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“Kinetic and thermodynamic study for the oxidation of alanine by dibromo dimethyl hydantoin in presence of Ru (III), concentration as homogeneous catalyst”

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ABSTRACT

Ru (III) chloride-catalyzed oxidation of alanine (Ala.) by DBDMH in aqueous acetic acid medium” has been carried out in presence of Ru (III) chloride in aqueous acetic acid medium, at 308 k. the reaction is fully Ru (III) chloride 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 alanine (Ala.) was identified as acetaldehyde 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, alanine (Ala.) 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 reactions¹. 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.

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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^[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 CO₂, NH₃, and aldehydes. Kinetics of oxidation of amino acids by Chloramines-T (CAT) in both acid and alkaline media has been studied^[13-15]. Catalyzed 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 has 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 Ru (III) chloride catalyzed oxidation of alanine (Ala.) (an α -Amino acid) by DBDMH in aqueous acetic acid medium.

Materials and methods

In the Present kinetic investigation of Ru (III) 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 employed for the preparation of these solutions and for the kinetic study mentioned in the following sections:

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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% CH₃COOH (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 H₂SO₄ added to it. The liberated iodine was titrated against standard sodium thiosulphate (hypo) solution using starch solution as an indicator ^[24]. alanine (Ala.) (anal. grade)) was used as substrates for the preparation of solutions. The solution of alanine (Ala.) 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 K₂Cr₂O₇ solution iodometrically^[26]. The standard solution of K₂Cr₂O₇ 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 H₂O; 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.

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- (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 alanine (Ala.) 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 Ru(III) chloride solution (dissolved in solvent mixture of HCl acid-H₂O) 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 –

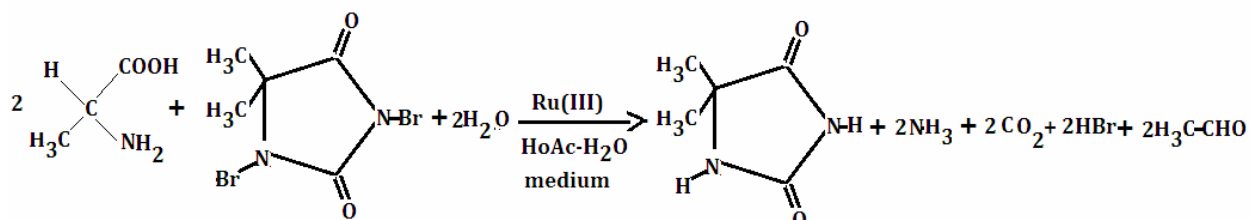
$$k_1 = 2.303/t. \log a/(a-x)$$

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 alanine (Ala.) consumes one mole of DBDMH. The acetaldehyde was found as the end-product of oxidation. These

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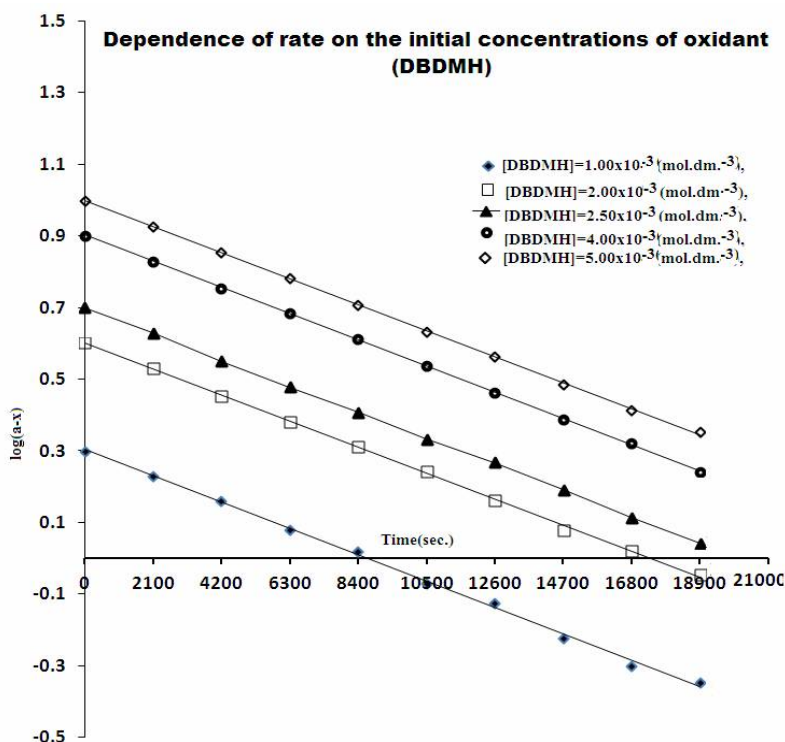
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product was identified by forming their 2,4-dinitrophenylhydrazone (2,4-DNP, which was characterized by their melting point, spot test^[27-28] and existing conventional method.



Results and discussions

The experimental kinetic data have been collected for variant concentrations of oxidant (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.



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	[DBDMH]	=	2.50X10 ⁻³ (mol.dm. ⁻³)	
	[Ru (III)]	=	1.25X10 ⁻³ (mol.dm. ⁻³)	
Fig.1: Dependence of oxidation reaction on concentration of	HOAc-H ₂ O	=	30%(v/V),	rate of the initial oxidant
	Temperature	=	308 K.	
(DBDMH)				

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-axis tends 1 to 0 orders. Therefore, $\text{rate} = k_1[\text{Ala.}]^{1/3}$. 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. 2).

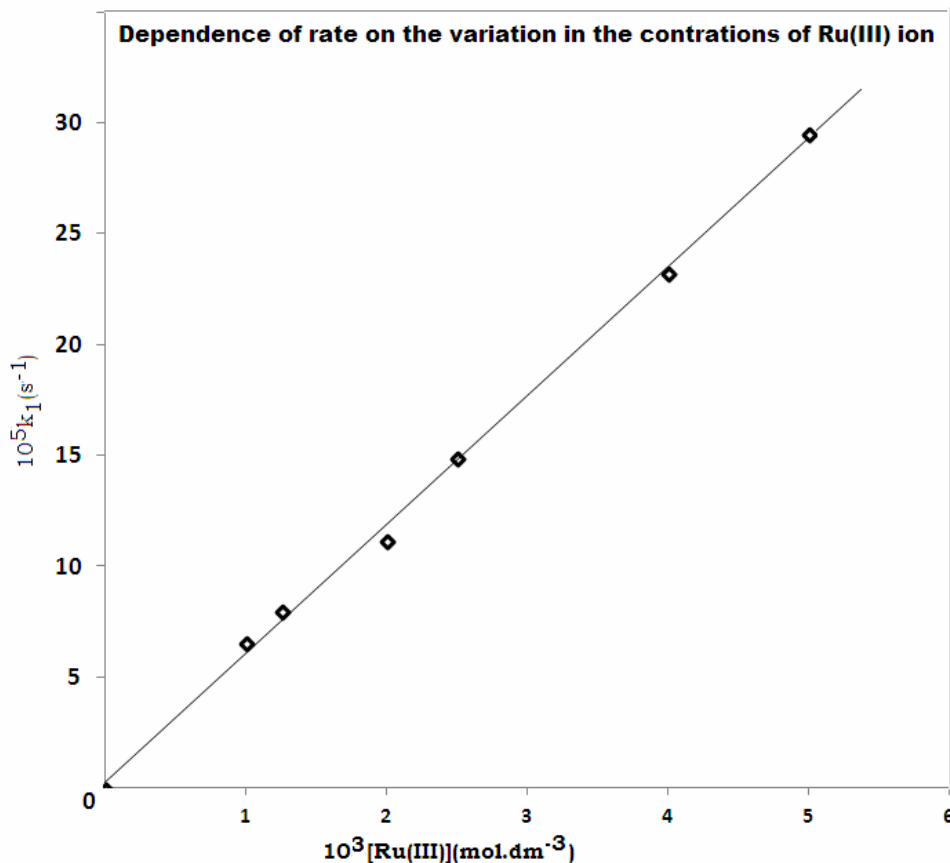


Fig.2: Dependence of oxidation reaction on concentration of

[DBDMH]	=	2.50X10 ⁻³ (mol.dm. ⁻³)
[Ala]	=	1.25X10 ⁻² (mol.dm. ⁻³)
HOAc-H ₂ O	=	30%(v/V),
Temperature	=	308 K.

rate of the initial [Ru(III)]ion

Reaction is fully Ru (III) chloride catalysed but velocity of the reaction increases with increase the concentration of Ru (III) chloride. The plot of k_1 vs. [Ru (III)] chloride and plot of $\log k_1$ vs. $\log [\text{Ru (III)}]$ is obtain linear with the positive unit slope, confirming that the reaction fully catalyzed(Fig. 2).

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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 presence of free radicals in the system understudy was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and white precipitate clearly indicates the absence of free radicals in the system.

Table: 1

Thermodynamics parameters

[DBDMH]	=	2.50×10^{-3} (mol.dm. ⁻³)
[Ala.]	=	1.25×10^{-2} (mol.dm. ⁻³)
[Ru (III)]	=	2.00×10^{-3} (mol.dm. ⁻³)

Substrate	E_a kJ/mol.	A (s ⁻¹)	ΔH^\ddagger kJ/mol.	$-\Delta G^\ddagger$ kJ/mol.	$-\Delta S^\ddagger$ JK/mol.
Alanine	57.65 ±0.46	4.11×10^5 ±0.89	65.02 ±0.49	90.16 ±0.72	99.36 ±0.87

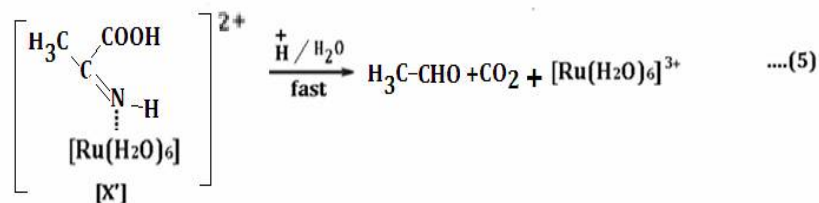
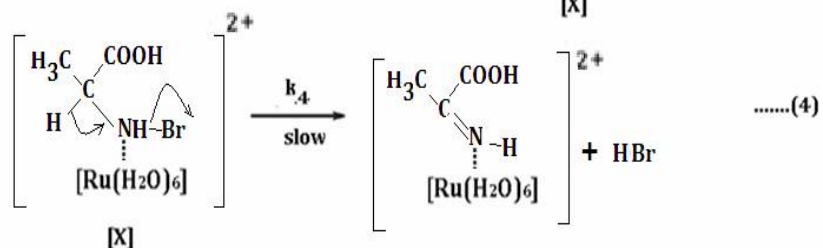
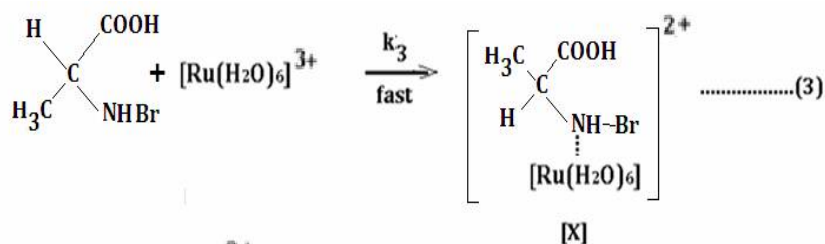
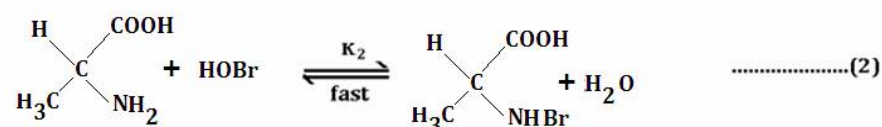
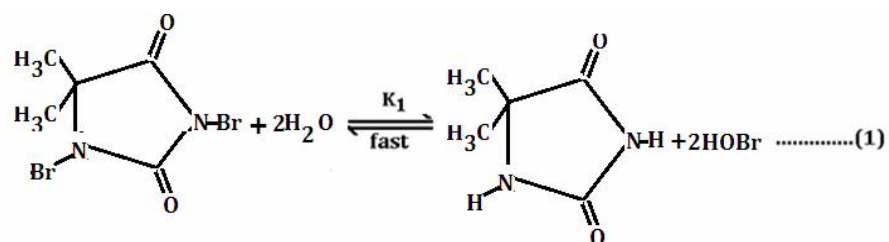
Various activation parameters namely temperature coefficient, energy of activation (E_a), frequency factor (A), enthalpy of activation (ΔH^\ddagger), free energy of activation (ΔG^\ddagger), and entropy of activation (ΔS^\ddagger) for each reaction are calculated for glycine–DBDMH system (Table:1) and according to the reaction mechanism, rate equation and order of reaction have been discussed. The iso-kinetic and Exner's have been explained

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Mechanism

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



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Rate law:

Derive rate law is given as:

$$k_{\text{obs.}} = \frac{K_3 K_1 K_2 [\text{Ala.}] [\text{DBDMH}]^t [\text{Ru(III)}]}{\{1 + K_1\} + \{K_1 K_2 [\text{Ala.}]\}} \dots\dots\dots (6.)$$

The rate law (Eq. (6)) is good agreement with the observed kinetic data.

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 ΔS^\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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