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"Ir (III) ION CATALYZED KINETICS AND MECHANISTIC STUDY OXIDATION OF ALANINE BY N-CHLOROSACCHARIN"

Umesh Pandey[1], S.K. Singh[1*], Manju Pandey[1], ,H.D.Gupta[2], Arshi Gautam[1]

[1]Govt. T. R.S. (Auton.) College, Rewa (M.P.) India

[2]Govt. Girls Degree College,Sidhi (M.P.) India

*Corresponding author : sanjaysinghchemtrs@gmail.com

ABSTRACT

Alanine 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 Alanine by N-Chlorosaccharin acid which has been investigated in water-HOAc medium. The reaction is of pseudo first-order in [NCSA], fractional order in [Alanine] 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. Acetaldehyde was identified as an end-product of oxidation.

Key words: Alanine; Ir(III) catalyzed; fractional order; Dielectric constant of medium; thermodynamic parameters

INTRODUCTION

The elucidation of reaction mechanism is still one of the most fascinating problems in inorganic and organic chemistry. 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 explored the kinetics and mechanistic path of oxidation of Alanine by NCSA. I have chosen NCSA. as an oxidant to oxidized Alanine. NCSA act an oxidant because >N-Cl bonds are polar easily undergo heterolytic fission in polar medium[11].

MATERIALS AND METHODS

The solution of NCSA (sigma-Aldrich china sample) so obtained was prepared by dissolving its weighed quantity in 100% CH_3COOH (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 solution of Alanine was prepared in requisite volume of glacial acetic acid. Other reagents are grade chemicals and doubly distilled water was used throughout the experiments.

METHOD

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^{0}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 NCSA 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 NCSA. 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 -

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

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Found fairly constant within the experimental error suggested that each reaction obeys first-order kinetics. The effect of [Ir (III)] on the oxidation of Alanine was determined by adding different

RESULT AND DISCUSSION

Effect of oxidant: 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).

Effect of substrate: 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 (NCSA) and appeared before the slow step (Fig.1).

Effect of [Ir(III)]: 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).
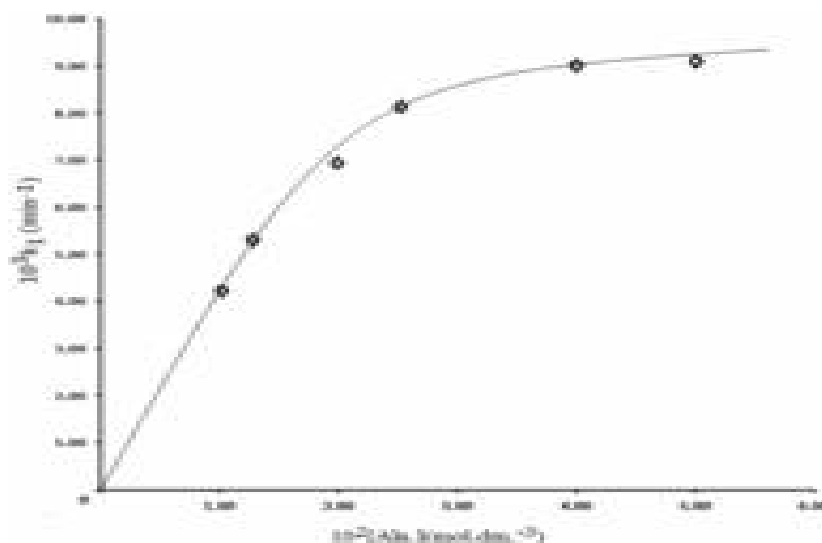

Fig. 1: Dependence of rate on concentration of Alanine

Effect of [H$^+$]: Reaction rate increases with increase the concentration of hydrochloric acid.
The plot of k_1 vs. [H$^+$] ion is obtained linear with the positive unit slope, confirming that the
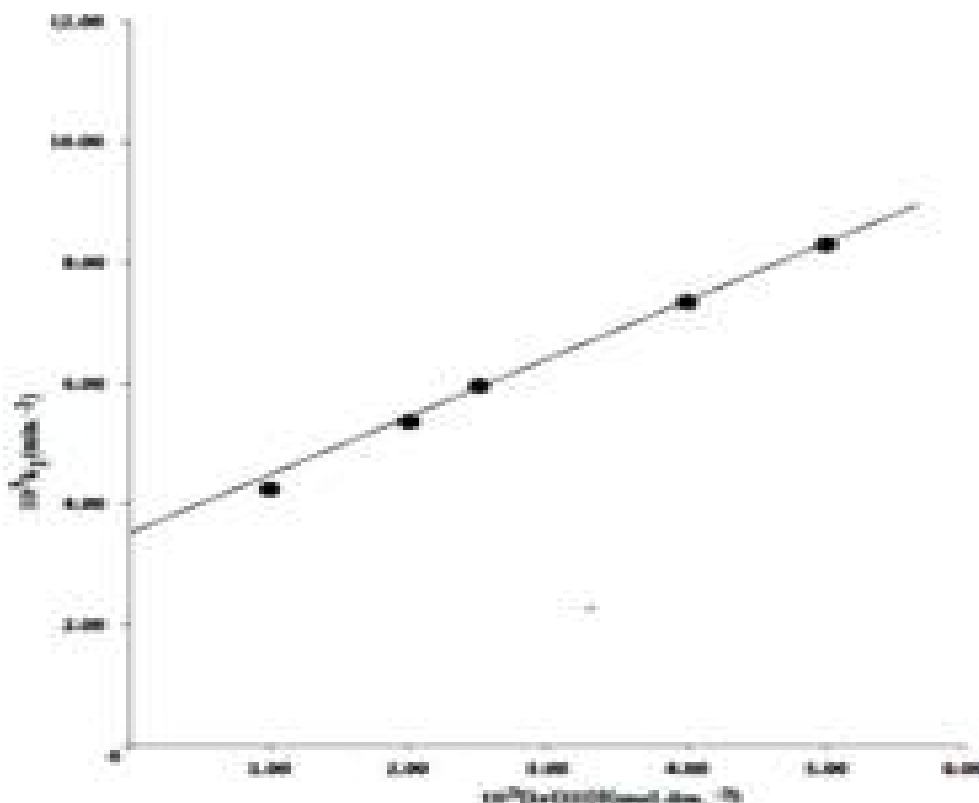reaction fully catalyzed.

Fig. 2: Dependence of rate on concentration of Ir(III)chloride

Effect of dielectric constant of the medium: first-order rate constant slightly increases with
increase composition of acetic acid i.e. rate slightly accelerated with increase in dielectric
constant of the medium (Table: 2).

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Table:1

[Ala]	=	1.75×10^{-2} (mol.dm^{-3})
[Cr (III)]	=	2.00×10^{-3} (mol.dm^{-3})
[H$^+$]	=	1.75×10^{-3} (mol.dm^{-3})
HOAc- H$_2$O	=	40%(v/v)
Temperature	=	313 K

[NCSA]×10^3 (mol.dm^{-3})	10^{3}k$_2$(min^{-1})
1.00	5.38
2.00	5.36
2.50	5.38
4.00	5.39
5.00	5.37

Table: 2

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

[NCSA]	=	2.50×10^{-3} (mol.dm^{-3})
[Ala]	=	1.75×10^{-2} (mol.dm^{-3})
[Cr (III)]	=	2.00×10^{-3} (mol.dm^{-3})
[H+]	=	1.75×10^{-3} (mol.dm^{-3})
Temperature	=	313 K

HOAc-H$_2$O % (V/V)	10^2/D	10^{3}k$_2$(min^{-1})
20	17.17	5.06
30	19.15	5.20
40	21.98	5.38
50	25.64	5.60
60	30.36	5.99
70	38.04	6.49

Acetaldehyde was formed as the end-product of oxidation of alanine, which was identified by the determination of melting points of 2, 4-dinitrophenylhydrazone derivatives (mp.164°C) of oxidation products and existing conventional methods.

Absence of free radical in the system:

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.
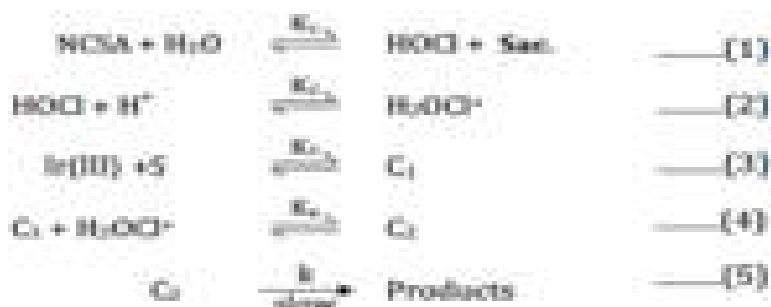
Various activation parameters namely temperature coefficient, energy of activation (Ea) , frequency factor (A), enthalpy of activation ($\Delta H^{\#}$), free energy of activation ($\Delta G^{\#}$), and entropy of activation ($\Delta S^{\#}$) for each reaction are calculated for Alanine –NCSA system and according to the reaction mechanism, rate equation and order of reaction have been discussed(Table:3).

Table 3
Thermodynamics parameters

Substrate	Ea kJ/mol	A (s⁻¹)	$\Delta H^{\#}$ kJ/mol	$\Delta G^{\#}$ kJ/mol	$\Delta S^{\#}$ J/mol
Alanine	55.17 ±0.06	0.21332×10⁷ ±0.08	58.61 ±0.04	88.13 ±0.27	154.96 ±0.07

MECHANISM

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

$$NCSA + H_2O \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} HOCl + Sac. \qquad \text{[1]}$$

$$HOCl + H^+ \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} H_2OCl^+ \qquad \text{[2]}$$

$$Ir(III) + S \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} C_1 \qquad \text{[3]}$$

$$C_1 + H_2OCl^+ \underset{K_{-4}}{\overset{K_4}{\rightleftharpoons}} C_2 \qquad \text{[4]}$$

$$C_2 \xrightarrow[slow]{k} Products \qquad \text{[5]}$$

where,

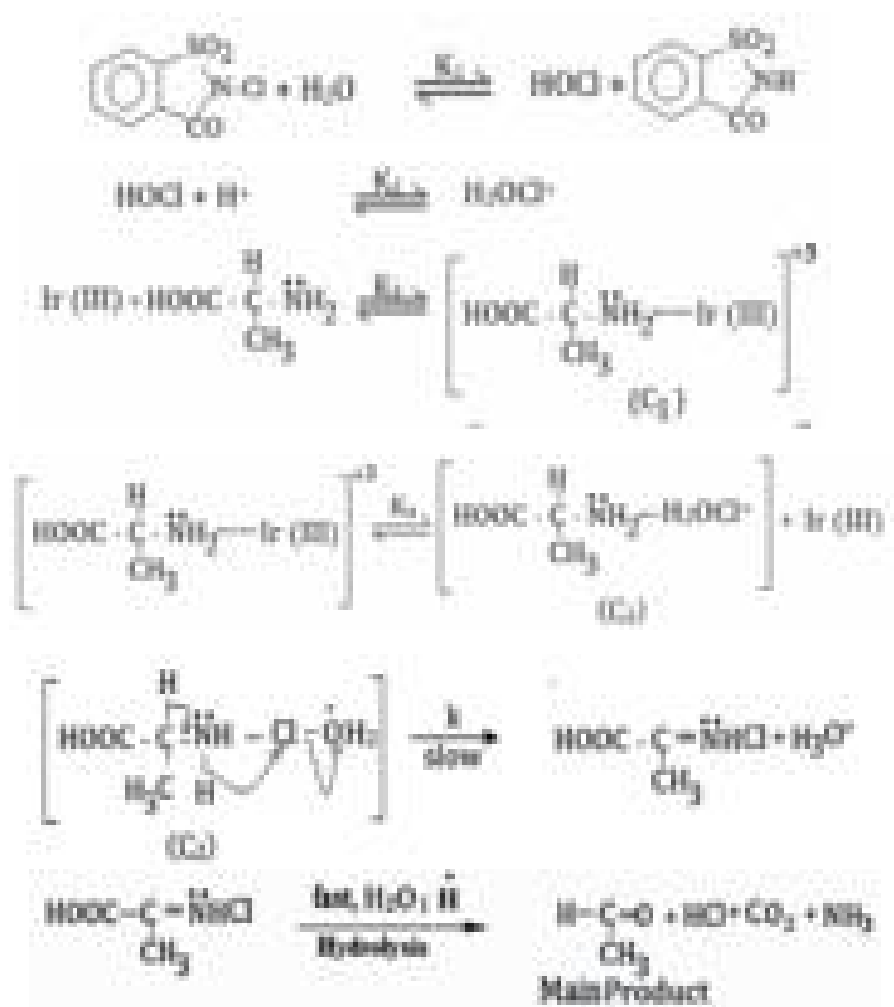S stands for substrate(Alanine)

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Derived Rate law:

$$Rate = \frac{k K_1 K_2 K_3 K_4 [S]_T [H^+]_T [NCSA][Ir(III)]}{[1 + K_3[Ir(III)]] \ [1 + K_2[NCSA]][1 + K_1[H^+]]} \quad ...(6)$$

Equation (6) is in good agreement with the observed experimental data and results

Mechanism can also explain as following:

CONCLUSIONS

Kinetic studies utilizing NCSA 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 NCSA 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 industries[12-16].

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