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Ir (III) ION CATALYZED KINETICS AND MECHANISTIC STUDY OXIDATION OF LEUCINE BY TRICHLOROISOCYANURIC ACID"

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Received: 15/12/2017	Revised: 23/12/2017	Accepted: 28/12/2017
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ABSTRACT

Leucine is an α -amino acid that is used in the biosynthesis of proteins. It contains an α -amino group, an α -carboxylic acid group, and a side chain isobutyl group, making it a non-polar aliphatic amino acid. In present paper explored kinetics and Mechanistic study of oxidation of Leucine by Trichloroisocyanuric acid which has been investigated in water-acetic acid medium. The reaction is of pseudo first-order in [TCIA], fractional order in [Leucine] and first-order in [Ir (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: Leucine; Ir(III) catalyzed; fractional order; Dielectric constant of medium; thermodynamic parameters

INTRODUCTION

Chemical Kinetics has furnished a pool of precious wealth of information about the nature and in course of a reaction^[1-4] 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

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reaction. The above study leads to work at stoichiometry, identification of intermediates and isolation of end products as an indirect support to reaction mechanism. A number of reports on the oxidation of organic compounds by different oxidants are available in the literature^[5-10]. In the present work, kinetics and mechanistic study of oxidation of leucine by TCIA in presence of Ir(III)chloride first time. I have chosen TCIA as an oxidant to oxidized Leucine. TCIA act an oxidant because >N-Cl bonds are polar easily undergo heterolytic fission in polar medium¹¹.

MATERIALS AND METHODS

The solution of TCIA (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 TCIA 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. Leucine (anal. grade)) was used as substrates for the preparation of solutions. The solution of Leucine 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 Ir(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 TCIA 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 TCIA. These readings are the values of (a-x) at time "t". The experimental data were fed into

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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 within the experimental error suggested that each reaction obeys first-order kinetics. The effect of [Ir (III)] on the oxidation of Leucine was determined by adding different concentrations of Ir (III). 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 TCIA over and Ir (III), for 24 hrs. at 308K. The un-reacted oxidant (TCIA) was determined by iodometrically. The estimated amount of un-reacted TCIA showed that three moles of Leucine consumes one mole of TCIA.



RESULT AND DISCUSSION

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

The reaction rate increased with increase in [leucine]. Plot of k_1 versus [leucine] 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 Leucine

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and oxidant (TCIA) and appeared before the slow step. Furthermore confirming the fractional order dependence on [Leucine]. Fractional slopes of the plots indicate a fractional order dependence on [Leucine] (Fig.1), this implies that, rate is proportional to [Leucine]. Therefore, $\text{rate} = k_1 [\text{Leucine}]^{0.66-0.87}$, this explains that the influence of substrate concentration on the rate is low. Reaction is fully Ir(III)ion catalyzed and velocity of the reaction increases with increase the concentration of Ir(III) ion. The plot of k_1 vs. [Ir(III)] ion is obtained linear with the positive unit slope, confirming that the reaction fully catalyzed. (Fig.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 (Table: 2). the plot of $\log k_1$ versus $10^3/D$ were obtained linear with positive slope.

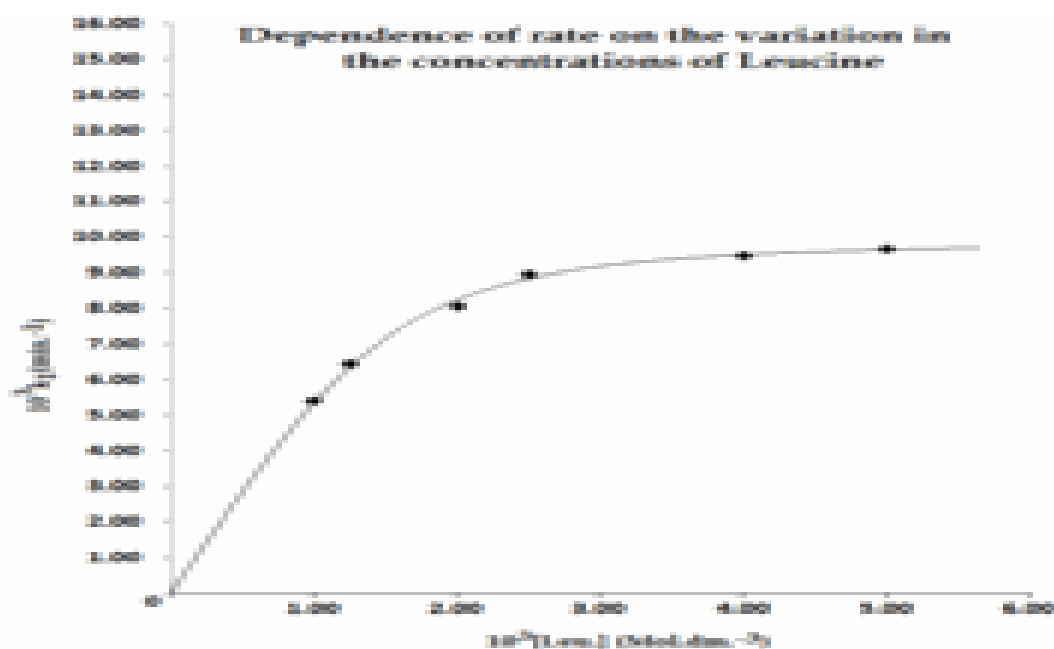


Fig.1: Dependence of rate on variation in the concentrations leucine

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

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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 Leucine –TCIA system and according to the reaction mechanism, rate equation and order of reaction have been discussed.

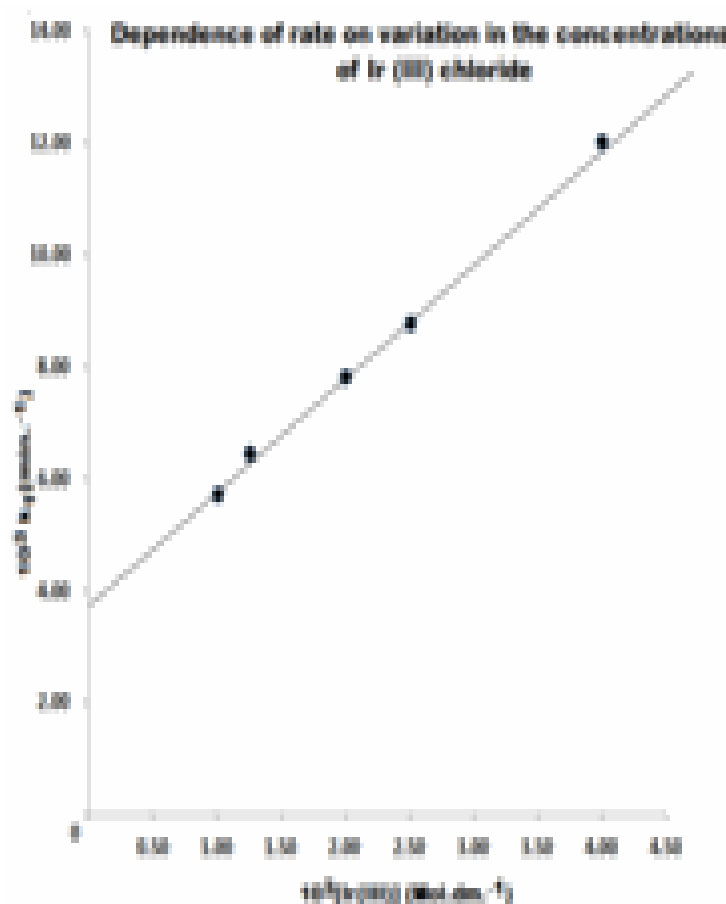


Fig.2: Dependence of rate on variation in the concentrations of [Ir(III)]ion

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Table: 1

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

[Leu]	=	1.25×10^{-2} (mol.dm ⁻³)
[Ir (III)]	=	1.25×10^{-2} (mol.dm ⁻³)
HClAc-H ₂ O	=	10% (v/v)
Temperature	=	300 K.

[TCIA] 10^2 (mol.dm ⁻³)	Leucine
	$10^3 k_2$ (min. ⁻¹)
1.00	6.45
2.00	6.43
2.50	6.46
4.00	6.47
5.00	6.44

Table: 2

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

[TCIA]	=	2.50×10^{-2} (mol.dm ⁻³)
[Leu]	=	1.25×10^{-2} (mol.dm ⁻³)
[Ir (III)]	=	1.25×10^{-2} (mol.dm ⁻³)
Temperature	=	300 K.

HClAc-H ₂ O % (v/v)	$\frac{10^3}{D^2}$	$10^3 k_2$ (min. ⁻¹)
20	17.17	6.16
30	19.15	6.46
40	21.98	6.56
50	25.64	7.46
60	30.36	8.19

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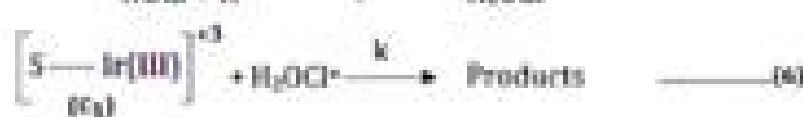
Table: 3

THERMODYNAMIC PARAMETER

Substrate	ΔH kJ/mol	ΔS (J/mole. $^{\circ}$ K)	ΔG° kJ/mol	$-\Delta H^{\circ}$ kJ/mol	$-\Delta S^{\circ}$ J/mole.K
Leucine	51.98 +18.32	104.3129 +16.96	51.98 +18.32	88.46 +16.25	100.23 +18.36

MECHANISM

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



Where, S stands for Leucine

RATE LAW EXPRESSION

$$\text{Rate} = \frac{-d(\text{TCIA})}{dt} = kK_1K_2K_3[\text{S}][\text{Ir(III)}][\text{TCIA}] \quad \text{---(7)}$$

Equation (7) is in good agreement with the observed experimental data and results.

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CONCLUSIONS

Kinetic studies utilizing TCIA 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 TCIA 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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