

## Kinetics and Mechanism of Oxidative Decarboxylation of Glycine by Bi(V) in Phosphoric Acid Medium

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Kinetics of oxidative decarboxylation of glycine by Bi(V)-phosphato complex have been investigated in phosphoric acid-perchloric acid mixture. The products are ammonia, carbon dioxide and formaldehyde. The reaction shows first order kinetics in [oxidant] and [substrate] as well as to  $[H^+]$ . Ionic strength has inverse effect on the reaction rate. The effect of Bi(III) is found to be negligible. Thermodynamic activation parameters have been evaluated. An outer sphere mechanism involving fission of C—C bond and consistent with the observed kinetics has been probed and the rate law derived as:

$$\frac{1}{K_{obs}} = \frac{1}{K_1 K_2 k_3 [S][H^+]} + \frac{1}{k_3}$$

**Key Words:** Kinetics, Mechanism, Decarboxylation, Glycine, Bi(V).

### INTRODUCTION

Amino acid reactions have drawn the attention of many investigators due to their biological activity. Mechanism of oxidative decarboxylation of amino acids has attracted the attention of many workers. It is one of the important biochemical processes and is a potential area for intensive investigation. Although the kinetics of oxidation of amino acids with various oxidants<sup>1-3</sup> have been studied, but the oxidation kinetics of amino acids has not been probed with Bi(V) as oxidant. Herein, the kinetics of oxidation of glycine by Bi(V) in  $H_3PO_4$ - $HClO_4$  mixture is reported.

### EXPERIMENTAL

Sodium bismuthate BDH (AnalaR) was the source of Bi(V) and the sample was employed as supplied without any further treatment. Bismuth nitrate (BDH AnalaR) was used for Bi(III). Phosphoric acid was of E. Merck grade. Doubly distilled  $CO_2$ -free water was used throughout the study. Corning glassware was employed for both storing the solution and for studying kinetics of reactions

unless specified otherwise. All other chemicals were of either AnalaR or GR grade.

A requisite quantity of sodium bismuthate was taken in the mixture of  $\text{H}_3\text{PO}_4$  ( $0.55 \text{ mol dm}^{-3}$ ) and  $\text{HClO}_4$  ( $1.0 \text{ mol dm}^{-3}$ ) and stirred for 30 min constantly. The solution was filtered off from undissolved salts. The pink coloured solution so obtained was quite stable at room temperature for hours but the same was stable for long when it was refrigerated below  $10^\circ\text{C}$ . The solution of Bi(V) was standardized by modified iodometric method<sup>4</sup>.

A known volume (5.0 mL) of Bi(V) solution was added to KI ( $0.1 \text{ mol dm}^{-3}$ ) solution (5 mL) and the pH of the solution was adjusted between 2 and 3 by adding NaOH ( $1.0 \text{ mol dm}^{-3}$ ) and titrated in the presence of EDTA ( $0.01 \text{ mol dm}^{-3}$ ) solution (5 mL). EDTA was used to form complex with Bi(III) and liberate  $\text{I}_2$ . The liberated  $\text{I}_2$  was titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution with starch as indicator.

**Kinetic procedure:** The requisite quantities of various components of the reaction mixture except glycine were taken in a reaction cell. This mixture and the glycine solution were kept separately suspended in a thermostat maintained at desired temperature. The reaction was initiated by adding the requisite solution of the temperature-equilibrated glycine in the reaction mixture. The progress of the reaction was monitored by modified iodometric method of estimation of Bi(V). Aliquot samples (5 mL) of this mixture were withdrawn at regular intervals of time and then quenched in an ice-cold KI ( $0.1 \text{ mol dm}^{-3}$ ) solution. The liberated  $\text{I}_2$  was titrated against sodium thiosulphate solution using starch as indicator. Measurements in triplicate without any interference of the ingredients of the reaction mixture were in agreement within  $\pm 0.2\%$ . Initial rates were computed employing plane mirror method. Kinetic investigations were carried out under pseudo first order conditions taking [glycine] in excess over the oxidant Bi(V).

## RESULTS AND DISCUSSION

The stoichiometry of the reaction was ascertained by allowing the reactions to completion at 303 K at different [glycine]/[oxidant] ratio. The stoichiometry of the oxidation reaction with an excess of Bi(V) over [glycine] corresponds to the reaction represented by eqn. (1).



The higher ratio of  $\Delta[\text{HA}]/[\text{Bi(V)}]$  is due to the self-decomposition of Bi(V).

**Product analysis:** Under the kinetic condition the final oxidation products of glycine were  $\text{CO}_2$ , formaldehyde and ammonia. The presence of formaldehyde as the reaction product was detected by preparing 2,4-dinitrophenyl hydrazone derivative in presence of NaOH and by using Tollen's reagent and chromic acid test<sup>5</sup>.  $\text{NH}_3$  formed was detected by Nessler's reagent and quantitatively estimated by standard micro-Kjeldahl procedure. The low yield of formaldehyde indicated

that it combines with  $\text{NH}_3$  formed during the reaction. For this reason formaldehyde is detected in presence of  $\text{NaOH}$  because the latter facilitates the evolution of  $\text{NH}_3$ .  $\text{CO}_2$  was detected by the conventional limewater test.

**Bi(V) dependence:** The concentration of  $\text{Bi(V)}$  was varied from  $3 \times 10^{-4}$  to  $3 \times 10^{-3} \text{ mol dm}^{-3}$  at fixed [glycine] and also at fixed  $[\text{HClO}_4] = 0.50 \text{ mol dm}^{-3}$  and  $[\text{H}_3\text{PO}_4] = 1.0 \text{ mol dm}^{-3}$ . The plot of the initial rates calculated by plane mirror method<sup>6</sup> against  $[\text{Bi(V)}]$  was linear passing through the origin indicating that the order in  $[\text{Bi(V)}]$  is one. Further, pseudo-first order rate constants calculated were found to be independent of initial  $[\text{Bi(V)}]$  (Table-1).

**Glycine dependence:** [Glycine] was varied in the range  $4.0 \times 10^{-3}$  to  $2.5 \times 10^{-2} \text{ mol dm}^{-3}$  at fixed  $[\text{Bi(V)}] = 8.8 \times 10^{-3} \text{ mol dm}^{-3}$  and also at fixed  $[\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$  and  $[\text{H}_3\text{PO}_4] = 1.0 \text{ mol dm}^{-3}$ .

The plot of initial rate against the concentration of glycine was linear with non zero intercept on ordinate indicating fractional order in [glycine].

**$[\text{H}^+]$  dependence:** Perchloric acid was employed to study the effect of  $[\text{H}^+]$  on the reaction rate. The  $[\text{HClO}_4]$  was varied from 0.5 to 2.0  $\text{mol dm}^{-3}$  at fixed [glycine] =  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  and also at  $[\text{Bi(V)}] = 8.8 \times 10^{-3}$  keeping  $[\text{H}_3\text{PO}_4] = 1.0 \text{ mol dm}^{-3}$ . The ionic strength was maintained constant at 2.0 (adjusted with  $\text{LiClO}_4$ ). The initial rates (IR) increased with increase in  $[\text{HClO}_4]$ .

However,  $[\text{H}^+]$  contributed by  $\text{H}_3\text{PO}_4$  was not ignored in the subsequent calculations of the total  $[\text{H}^+]$  in the reaction mixture.

**Ionic strength dependence:** Ionic strength was varied in the range 1.0–2.4  $\text{mol dm}^{-3}$  by adding requisite quantity of  $\text{LiClO}_4$  at a fixed  $[\text{Bi(V)}] = 8.8 \times 10^{-3} \text{ mol dm}^{-3}$ , [glycine] =  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  keeping  $[\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$  and  $[\text{H}_3\text{PO}_4] = 1.0 \text{ mol dm}^{-3}$ .

The reaction rate decreased with the increase in ionic strength indicating reactive species of opposite charge.

**Bi(III) dependence:** The concentration of  $\text{Bi(III)}$  over and above already present in the solution of  $\text{Bi(V)}$  was varied keeping the concentration of  $\text{Bi(V)}$ , glycine,  $\text{H}_3\text{PO}_4$  and  $\text{HClO}_4$  constant. The reaction rate remained unchanged with the change in the concentration of  $\text{Bi(III)}$ . Such an observation rules out any equilibrium involving  $\text{Bi(III)}$  preceded by the rate-determining step in the reaction mechanism.

The most important consideration in devising the reaction mechanism is to define the reactive species of glycine and  $\text{Bi(V)}$  in  $\text{H}_3\text{PO}_4$ - $\text{HClO}_4$  mixture. Glycine dissociates as follows:

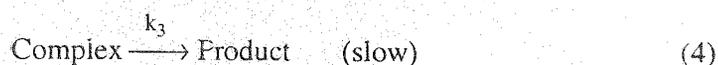
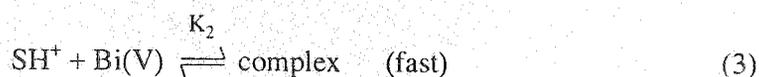
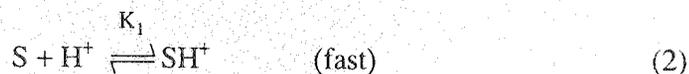


A consideration of isoionic point leads to the conclusion that in strong acidic solution as employed in the present study, the cationic form of glycine is the active species. The speciation of phosphate-bismuth(V) species in the strong acidic solution is impossible. However, the information about fluoro antimony(V)

species<sup>7-9</sup> can be used as a clue considering their group affinity in the periodic table. Bi(V), by analogy, might be in the form of phosphate or aquaphosphato complex. Since hydrolysis of  $[\text{SbCl}_6^-]$  is slow, the hydrolysis of phosphate Bi(V) complex is likely to be very slow. Further, the phosphate ions do not affect the rate as either all phosphato-Bi(V) species are reactive equally or Bi(V) species are fully saturated with phosphate ions.

The consideration of electronic configuration of Bi(V) negates the probability of cationic form of phosphato-Bi(V) complexes. Thus the reactive form of Bi(V) in phosphoric acid medium should be anionic, such as  $[\text{Bi}(\text{PO}_4)_n]^{(5-n)-}$ . For the sake of convenience it is written as Bi(V). Further the reaction rate is independent of Bi(III); therefore, it cannot be a part of the transition state.

Considering all these observations and also accounting for the experimental findings a plausible reaction mechanism consisting of steps (2)–(4) can be suggested.



where  $\text{S} = \text{NH}_2\text{---CH}_2\text{---COOH}$ .

The rate law (5) or (6) can be derived as

$$\begin{aligned} \frac{-d[\text{Bi(V)}]}{dt} &= \frac{K_2 k_3 [\text{Bi(V)}][\text{SH}^+]}{1 + K_2 [\text{SH}^+]} \\ &= \frac{K_1 K_2 k_3 [\text{Bi(V)}][\text{S}][\text{H}^+]}{1 + K_1 K_2 [\text{S}][\text{H}^+]} \end{aligned} \quad (5)$$

$$\frac{1}{K_{\text{obs}}} = \frac{1}{K_1 K_2 k_3 [\text{S}][\text{H}^+]} + \frac{1}{k_3} \quad (6)$$

Plot of  $1/K_{\text{obs}}$  vs.  $1/[\text{S}]$  and plot of  $1/K_{\text{obs}}$  vs.  $1/[\text{H}^+]$  were linear with intercept on ordinate in conformity with rate law (6).

Reciprocal of the intercept yields the values of  $k_3$  from both plots. The values are  $1.08 \times 10^{-2} \text{ s}^{-1}$  and  $1.09 \times 10^{-2} \text{ s}^{-1}$ . Both the values are the same in the error limit. Almost constant value of  $k_3$  is obtained from the plot of  $1/K_{\text{obs}}$  vs.  $1/[\text{S}]$  and  $1/K_{\text{obs}}$  vs.  $1/[\text{H}^+]$  support rate law (6) and hence the proposed mechanism. The values of ( $k_3$ ) at different temperatures were computed by varying  $[\text{S}]$  at each temperature. Activation parameters were calculated from the plot of  $\log k_3$  vs.  $1/T$  and  $(\log k_3/T)$  vs.  $1/T$ . The values of energy of activation, frequency factor and entropy of activation were found to be  $57.35 \text{ kJ mol}^{-1}$ ,  $6.2 \text{ s}^{-1}$  and  $41.20 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

The low value of ( $E_a$ ) and negative value of  $\Delta S^\ddagger$  suggest that the degree of freedom of intermediate complex is less than that of the reacting molecules and the intermediate complex permits a facile electron transfer from the substrate to Bi(V).

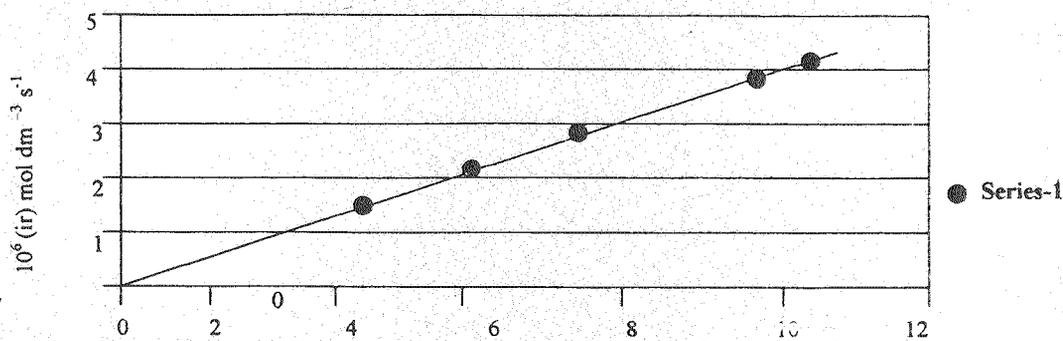


Fig. 1. Plot of initial rate vs. [Bi(V)]; [S] =  $10 \times 10^{-2}$  mol dm<sup>-3</sup>; [H<sub>3</sub>PO<sub>4</sub>] = 1.0 mol dm<sup>-3</sup>; [HClO<sub>4</sub>] = 0.5 mol dm<sup>-3</sup> [• Series 1]

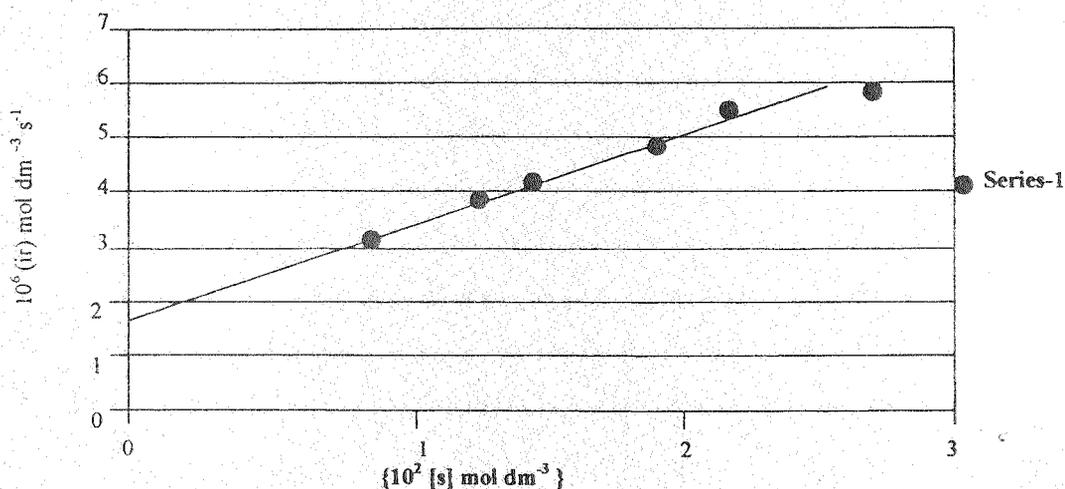


Fig. 2. Plot of initial rate vs. [S]<sup>-1</sup>; [Bi(V)] =  $8.8 \times 10^{-3}$  mol dm<sup>-3</sup>; [H<sub>3</sub>PO<sub>4</sub>] = 1.0 mol dm<sup>-3</sup>; [HClO<sub>4</sub>] = 0.5 mol dm<sup>-3</sup> [• Series 1]

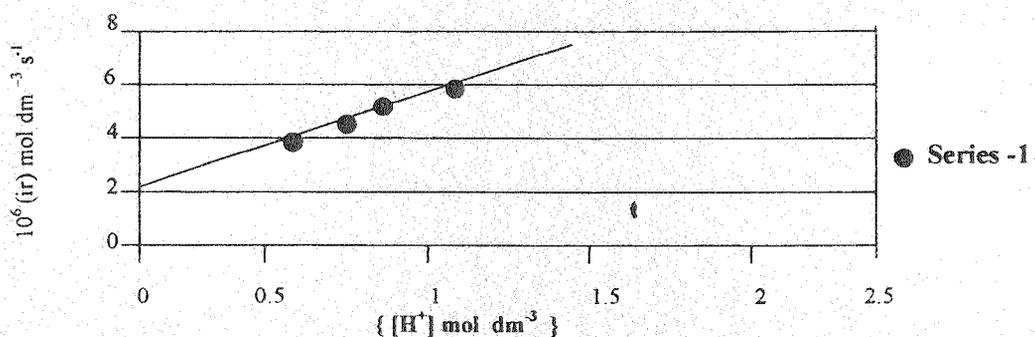


Fig. 3. Plot of initial rate vs. [H<sup>+</sup>]<sup>-1</sup>; [Bi(V)] =  $8.8 \times 10^{-3}$  mol dm<sup>-3</sup>; [H<sub>3</sub>PO<sub>4</sub>] = 1.0 mol dm<sup>-3</sup>; [HClO<sub>4</sub>] = 0.5 mol dm<sup>-3</sup> [• Series 1]

TABLE-1  
PSEUDO-FIRST ORDER RATE CONSTANT ( $k_0$ ) FOR OXIDATION OF GLYCINE (S)  
BY Bi(V) IN PHOSPHORIC ACID (1.0 mol dm<sup>-3</sup>) AND  
PERCHLORIC ACID (0.5 mol dm<sup>-3</sup>) MIXTURE

$10^4$ [Bi(V)] (mol dm <sup>-3</sup> )	$10^2$ [S] (mol dm <sup>-3</sup> )	[H <sup>+</sup> ] (mol dm <sup>-3</sup> )	$10^6$ [IR] (mol dm <sup>-3</sup> )	$k_0$ (S <sup>-1</sup> )
3.0	1.00	0.5	1.25	
5.0	1.00	0.5	2.10	
6.0	1.00	0.5	2.50	
8.8	1.00	0.5	3.45	
9.0	1.00	0.5	3.80	
10.0	1.00	0.5	4.25	
8.8	0.80	0.5	3.14	
8.8	1.00	0.5	3.70	
8.8	1.25	0.5	4.17	$k_0 = 4.2 \times 10 \times 10^{-3} \text{ S}^{-1}$
8.8	1.67	0.5	4.76	
8.8	2.00	0.5	5.26	
8.8	2.50	0.5	5.71	
8.8	1.00	0.6	4.00	
8.8	1.00	0.8	4.76	
8.8	1.00	1.0	5.40	
8.8	1.00	1.25	5.88	
8.8	1.00	2.0	7.14	

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(Received: 23 February 2005; Accepted: 21 March 2006)

AJC-4751