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“Ru (III) CHLORIDE-CATALYZED OXIDATION OF GLYCINE (GLY) BY N-CHLOROPHTHALIMIDE IN ACID MEDIUM: MECHANISTIC INVESTIGATION AND KINETIC MODELING”

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Abstract

The kinetics of oxidation of Glycine (Gly) by N-Chlorophthalimide (NCP) with Ru (III) catalysis has been investigated in aqueous HOAC-HCl medium. The reaction is of pseudo first order in [NCP], first order in [Glycine] and first order in [Ru (III)] ion. The velocity of the reaction increases with increase in the concentration of HCl acid. Effect of temperature has been studied and thermodynamic parameters are calculated and a suitable mechanism has been suggested.

Key words: Glycine; N-Chlorophthalimide; pseudo first order; Ru(III) catalysis; thermodynamic parameters

INTRODUCTION

N- Halo compounds, which are good sources of positive halogen in polar solvents have been extensively employed as halogenating and oxidizing agents for organic substrate¹. Amongst the N-chloro compound N-Chlorophthalimide² (NCP) has wide synthetic utility as it has the most polar N-X bond among the series TCIA, N-chlorobarbitol, NCS and NBS³. TCICA has been used in synthetic organic chemistry as an oxidizing and halogenating reagent⁴⁻⁷. 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 reactions, 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 conformation 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 interesting because different products are obtained with different oxidants⁸⁻¹⁴. The kinetics of oxidation of several Amino acids by a number of oxidants has been reported¹⁵⁻¹⁹. These reports are not sufficient to understand Ru (III) catalyzed reaction in acidic medium. Therefore, we reported in this paper detailed reaction mechanism of Ru(III) chloride catalyzed oxidation of glycine by N-Chlorophthalimide in aqueous HCl medium.

EXPERIMENTAL

Materials

Glycine was purchased from Sigma Chemicals (St. Louis, MO) were of acceptable grades of purity and were used as received. Aqueous solutions of the compounds are employed. An aqueous solution of NCP was prepared, standardized iodometrically and stored in amber colored stopper bottles until further use. The concentration of stock solutions was periodically. A solution of RuCl₃ (Merck) in HCl was used as the catalyst. Allowance was made for the amount of HCl present in catalyst solution, while preparing solution for kinetic runs. Reagent grade chemicals and doubly distilled water were used throughout the experiments.

Kinetic measurements

The reactions were carried out under pseudo first-order condition by taking a known excess of [l-Glycine] over [Oxidant] at 313 K. 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 $\pm 0.1^{\circ}\text{C}$. After the equilibrium of the temperature, the both solutions were mixed and aliquot was withdrawn immediately and was quenched. The amount of unreacted NCP 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."

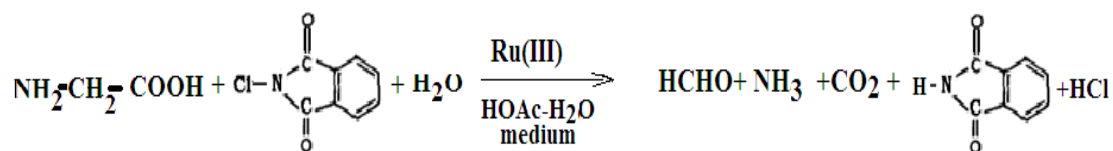
The aliquots were withdrawn at regular intervals and were estimated for un-reacted N-chlorophthalimide. These readings are the values of (a-x) at time "t". The experimental data

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 –

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

The rate constant k was found fairly constant within the experimental error suggested that each reaction obeys first-order kinetics. The effect of $[HCl]$ on the oxidation of Glycine was determined by adding different concentrations of HCl . The effect of phthalimide also investigated. Different composition of binary solvent mixtures of acetic acid-water was used to study the effect of variation of dielectric constant of the medium.

Stoichiometry and end-product analysis: stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of N -chlorophthalimide over glycine and $RuCl_3$ in HCl acid, for 24 hrs. at 313K. the un-reacted oxidant (N -chlorophthalimide) was determined by iodometrically. The estimated amount of un-reacted N -chlorophthalimide showed that one mole of glycine consumes one mole of N -chlorophthalimide.



Formaldehyde is identified as the main product of oxidation which was identified by existing conventional methods^[20-26].

RESULTS AND DISCUSSIONS

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

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. This confirmed the existence of equilibrium between glycine (Gly) and oxidant (NCP) and appeared before the slow step. Furthermore confirming the fractional order dependence on [Gly.]. (Fig. 2; $r > 0.9745$). Fractional slopes of the plots indicate a fractional order dependence on [Gly.]. (Table :1). This implies that, rate is proportional to [Gly.]. Therefore, rate = $k_1[\text{Gly.}]^{0.33-0.66}$. This explains that the influence of substrate concentration on the rate is low. Reaction is fully Ru (III) chloride catalyzed and velocity of the reaction increases with increase the concentration of Ru (III) chloride. The plot of k_1 vs. [Ru (III)] chloride is obtained linear with the positive unit slope, confirming that the reaction fully catalyzed. (Fig.3); 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 plot of k_1 vs. [HCl] is obtained linear with the positive unit slope, confirming that the reaction is acid catalyzed (Fig.4). The reaction rate ebbs when the concentration of phthalimide 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. Various activation parameters namely temperature coefficient, energy of activation (E_a) (Fig.5), 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–NCP system and according to the reaction mechanism, rate equation and order of reaction have been discussed.

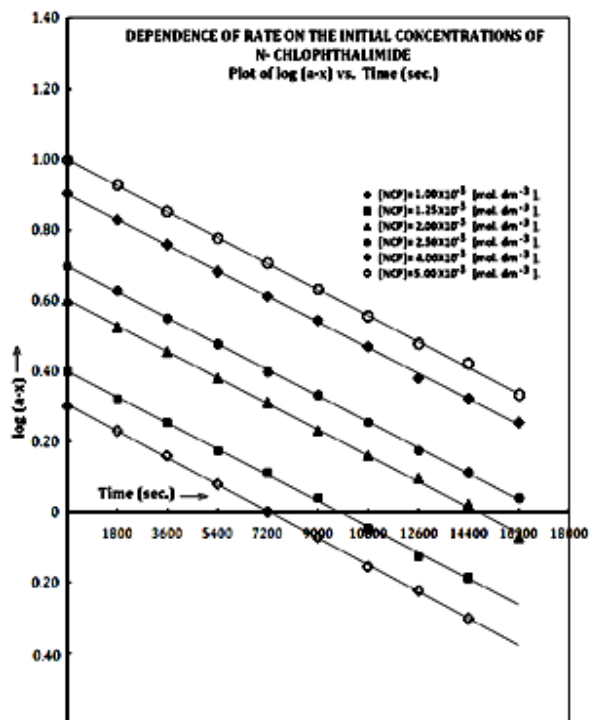


Fig.1

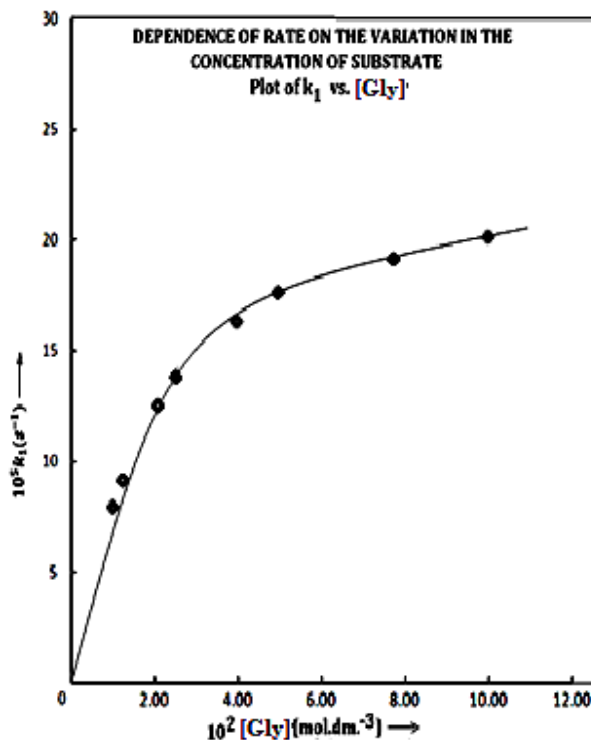


Fig.2

Table:1

[NCP] = 2.50×10^{-3} (mol.dm.⁻³)
 [Ru (III)] = 2.00×10^{-3} (mol.dm.⁻³)
 HOAc-H₂O = 40%(v/V),
 Temperature = 313 K.

[Gly]10 ² (mol.dm. ⁻³)	$\frac{10^{-2}}{[Gly]}$ (mol.dm. ⁻³)	Glycine		
		$10^5 k_1 (s^{-1})$	$\frac{10^5}{k_1} (s^{-1})$	$1000k_2 = \frac{k_1}{[Gly]}$ l.mol. ⁻¹ (s ⁻¹)
1.00	1.00	8.39	0.119	8.39
1.25	0.80	9.33	0.107	7.54
2.00	0.50	12.38	0.081	6.19
2.50	0.40	13.52	0.074	5.40
4.00	0.25	16.25	0.061	4.06
5.00	0.20	17.29	0.058	3.45
8.00	0.13	19.05	0.052	2.38
10.00	0.10	19.59	0.051	1.96

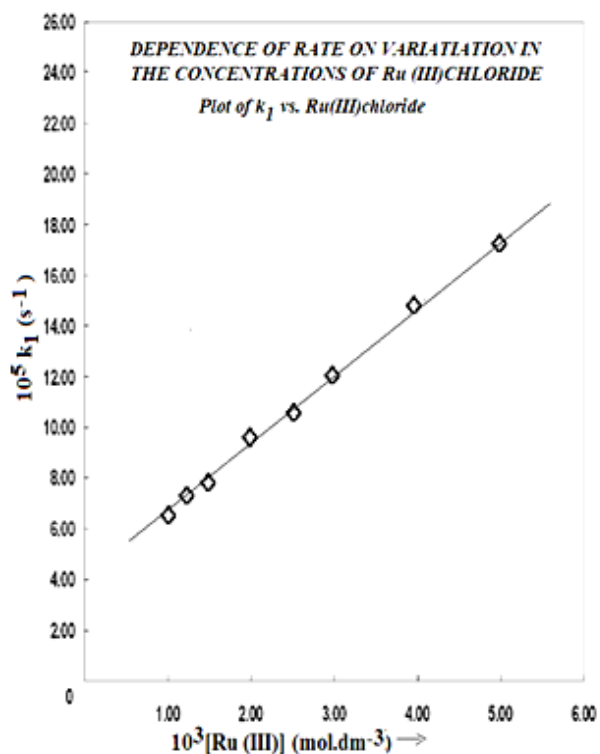


Fig.3

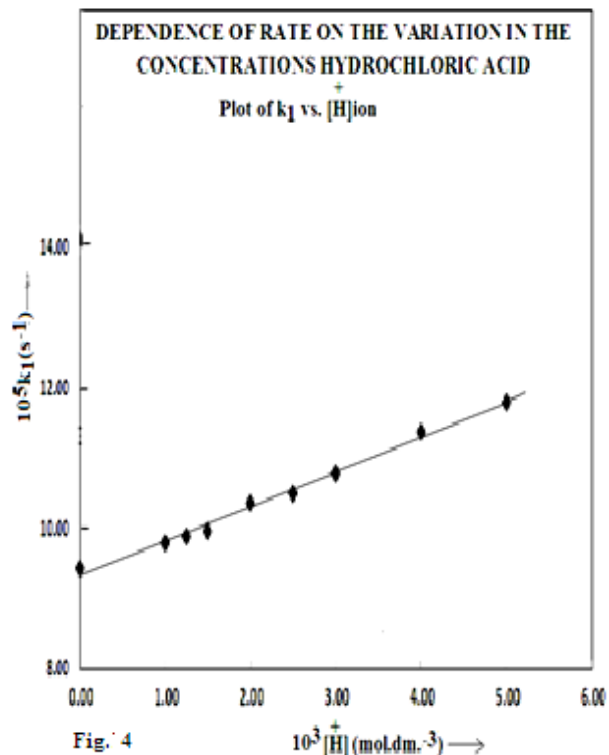


Fig. 4

Table :2

Dependence of rate on the variation of the composition of binary solvent polarity.

[NCP] = 2.50×10^{-3} (mol.dm⁻³)
 [Gly.] = 1.25×10^{-2} (mol.dm⁻³)
 [Ru(III)] = 2.00×10^{-3} (mol.dm⁻³)
 Temperature = 313 K.

HOAc-H ₂ O % (v/v)	$\frac{10^3}{D^\#}$	$10^5 k_1 \text{ (s}^{-1}\text{)}$
20	17.17	8.04
30	19.15	8.81
40	21.98	9.43
50	25.64	10.96
60	30.36	13.09
70	38.04	13.99

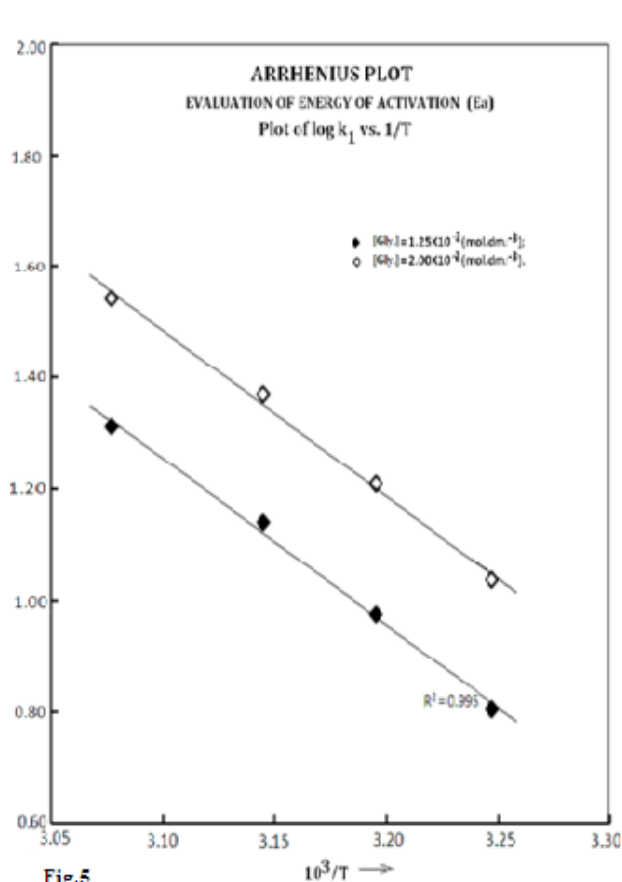


Fig.5

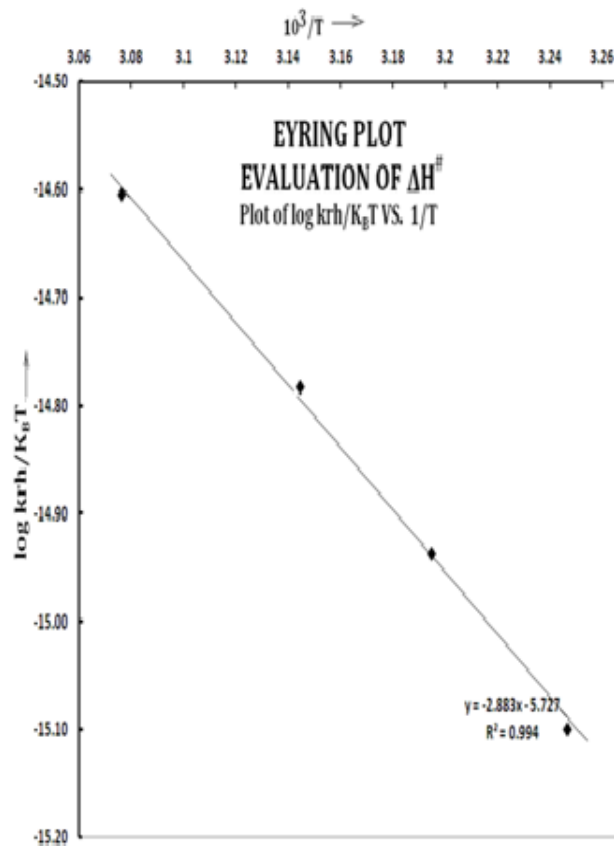


Fig.6

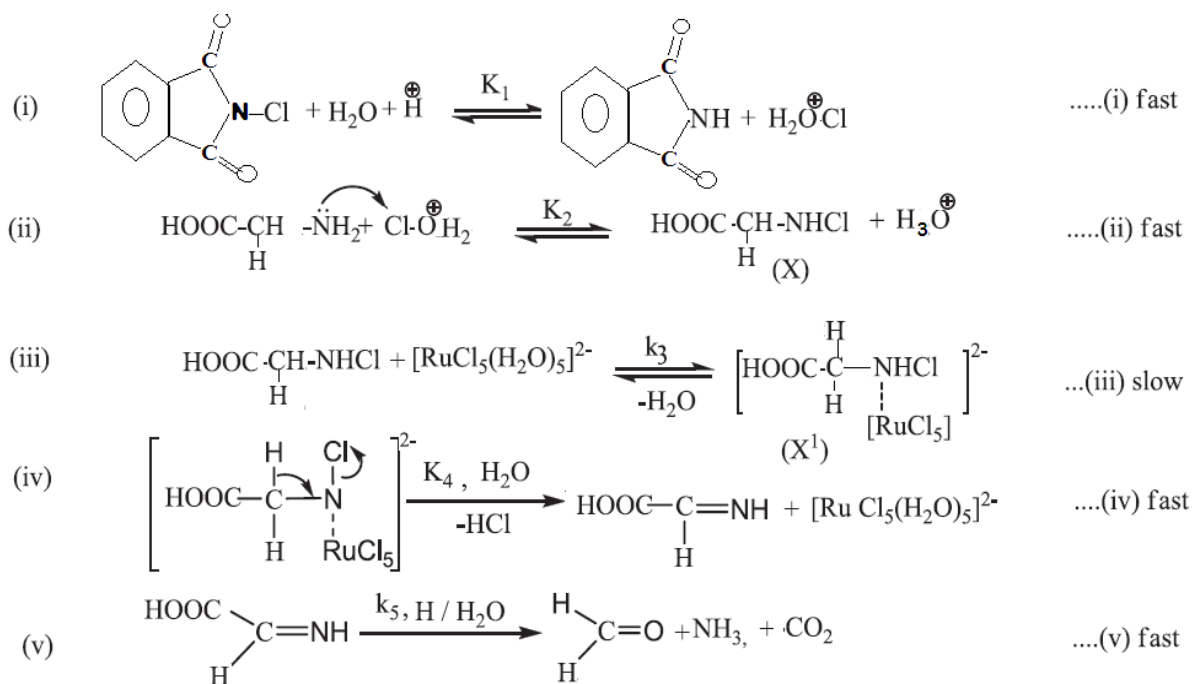
Table: 3
Thermodynamics parameters

Substrate	E_a kJ/mol.	A (s^{-1})	ΔH^\ddagger kJ/mol.	$-\Delta G^\ddagger$ kJ/mol.	$-\Delta S^\ddagger$ JK/mol.
Glycine	53.27 ± 0.64	3.21×10^5 ± 0.98	56.03 ± 0.94	87.23 ± 0.27	104.89 ± 0.87

The Arrhenius plot had been drawn between $\log k_1$ vs. $1/T$, the reciprocal of absolute temperature, (Fig.5) the value of energy of activation (E_a) is calculated from the slope of Arrhenius plot. The frequency factor (A) computed using graphical value of E_a . The enthalpy of activation (ΔH^\ddagger) is evaluated from the slope of the plot between $\log krh/K_B T$ vs. $1/T$. (Fig. 6).

MECHANISM

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



Rate law:

$$\text{rate} = \frac{d[\text{NCP}]_t}{dt} = \frac{K_1 K_2 [\text{Gly.}] [\text{H}^+] [\text{NCP}]_t [\text{Ru(III)}]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{Gly.}] [\text{H}^+]} \quad \dots \text{(vi)}$$

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

CONCLUSIONS

The kinetics of the ruthenium (III) chloride catalyzed oxidation of glycine, by NCP in aqueous acid medium at 313 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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