

***Mn (II) chloride-catalyzed oxidation of Glycine by N,N-DBDMH in aqueous acetic acid-HCl medium"***H.D.Gupta<sup>1\*</sup>, J.P.Tiwari<sup>1</sup>, A.Gupta, Akhilesh Kumar<sup>1</sup>, A Pandey<sup>1</sup>, P.Satnami<sup>1</sup>

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Received: 17/03/2017

Revised: 22/03/2017

Accepted: 23/03/2017

**ABSTRACT**

*Mn (II) chloride* -catalyzed oxidation of Glycine by Dibromo dimethyl hydantoin in aqueous acetic acid medium" has been carried out in presence *Mn (II) chloride* in aqueous acetic acid medium, at 313 K. the reaction is fully *Mn (II) chloride* catalyzed and the reaction rate ebbs when the concentration of Dimethyl hydantoin (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: *Mn (II)*, catalyzed, Dibromo dimethyl hydantoin, Glycin dielectric permittivity .

**INTRODUCTION**

Man knew chemical reactions long before chemistry had attained the status of science and sensed that substances changed their properties under certain external conditions, which is a characteristic of chemical reactions <sup>[1]</sup>. 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

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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.

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<sup>[2-7]</sup>. The kinetics of oxidation of several amino acids by a number of oxidants has been reported<sup>[8-12]</sup>. 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<sup>[13-15]</sup>. Catalysed oxidation of amino acids by Chloramine-T in aqueous acid medium as well as in alkali medium have been reported in the literature <sup>[16-23]</sup>. But no works have been seen or reported *Mn (II) chloride* 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 *Mn (II) chloride* catalyzed oxidation of glycine (an  $\alpha$ -Amino acid) by DBDMH in aqueous acetic acid medium.

## Materials and methods

In the Present kinetic investigation of *Mn (II) chloride* 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

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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<sup>[24]</sup>. 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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution iodometrically<sup>[24]</sup>. The standard solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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<sup>[25]</sup>.

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

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- (1) dimethyl hydantoin (sigma china ) is sparingly soluble in H<sub>2</sub>O; 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 <sup>[27-28]</sup> 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 Ru (III) Chloride, 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.

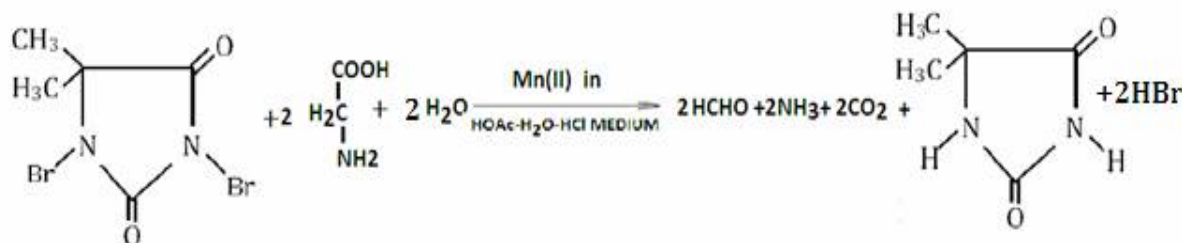
The known volume of oxidant dissolved in aqueous acetic acid binary solvent and *Mn (II) chloride* solution (dissolved in solvent mixture of HCl acid-H<sub>2</sub>O) were taken in a conical flask while substrate and rest amount of water were in another conical flask. These two-stopper flasks were placed at experimental temperature in a thermostat of sensitivity  $\pm 0.10\text{C}$ . 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 –

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

**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<sup>[27-28]</sup> and existing conventional method.



## Results and discussions

The experimental kinetic data have been collected for variant concentrations of oxidant (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 (Fig.1). 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**

**Summary: Dependence of rate of oxidation reaction on the initial concentration of oxidant**

[Gly]	=	$2.50 \times 10^{-2}$ (mol.dm. <sup>-3</sup> )
[Mn (II)]	=	$2.00 \times 10^{-3}$ (mol.dm. <sup>-3</sup> )
[H <sup>+</sup> ]	=	$2.00 \times 10^{-3}$ (mol.dm. <sup>-3</sup> )

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HOAc-H <sub>2</sub> O	=	40%(v/V),
Temperature	=	313 K.

The reaction rate increased with increase in [Gly.]. Plot of  $k_1$  versus [Gly.] initially linear passing through origin at low concentrations but at higher concentrations of substrate it bent to x-

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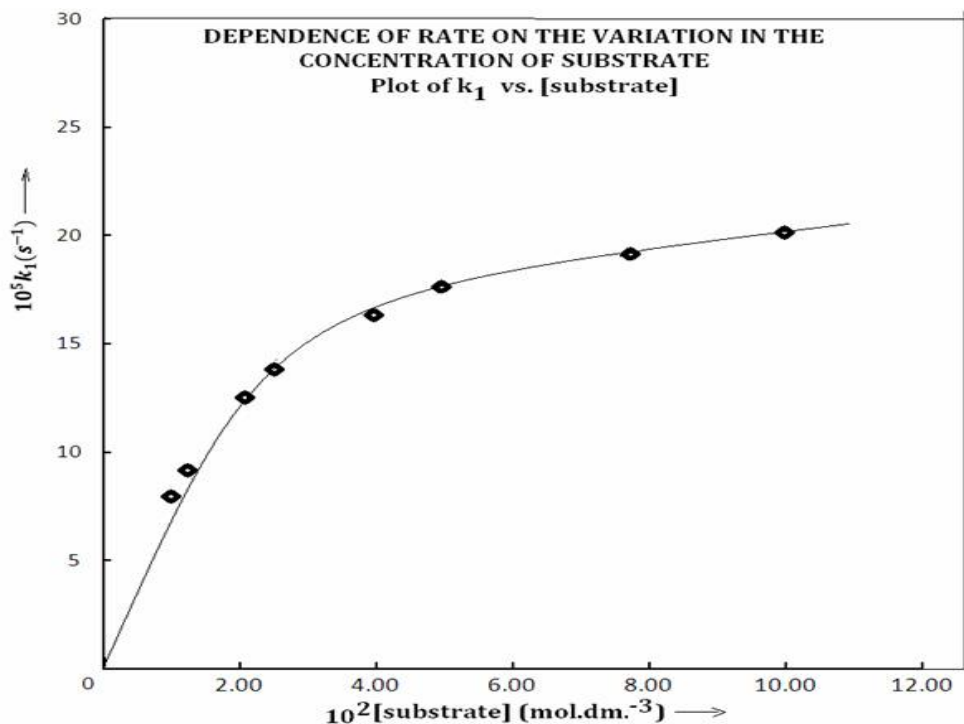
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[ N,N-DBDMH ] $10^3$ (mol.dm. <sup>-3</sup> )	Glycine
	$10^5 k_1 (s^{-1})$
1.00	9.40
1.25	9.33
2.00	9.37
2.50	9.43
4.00	9.38
5.00	9.36

refore, rate =  $k_1[\text{Gly.}]^{1/3}$ . This explains that the influence of substrate concentration on the rate is low. 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, Suggested that the formation of a complex during the course of the reaction (Fig. 1).

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[N,N-DBDMH]	=	$2.50 \times 10^{-3} (\text{mol.dm}^{-3})$
[Gly.]	=	$1.25 \times 10^{-3} (\text{mol.dm}^{-3})$
[H <sup>+</sup> ]	=	$2.00 \times 10^{-3} (\text{mol.dm}^{-3})$
HOAc-H <sub>2</sub> O	=	40%(v/V),
Temperature	=	313 K.

Reaction is fully Mn (II) chloride catalyzed but velocity of the reaction increases with increase the concentration of Mn (II) chloride. The plot of  $k_1$  vs. [Mn (II)] and plot of  $\log k_1$  vs.  $\log$  Mn (II) chloride is obtain linear with the positive unit slope, confirming that the reaction fully catalyzed(Table-2).

The first-order rate constant increases with increase composition of acetic acid i.e. rate accelerated with increase in dielectric constant of the medium. The plot of  $\log k_1$  versus  $10^3/D$  were obtained linear with positive slope. The velocity of the reaction increases with increase the concentration of HCl acid. The reaction rate ebbs when the concentration of DMH added. The

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presence of free radicals in the system under study was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method.

Table-2: Dependence of rate on the variation in the concentrations of Mn(II) chloride

$10^3[\text{Mn (II)}]$ (mol.dm. <sup>-3</sup> )	$10^5 k_1(\text{s}^{-1})$
1.00	6.70
1.25	7.42
1.50	7.98
2.00	9.43
2.50	10.77
3.00	12.04
4.00	14.93
5.00	17.38

The non-occurrence of turbidity and white precipitate clearly indicates the absence of free radicals in the system. 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. The iso-kinetic and Exner's have been explained

## Mechanism

In view of the above experimental kinetic data, facts and finding, a suitable mechanism has been proposed for the oxidation of Glycine – DBDMH system as:

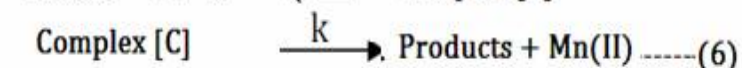
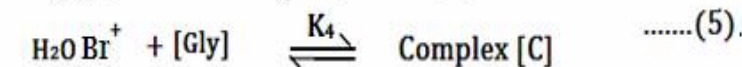
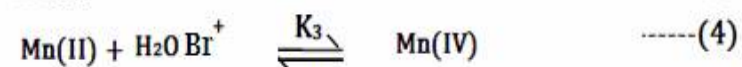
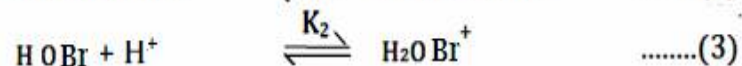
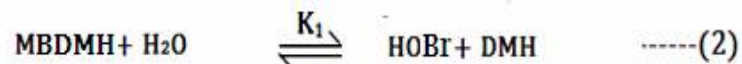


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Rate law:



$$\text{rate} = kC \quad \text{---(7)}$$

$$= kK_4[Gly][Mn(IV)] \quad \text{---(8)}$$

$$= kK_4[Gly.][H_2OBr^+][Mn(II)] \quad \text{---(9)}$$

$$= \frac{kK_3K_4[Gly.][H_2OBr^+]_T[Mn(II)]}{[1+K_3][Mn(II)]} \quad \text{---(10)}$$

$$k_{\text{obs}} = \frac{kK_3K_4[Gly.][H^+][N,N'-DBDMH]_T[Mn(II)]}{\{[1+K_2[N,N'-DBDMH]_T[1+K_3][Mn(II)]] [1+K_2[H^+]]\}} \quad \text{---(11)}$$

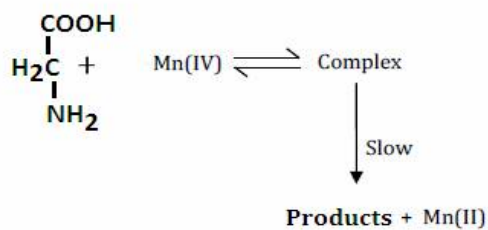
The above rate law possibly explains all the experimental kinetic observations.

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

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## CONCLUSION

The kinetics of the Mn (II) chloride catalyzed oxidation of glycine, by N,N-DBDMH in aqueous acid medium at 313 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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