4 – HF mixtures have been reported², but the problem of species of Bi(V) species still remain unsolved. We attempt to get Bi(V) as solution by using aqueous phosphoric acid. The requisite quantity of sodium bismuthate was digested in aqueous H_3PO_4 (3.0 mol dm^{-3}). Solution for 20 minutes after filtration a pink coloured solution were obtained. The solution was standardized iodometrically³⁻⁶.

All the other materials used were of Anala R grade doubly distilled water was used throughout the investigation.

Kinetic Procedure

The requisite quantities of various components of the reaction mixture, except Glutamic acid, were taken in glass – stoppered Erlenmeyer flasks, which were then suspended in a water bath thermostated at the desired temperature $\pm 0.1^\circ\text{C}$ unless stated otherwise. The reaction was initiated by adding the requisite solution of the temperature pre-equilibrated Glutamic acid into the reaction mixture, and the time of initiation was recorded when

half of the contents from the pipette were released. Aliquot samples (5 to 10 cm^{-3}) were withdrawn at different intervals of time and then quenched in an ice-cold KI (10%) solution; the liberated iodine was titrated against thiosulphate solution using starch as an indicator. Measurements in triplicate without any interference from the ingredients of the reaction mixture were in agreement to within $\pm 5\%$. Initial rates were computed employing plane mirror method⁷.

RESULTS

Stoichiometry

Several reaction mixtures with an excess of Bi(V) over Glutamic acid (GA) at fixed concentration of Phosphoric acid (3.0 mol dm^{-3}) were allowed to react in a water bath thermostated at $35 \pm 0.1^\circ\text{C}$. They were kept for 8 hrs. and excess of Bi(V) was estimated iodometrically after ensuring the completion of the reaction. The stoichiometry of the reaction was formed as (Table 1) as represented by the equation (1).

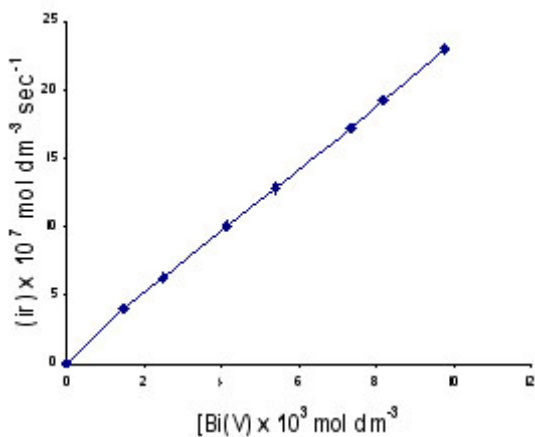
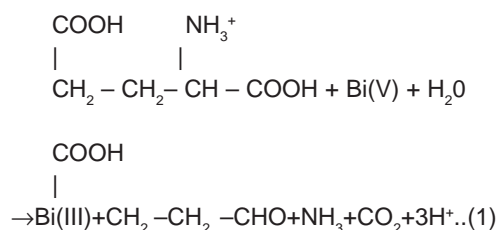


Fig 1. A Plot of (ir) Vs [Bi(V)] at fixed concentration H_3PO_4 at 35°C [Glutamic acid] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$

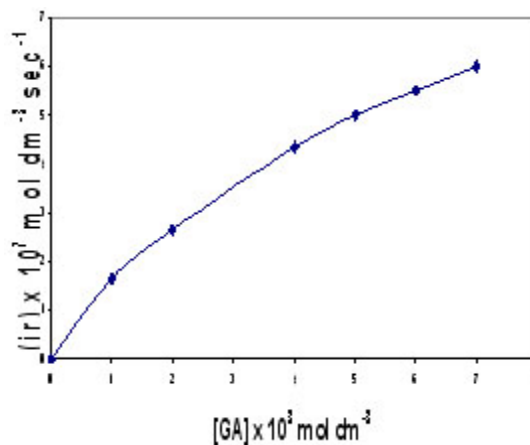


Fig 2. A Plot of (ir) Vs [Glutamic acid] fixed concentration H_3PO_4 at 35°C [GA] = $1.53 \times 10^{-3} \text{ mol dm}^{-3}$

Table 1 : Stoichiometric results of oxidation of (glulamic acid) with Bi(V) in Phosphoric acid (3.0 mol dm⁻³), temp. – 25°C

[Bi(v)]×10 ³ mol dm ⁻³ taken	[GA]×10 ³ mol dm ⁻³ taken	[Bi(V)]×10 ³ mol dm ⁻³ (measured)	$\frac{\Delta[Bi(V)]}{\Delta[GA]}$
1.25	1.0	1.13	1.13
2.25	1.0	1.08	1.08
2.25	1.5	1.7	1.133
2.25	1.5	1.61	1.07
3.375	1.5	1.60	1.06
3.375	2.0	2.31	1.15
3.375	2.0	2.23	1.15
4.5	2.0	2.23	1.15
5.625	2.0	2.25	1.124
5.625	2.5	2.81	1.124
4.5	2.5	2.84	1.136

The slightly higher ratio is due to itself decomposition of Bi(V). The oxidation product a aldehyde was detected by spot test⁸. The oxidation product of amino acid has been identified as an aldehyde by other reactions.

Bi(v) and Glutamic Acid [Ga] Dependence

The concentration of Bi(V) an Glutamic acid were varied in the range of (1.5 – 9.8) × 10³ mol dm⁻³ and (1.0–20.0) × 10³ mol dm⁻³ respectively at fixed concentration of Phosphoric acid (3.0 mol dm⁻³). The initial rate (ir) were computed by plane mirror method⁷. The plot of initial rate (ir) against the concentration of Bi(V) yielded a straight line while in the case of the substrate it is a curve. Thus the reaction order with respect to oxidant is one and the order with respect to Glutamic acid seemed to be complex one (Table 2, 3, Fig 1,2).

The concentration of Glutamic acid was varied from (2–10) 10⁻² mol dm⁻³ at five different concentration of Bi(V) and also at fixed concentration of Phosphoric acid 3.0 mol dm⁻³.

The initial rates were calculated by plane mirror method. The reaction rate initially increases and finally ends towards a limiting value.

Ionic Strength Dependence

Investigations were carried out at different ionic strength, reaction rates increases with increasing ionic strength

Table 2: [GA] = 5.0 × 10⁻³ mol dm⁻³ Temp. – 35°C, [H₃PO₄] = 3.0 mo; dm⁻³ Aliquot – 5 ml

[Bi(v)]×10 ³ mol dm ⁻³	[GA]×10 ³ mol dm ⁻³	(ir)×10 ⁷ mol dm ⁻³ sec ⁻¹
1.5	5.0	4.0
2.5	5.0	6.33
3.3	5.0	7.8
4.16	5.0	10.0
5.4	5.0	12.8
7.35	5.0	17.2
8.2	5.0	19.2
9.8	5.0	23.0

Hydrogen Ion Dependence

Hydrogen ion concentration were varied from 0.5 to 2.0 mol. dm⁻³ by adding [HClO₄] at constant ionic strength. Reaction rate decreases with increasing H⁺ ion concentration.

Bi(III) dependence

Reaction rate were independent of Bi (III) ion.

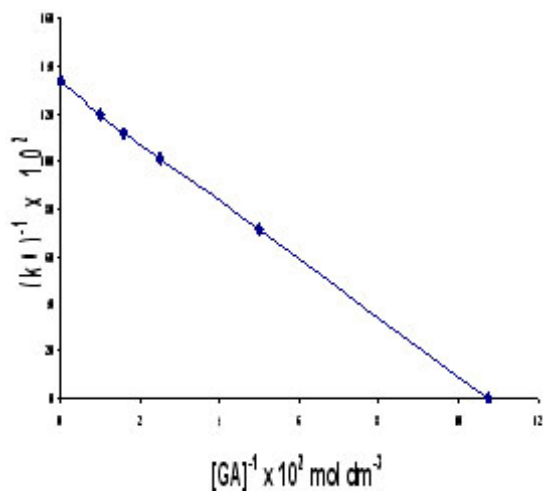


Fig 3. A Plot of $(k_0)^{-1}$ Vs $[\text{Glutamic acid}]^{-1}$ at fixed concentration of hydrogen ion at 35°C

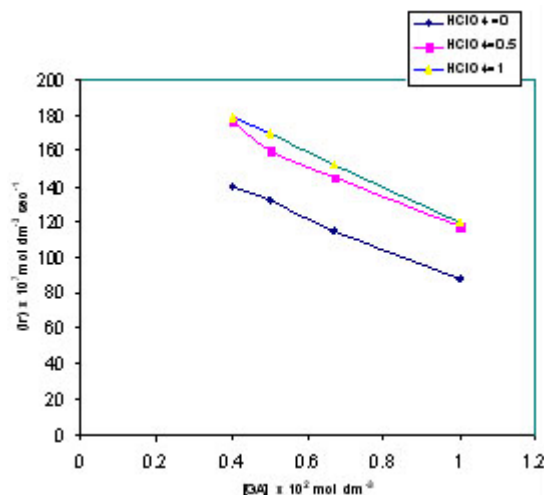


Fig 4. Graph showing Glutamic acid dependence

Table 3: $[\text{Bi(V)}] = 1.63 \times 10^{-3} \text{ mol dm}^{-3}$ Temp. – 35°C
 $[\text{H}_3\text{PO}_4] = 3.0 \text{ mol dm}^{-3}$ Aliquot – 5 ml

$[\text{GA}] \times 10^3$ mol dm^{-3}	$[\text{Bi(v)}] \times 10^3$ mol dm^{-3}	$(ir) \times 10^7 \text{ mol}$ $\text{dm}^{-3} \text{ sec}^{-1}$	$k_0 \times 10^4$ sec^{-1}
1.0	1.63	1.66	1.66
2.0	1.63	2.66	1.33
3.0	1.63	3.33	1.11
4.0	1.63	4.33	1.08
5.0	1.63	5.00	1.0
6.0	1.63	5.50	.91
7.0	1.63	6.00	0.86

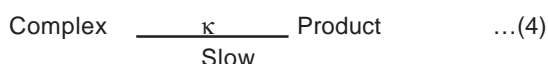
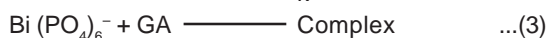
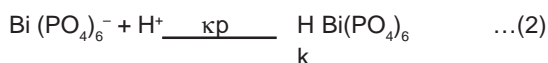
Table 4: Glutamic acid dependence
 $[\text{Bi(V)}] = 1.63 \times 10^{-3} \text{ mol dm}^{-3}$, Temp. – 35°C
 $[\text{H}_3\text{PO}_4] = 3.0 \text{ mol dm}^{-3}$
 $\text{HClO}_4 = 0.0, 0.5, 1.0 \text{ mol dm}^{-3}$ $I = 3.0 \text{ mol dm}^{-3}$

$[\text{GA}] \times 10^2$ mol dm^{-3}	$\text{HClO}_4 = 0.0$ mol dm^{-3}		$\text{HClO}_4 = 0.5$ mol dm^{-3}		$\text{HClO}_4 = 1.0$ mol dm^{-3}	
	$(ir) \times 10^7 \text{ mol}$ $\text{dm}^{-3} \text{ sec}^{-1}$	$k_0 \times 10^5$ sec^{-1}	$(ir) \times 10^7 \text{ mol}$ $\text{dm}^{-3} \text{ sec}^{-1}$	$k_0 \times 10^5$ sec^{-1}	$(ir) \times 10^7$ $\text{mol dm}^{-3} \text{ sec}^{-1}$	$k_0 \times 10^5$ sec^{-1}
1.0	11.3	11.3	8.5	8.5	7.8	7.8
1.5	12.9	8.6	10.33	6.89	9.85	6.57
2.0	14.8	7.4	12.5	6.25	10.3	5.88
2.25	16.2	7.2	13.72	6.09	12.84	5.71
2.5	17.5	7.0	14.1	5.64	13.95	5.58

DISCUSSION

Oxidation kinetics of amino acid has been studied by some workers⁹⁻¹⁸ and it has been observed that oxidative decarboxylation is followed by deamination.

Considering all these observations and also accounting for the experimental findings a probable reaction mechanism can be proposed as follows



The rate law can be derived considering equation (4) as rate determining step.

$$\frac{-d[\text{Bi}(\text{V})]}{dt} = \frac{k k [\text{Bi}(\text{V})][\text{GA}]}{1 + k[\text{GA}]} \cdot \frac{1}{1 + k_p[\text{H}^+]}$$

$$\frac{-d[\text{Bi}(\text{V})]}{dt} / [\text{Bi}(\text{V})] = \frac{k k [\text{GA}]}{1 + k[\text{GA}]} \cdot \frac{1}{1 + k_p[\text{H}^+]} = k_o$$

$$k_o = \frac{k k [\text{GA}]}{1 + k[\text{GA}]} \cdot \frac{1}{1 + k_p[\text{H}^+]}$$

k_o = observed first order rate constant

$[\text{GA}]$ = Equilibrium concentration

$[\text{Bi}(\text{V})]$ = Total gross concentration of all phosphato species of Bi(V)

$$\frac{1}{k_o} = \left\{ \frac{1 + k[\text{GA}]}{k k [\text{GA}]} \right\} \cdot (1 + k_p[\text{H}^+])$$

$$= \left\{ \frac{1}{k k [\text{GA}]} + \frac{1}{k} \right\} \cdot (1 + k_p[\text{H}^+])$$

$$\frac{1}{k_o} = \frac{1 + k_p[\text{H}^+]}{k k [\text{GA}]} + \frac{1 + k_p[\text{H}^+]}{k}$$

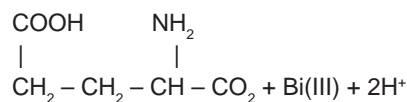
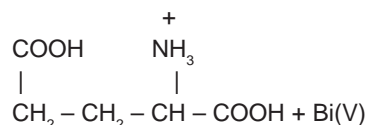
A plot of $1/k_o$ vs $1/[\text{GA}]$ at constant $[\text{H}^+]$ concentration was constructed from the equation (Table 3, Fig.-3). Again a plot of $1/k_o$ vs $1/[\text{GA}]$ at different concentration of $[\text{H}^+]$ ion was also constructed (Table 4, Fig. 4).

Plot of intercept $\frac{1 + k_p[\text{H}^+]}{k}$ and gradient

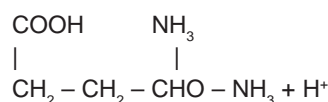
$\frac{1 + k_p[\text{H}^+]}{k k}$ against $[\text{H}^+]$ were further constructed.

The value of k and k_p were calculated from the ratio of intercept and gradient as $4.1 \text{ dm}^3 \text{ mol}^{-1}$ and $1.2 \text{ dm}^3 \text{ mol}^{-1}$.

The mode of electron transfer is through an intermediate to be formed in two equivalent steps taking decarboxylation of α -carboxylic group and the intermediate can opt out a path for the facile hydrolysis to an aldehyde. Thus the oxidation of Glutamic acid with Bi(V) in phosphoric acid medium takes place via decarboxylation of α -carboxylic group followed by deamination as follows :



Fast H_2O



The oxidation product of Glutamic acid has been found as an aldehyde in other reaction²⁰.

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