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“KINETICS AND MECHANISTIC INVESTIGATION RU (III) CHLORIDE CATALYZED OXIDATION OF L-ALANINE BY N-CHLOROBENZAMIDE IN ACID MEDIUM”

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Abstract

Mechanistic investigation of oxidation of of l-Alanine by N-Chlorobenzamide has been investigated in water-HOAc medium. The reaction is of pseudo first-order in [NCB], fractional order in [Alanine] and first-order in [Ru (III)] ion. The velocity of the reaction increases with increase the Dielectric constant of medium and solvent polarity. Effect of temperature has been studied and thermodynamic parameters are calculated and a suitable mechanism has been suggested.

Key words: Alanine; Ru(III)chloride catalyzed; fractional order; Di electric constant of medium; thermodynamic parameters

Introduction

Chemical Kinetics is a part of science of dynamics. It plays a key role in elucidation of reaction mechanism. It deals with the rate of chemical reactions, at various conditions such as concentration, temperature, influencing the rate of reaction, and the explanation of all the rates in terms of the reaction mechanism. The course of the products of the reaction is controlled by the relative rates of several competing reactions, which in turn depend on several factors. Studies on

the mechanism of a reaction are conveniently made by following the quantitative variation of the rate under the influence of varying conditions of concentrations and temperature¹⁻³.

The elucidation of reaction mechanism is still one of the most fascinating problems in inorganic and organic chemistry. Chemical Kinetics has furnished a pool of precious wealth of information about the nature and in course of a reaction^[4] viz. molecularity, concentration, reaction path, frequency of activated complex, mass, temperature and other properties such as influence of substituent groups and structural alterations, rate equation, salt effect, isotopic effect, activation parameters and various environmental changes etc, like solvent polarity, pH and catalytic changes in a reaction. The above study leads to work at stoichiometry, identification of intermediates and isolation of end products as an indirect support to reaction mechanism. The important prerequisite for an oxidant to be useful are its mildness, versatility, selectivity and operational simplicity. Varieties of oxidants have been used as mild and selective oxidizing reagents in synthetic organic chemistry. A number of reports on the oxidation of organic compounds by different oxidants are available in the literature⁵⁻¹⁰. Synthetic methodology, the building block of organic synthesis, continuously seeks for new reagents, better reaction conditions, and more efficient and selective methods. In this regard, a large group of compounds entitled N-halo reagents are widely used in fine organic synthesis. In the present kinetics and mechanistic investigation N-chlorobenzamide (NCB) chose as an oxidant to oxidized *L-Alanine*. N-chlorobenzamide (NCB) act an oxidant because >N-Cl bond are polar easily undergo heterolytic fission in polar medium¹¹.

Materials and methods

The solution of NCB (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 NCB 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 H₂ SO₄ added to it. The liberated iodine was titrated against standard sodium thiosulphate (hypo) solution using starch solution as an indicator. L-alanine (anal. grade)) was used as substrates for the preparation of solutions. The

solution of L-alanine was prepared in requisite volume of glacial acetic acid. Other reagents are grade chemicals and doubly distilled water was used throughout the experiments.

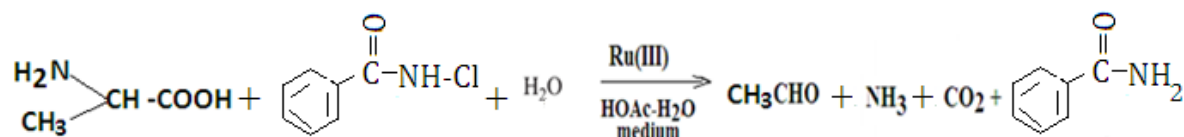
The known volume of oxidant, acetic acid and Ru(III) ion were taken in a conical flask while substrate and rest amount of water were in another conical flask. These two-stopper flasks were placed at experimental temperature in a thermostat of sensitivity $\pm 0.1^{\circ}\text{C}$. After the equilibrium of the temperature, the both solutions were mixed and aliquot was withdrawn immediately and was quenched. The amount of un-reacted N-chlorobenzamide 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-chlorobenzamide. 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 -

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

found fairly constant within the experimental error suggested that each reaction obeys first-order kinetics. The effect of [Ru(III)chloride] on the oxidation of L-alanine was determined by adding different concentrations of Ru (III)chloride. The effect of Benzamide was also investigated. Different compositions of binary solvent mixtures of acetic acid-water were 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-chlorobenzamide over L-alanine and Ru(III), for 24 hrs. at 308K. The un-reacted oxidant (N-chlorophthalimide) was determined by iodometrically. The estimated amount of un-reacted N-chlorobenzamide showed that one mole of L-alanine consumes one mole of N- chlorophthalimide.



Result and discussion

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

The reaction rate increased with increase in [Alanine]. Plot of k_1 versus [Alanine] 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 Alanine and oxidant (NCB) and appeared before the slow step. Furthermore con-firming the fractional order dependence on [Alanine]]. (Fig. 2; $r > 0.95$). Fractional slopes of the plots indicate a fractional order dependence on [SBL] (Fig.1, 2), this implies that, rate is proportional to [Alanine]. Therefore, $\text{rate} = k_1 [\text{Alanine}]^{0.66-0.97}$, this explains that the influence of substrate concentration on the rate is low. Reaction is fully Ru(III)ion catalyzed and velocity of the reaction increases with increase the concentration of Ru(III) ion. The plot of k_1 vs. [Ru(III)] Ion 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 (Table:2). The plot of $\log k_1$ versus $10^3/D$ were obtained linear with positive slope.

The reaction rate ebbs when the concentration of benzamide i.e. [$>NH$] is 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), 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 Alanine–NCB system and according to the reaction mechanism, rate equation and order of reaction have been discussed.

The Arrhenius plot had been drawn between $\log k_1$ vs. $1/T$, the reciprocal of absolute temperature, 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 $\log k_{rh}/K_B T$ vs. $1/T$.

Table: 1

Summary: Dependence of rate of oxidation reactions on the initial concentration of oxidant (NCB)

[Alanine] : $1.25 \times 10^{-2} (\text{mol} \cdot \text{dm}^{-3})$
[Ru(III)] : $1.25 \times 10^{-2} (\text{mol} \cdot \text{dm}^{-3})$
HOAc-H₂O : 30% (v/V) ;
Temp. : 308 K.

[NCB] $10^3(\text{mol} \cdot \text{dm}^{-3})$	$10^5 k_1(\text{s}^{-1})$
1.00	9.45
1.25	9.42
2.00	9.43
2.50	9.55
4.00	9.42
5.00	9.45

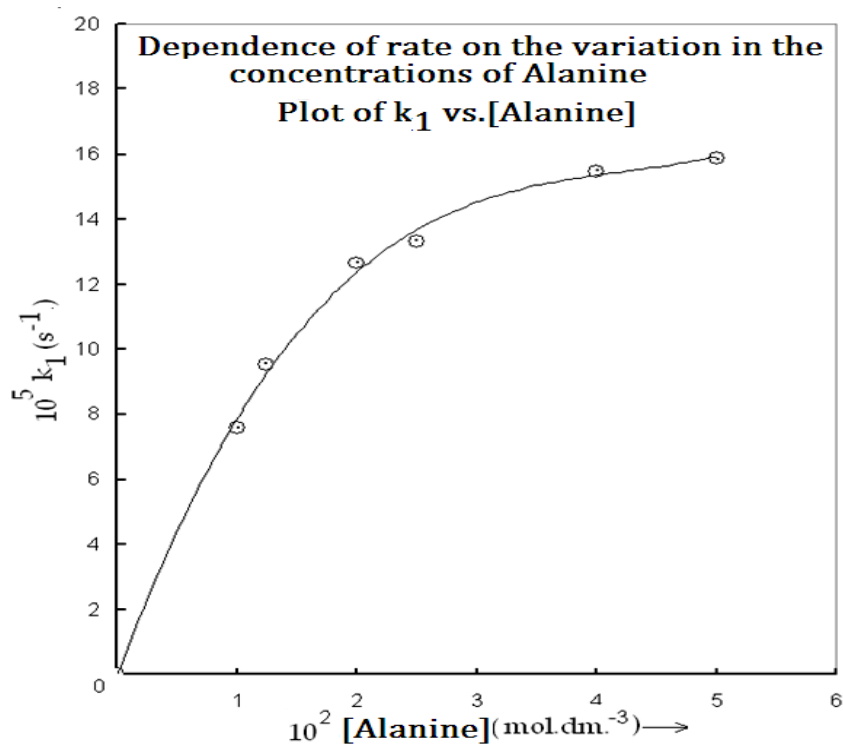


Fig.1

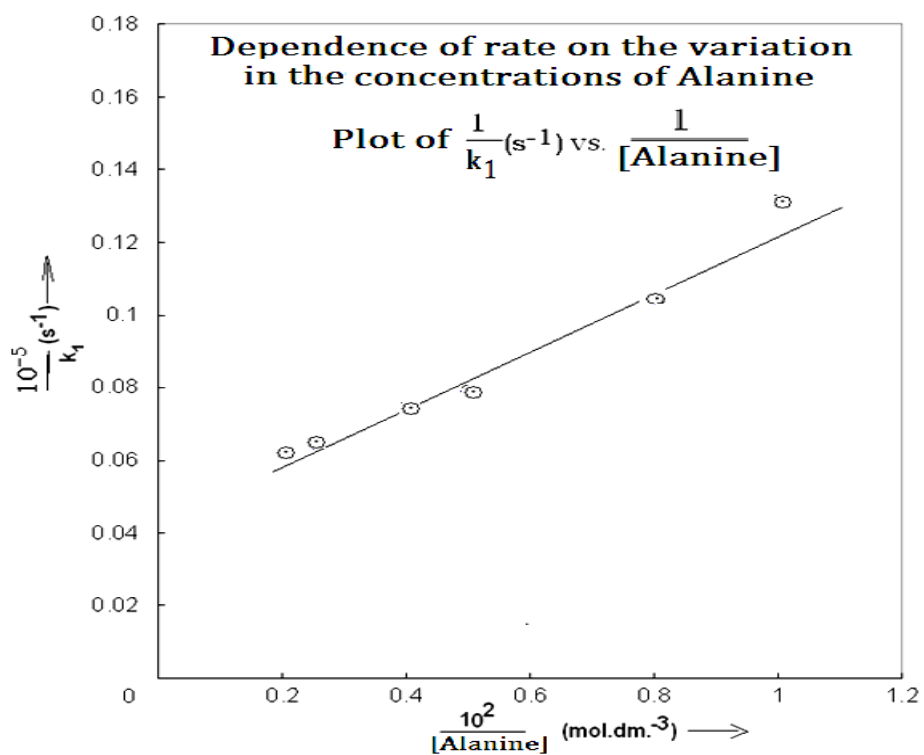


Fig.2

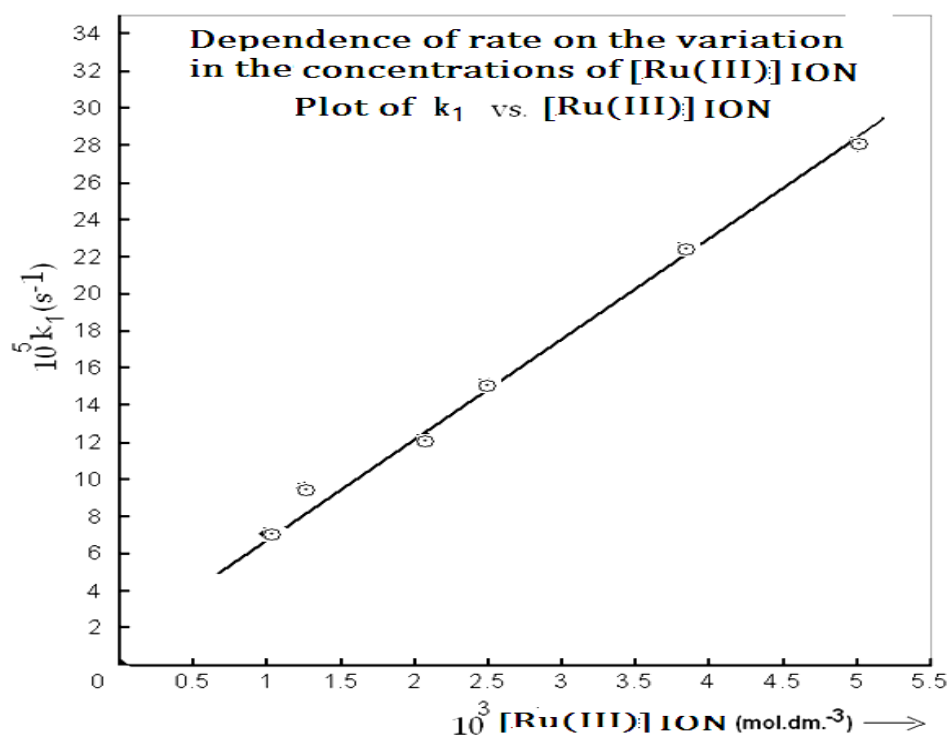


Fig.3

Table: 2

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

[NCB]	: 2.50X10 ⁻² (mol.dm ⁻³)
[Alanine]	: 1.25X10 ⁻² (mol.dm ⁻³)
[Ru(III)]	: 1.25X10 ⁻² (mol.dm ⁻³)
Temp.	: 308 K.

HOAc-H ₂ O % (V/V)	1/D	10 ⁵ k ₁ (s ⁻¹)
20	17.17	8.73
30	19.15	9.55
40	21.98	10.45
50	25.64	11.62
60	30.36	13.09

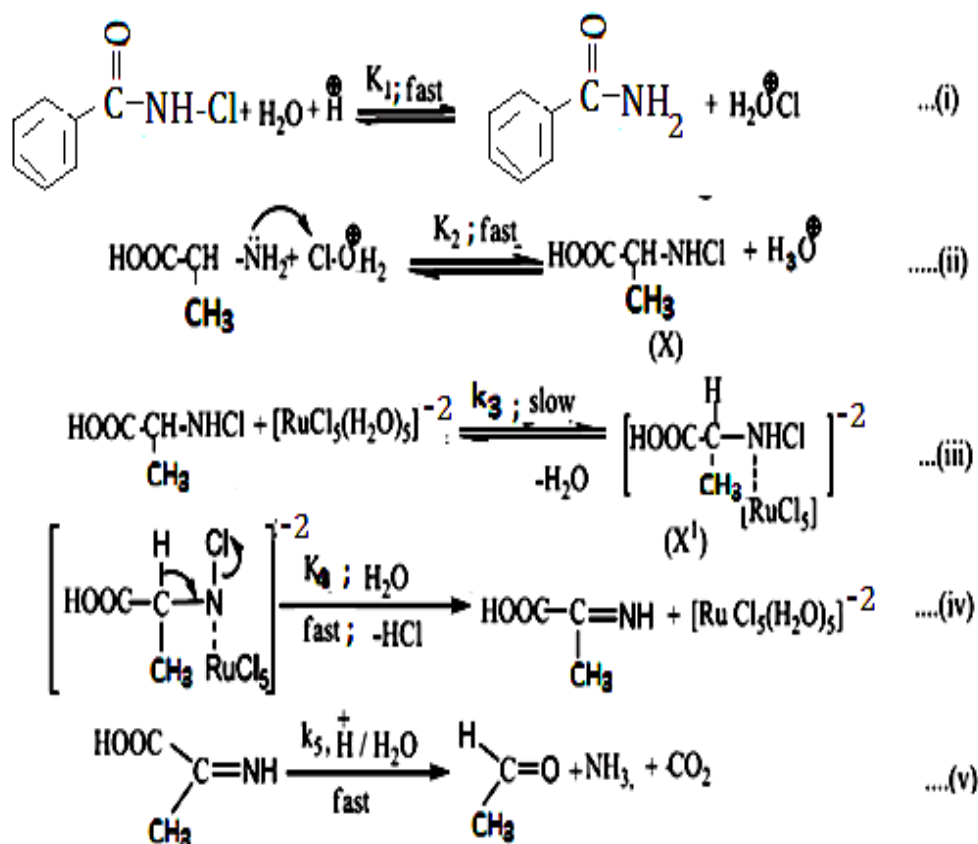
Table: 3

THERMODYNAMIC PARAMETER

Substrate	E _a kJ mol ⁻¹	A (s ⁻¹)	ΔH [#] kJ mol ⁻¹	ΔG [#] kJ mol ⁻¹	ΔS [#] JK mol ⁻¹
Alanine	50.64 ±0.98	3.34 x 10 ³ ±0.82	46.54 ±0.96	-77.33 ±0.59	-86.25 ±0.75

Mechanism

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



RATE LAW EXPRESSION

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

Equation (vi) is in good agreement with the observed experimental data and results.

CONCLUSIONS

Kinetic studies utilizing NCB as an oxidant in series of reaction lead us to conclude that the activity of it is much limited and needs to be explored in a Broadway. It possesses vital potentiality with two-electron system and displays interesting behaviors at moderate condition of temperature. The study will act as a milestone and will pave the way for future researcher to enlighten the mechanism utilizing NCB as an oxidant for some other organic compounds like disulphide, acetophenone and substituted acetophenones, aliphatic ketones, amines and amino

acids in the similar manners and also can be catalyzed by micelles like CTAB and phosphotungstic acid etc. The contribution and information through kinetic study will enrich chemical literature to a great extent in journals. Its applied aspects may be judged in lather industries, analytical, chemical separation, and identification of organic compounds and paper and pulp industries¹²⁻¹⁶.

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