

**“*O<sub>S</sub> (VIII) OXIDE CATALYZED OXIDATION OF GLYCINE BY DIBROMO DIMETHYL HYDANTOIN (DBDMH) IN ACID MEDIUM*”**

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## ABSTRACT

*O<sub>S</sub> (VIII) Oxide* -catalyzed oxidation of Glycine (Gly) by DIBROMO DIMETHYL HYDANTOIN in aqueous acetic acid medium” has been carried out in presence *O<sub>S</sub> (VIII) OXIDE* in aqueous acetic acid medium, at 308 k. the reaction is fully *O<sub>S</sub> (VIII) OXIDE* catalyzed and the reaction rate ebbs when the concentration of DMH added in reaction mixture. Increasing in dielectric permittivity of the medium; increases the rate oxidation. The stoichiometry of the reaction was found to be 1:1. The reported oxidation product of Glycine was identified as formaldehyde was formed as the end-product, which was detected by conventional methods and spot tests. Various activation parameters have been computed. The proposed mechanisms was good consistent with the observed experimental results.

Key words: DIBROMO DIMETHYL HYDANTOIN, DMH, formaldehyde, Amino acids

## INTRODUCTION

Kinetic studies are receiving much importance in the recent years. Since, it is such a part of science that deals with the rate of chemical reaction, with all factors, which influence the rate of reaction, and with the explanation of the rate in terms of the reaction mechanism. To many chemists the real heart of chemistry is the study of mechanisms. Thus, chemical kinetics can be defined as that branch of chemistry concerned with the study and prediction of time dependent systems<sup>1</sup>.

Amino acids are simple organic compounds. Their physical and chemical properties are due to the presence of both acidic and basic groups present in the same molecule. These simple molecules act not only as the building blocks of protein but also play a significant role in metabolism. In metabolism, amino acids are subjected to many reactions and can supply precursors for many endogenous substances, e.g. haemoglobin in blood. These small

molecules can undergo many reaction, depending on particular amino acid contains non-polar group or polar group. Amino acids are active site residues of enzymes, and help also in maintaining the correct con-formation of enzymes by keeping them in their proper ionic states. Thus, their oxidation may help in understanding enzyme kinetics. The oxidation of these molecules is interested because of different products are obtained with different oxidants [2-7]. The kinetics of oxidation of several amino acids by a number of oxidants has been reported [8-12]. The products of oxidations were generally CO<sub>2</sub>, NH<sub>3</sub>, and aldehydes. Kinetics of oxidation of amino acids by Chloramines-T (CAT) in both acid and alkaline media has been studied [13-15]. Catalysed oxidation of amino acids by Chloramine-T in aqueous acid medium as well as in alkali medium have been reported in the literature [16-23]. But no work have been seen or reported Ru (III) catalyzed oxidation of glycine with DBDMH in aqueous HCl medium. Therefore, all the facts are kept in mind; I have chosen this title of present paper to explore detailed reaction mechanism of *O<sub>s</sub> (VIII) Oxide* catalyzed oxidation of glycine (an  $\alpha$ -Amino acid) by DBDMH in aqueous acetic acid medium.

## Materials and methods

In the Present kinetic investigation of *O<sub>s</sub> (VIII) Oxide* catalyzed kinetics of oxidation of Glycine by Dibromo dimethyl hydantoin (DBDMH) in aqueous acetic acid medium in presence of hydrochloric acid, different chemicals were used in the form of solutions. The procedure employed for the preparation of these solutions and for the kinetic study mentioned in the following sections:

### A. Preparations of various solutions and their standardization

The solution of Dibromo dimethyl hydantoin (DBDMH) (sigma-Aldrich sample) so obtained was prepared by dissolving its weighed quantity in 100% CH<sub>3</sub>COOH (B.D.H.) and kept either amber colored flask or black paper wrapped around it to save it from the action of diffused day light which alters appreciably its concentrations.

The standardization of Dibromo dimethyl hydantoin (DBDMH) was done by taking one ml of its solution in conical flask to which 10 ml of 2% KI solution followed by 5ml of 2N H<sub>2</sub>SO<sub>4</sub> added to it. The liberated iodine was titrated against standard sodium thiosulphate (hypo) solution using starch solution as an indicator [24]. Glycine (anal. grade)) was used as

substrates for the preparation of solutions. The solution of Glycine was prepared in requisite volume of glacial acetic acid.

The solution on of sodiumthiosulphate was prepared by taking a (B.D.H. grade) sample in distilled water and standardized against standard  $K_2Cr_2O_7$  solution iodometrically[36]. The standard solution of  $K_2Cr_2O_7$  was prepared by dissolving the weighed amount of B.D.H. sample in distilled water. However, it was essential to prepare a fresh solution as it is reported that the spectra of this solution do not alter appreciably for over a period of days or weeks even in diffused day of light [25].

Stock solution of HCl acid (analytical grade) of appropriate strength was prepared by diluting the calculated volume (from specific gravity) of acid with distilled water and finally its concentration was determined by titrating it against standard NaOH solution using phenolphthalein as an indicator.

### **Preparation of other solutions**

- (1) dimethyl hydantoin (sigma china ) is sparingly soluble in  $H_2O$ ; hence, 0.016 M solution of dimethyl hydantoin was used.
- (2) Binary solvent mixtures of acetic acid-water were prepared by mixing known volume of these solvents.
- (3) The solution of acrylonitrile [27-28] was prepared by standard method for the identification of free radical formed during the course of oxidation.

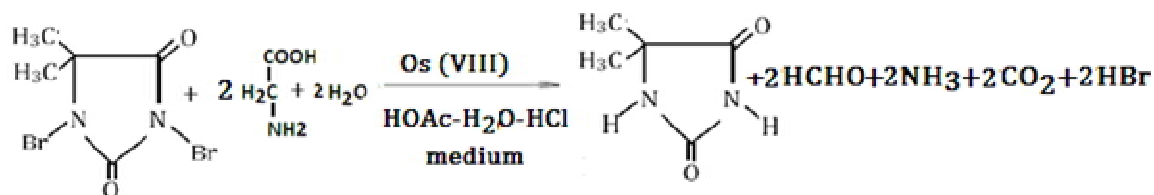
### **B. Kinetic studies**

Preliminary experiments for the oxidation of glycine with DBDMH was conducted to choose the appropriate conditions of concentration of the reactants and temperature under which these oxidation proceeds with measurable rate. It has been observed that in the presence of  $O_5$  (VIII) Oxide, the oxidation of these substrates proceeds at a measurable rate. The kinetic study of each system undertaken was carried out by integration and Oswald's isolation methods [29]. In each set of reaction, concentration of substrate was taken in large excess over the concentration of oxidant.

The known volume of oxidant dissolved in aqueous acetic acid binary solvent  $O_5$  (VIII) oxide solution (dissolved in solvent mixture of HCl acid- $H_2O$ ) were taken in a conical flask while substrate and rest amount of water were in another conical flask. These two-stopper flasks were placed at experimental temperature in a thermostat of sensitivity  $\pm 0.10C$ . After the equilibrium of the temperature, the both solutions were mixed and aliquot was withdrawn immediately and was quenched. The amount of un-reacted DBDMH was estimated iodometrically with the help of standard solution of sodium thiosulphate using starch as an indicator. The titre value at zero time was taken as "a". The aliquots were withdrawn at regular intervals and were estimated for un-reacted DBDMH. These readings are the values of (a-x) at time "t". The experimental data were fed into the integrated form of equation for first-order reactions. The values of pseudo first-order rate constant obtained from the rate equation –

$$k_1 = 2.303/t. \log a/(a-x)$$

**Stoichiometry and Product Analysis:** Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of DBDMH over glycine and 30 % acetic acid for 24 hrs. at 308 K. The un-reacted oxidant (DBDMH) was determined by iodometrically. The estimated amount of un-reacted DBDMH showed that one mole of glycine consumes one mole of DBDMH. The formaldehyde was found as the end-product of oxidation. These product was identified by forming their 2,4-dinitrophenylhydrazone (2,4-DNP, which was characterized by their melting point, spot test[27-28] and existing conventional method.



## RESULTS AND DISCUSSIONS

The experimental kinetic data have been collected for variant concentrations of oxidant (N,N-DBDMH) at fixed concentration of other reactants and temperature. The linear plots of  $\log (a-x)$  vs. Time, suggested that the first order rate dependency with respect to

oxidant. The value of first-order rate constant evaluated from the plot is excellently in good agreement with those calculated from first-order rate equation (Table-1).

**Table: 1**

[DBDMH] $10^3$ (mol.dm. <sup>-3</sup> )	Glycine
	$10^5 k_1$ (s <sup>-1</sup> )
1.00	13.89
2.00	13.97
2.50	13.99
4.00	14.04
5.00	14.01

[Gly] =  $1.25 \times 10^{-2}$  (mol.dm.<sup>-3</sup>)  
 [Os (VIII)] =  $1.25 \times 10^{-3}$  (mol.dm.<sup>-3</sup>)  
 [H<sup>+</sup>] =  $1.25 \times 10^{-3}$  (mol.dm.<sup>-3</sup>)  
 HOAc-H<sub>2</sub>O = 30%(v/v),  
 Temperature = 308 K.

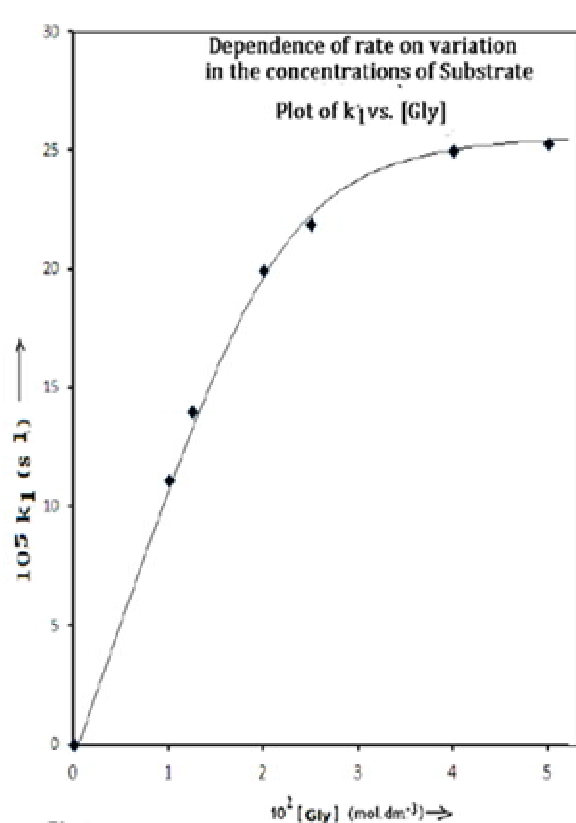


Fig.1

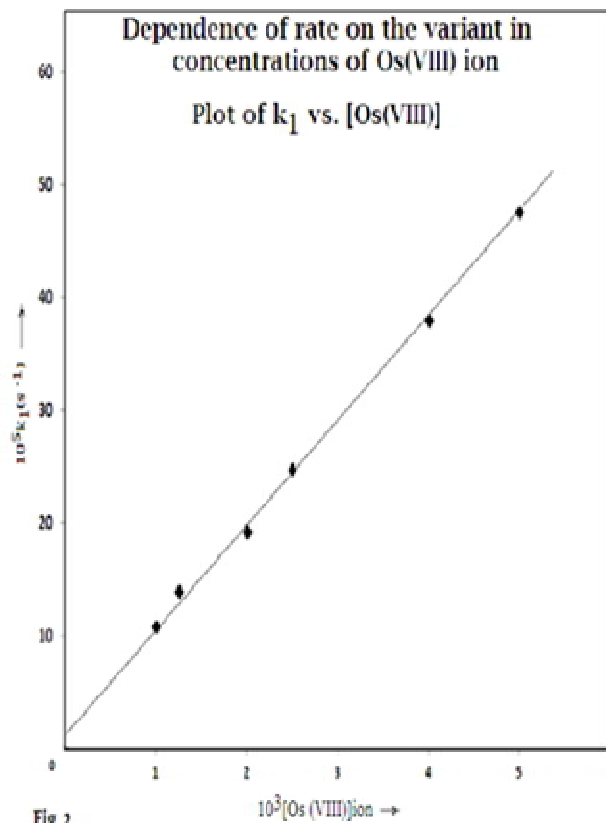
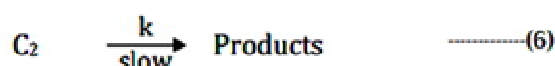
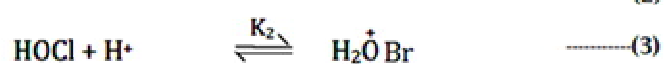
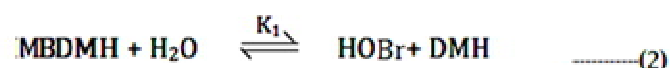
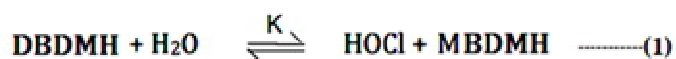


Fig.2

The pseudo first-order rate increases with increase in the concentration of substrate. The plot of  $k_1$  versus [substrate] are obtained linear passing through origin in lower concentrations, while it tend 1 to 0 orders at higher concentrations (Fig.1), Suggested that the formation of a complex during the course of the reaction. Reaction is fully Os (VIII) oxide catalyzed but velocity of the reaction increases with increase the concentration of Os (VIII) oxide. The plot of  $k_1$  vs. [Os (VIII)] is obtain linear with the positive unit slope, confirming that the reaction fully catalyzed(fig.2). Various activation parameters namely temperature coefficient, energy of activation ( $E_a$ ), frequency factor ( $A$ ), enthalpy of activation ( $\Delta H^\ddagger$ ), free energy of activation ( $\Delta G^\ddagger$ ), and entropy of activation ( $\Delta S^\ddagger$ ) for each reaction are calculated for glycine–DBDMH system and according to the reaction mechanism, rate equation and order of reaction have been discussed.

## MECHANISM

The relevant rate law to explain the kinetic orders and mechanistic sequences are given below.



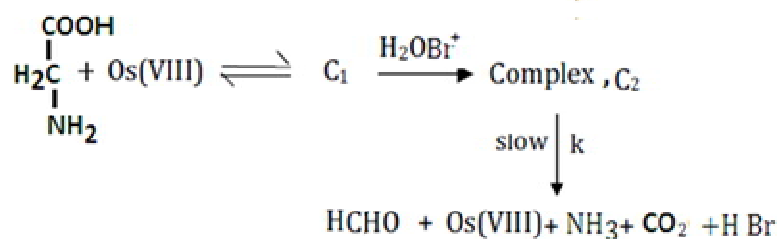
Where  
S stands for Substrate(Glycine)

**Rate law:**

$$\text{Rate} = k_{\text{obs}} = \frac{kK_1K_2K_3K_4[\text{S}]_T[\text{H}^+]_T[\text{DBDMH}][\text{Os(VIII)}]}{[1+K_3[\text{Os(VIII)}]][1+K_1K_2[\text{DBDMH}][1+K_5[\text{H}^+]]]} \quad \text{-----(6)}$$

The rate law (Eq. (13)) is good agreement with the observed kinetic data.

Mechanistically, the reaction sequence can be depicted as follows under the kinetic conditions of [substrate] > [oxidant]:



## CONCLUSIONS

The kinetics of the ruthenium (III) chloride catalyzed oxidation of glycine, by DBDMH in aqueous acid medium at 308 K, was discussed. A negative  $\Delta S^\ddagger$  value

indicates the formation of transition state fair and rapid with lower degree of freedom. Further, the high value of free energy of activation suggests a solvated activated complex. Formaldehyde is the main product of the reaction.



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