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"KINETICS AND MECHANISTIC STUDY OF Ir (III) CHLORIDE CATALYZED OXIDATION OF PHENYLALANINE BY DIMETHYL HYDANTOIN IN AQUEOUS ACETIC ACID MEDIUM"

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ABSTRACT

Kinetics and mechanistic study of oxidation of phenylalanine, a bioactive compound, with potent oxidant, Dibromo Dimethyl hydantoin has been carried out in the presence of Ir(III) Chloride in acetic acid-water medium, at 308 K. The reaction is fully Ir (III) chloride catalyzed and retardation of the added Dimethyl hydantoin. Variation of ionic strength of the medium shows negligible effect on rate of reaction. Decrease in dielectric permittivity of the medium decreased the rate. The stoichiometry of the reaction was found to be 2:1. The oxidation product of phenylalanine was identified as the benzaldehyde. The reactions were studied at different temperatures and the activation parameters have been evaluated. The reaction constants involved in the proposed mechanisms were computed. The proposed mechanisms and the derived rate.

Keywords: Dibromo Dimethyl hydantoin, phenylalanine, stoichiometry, benzaldehyde.

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INTRODUCTION

Environmental concern has forced the chemical industry to re-evaluate many of its processes to reduce or eliminate the formation of waste produced in the synthesis of organic products. This need is specially required in oxidation technology and can be addressed by the development of clean and safe oxidation Procedures. This is possible by establishment of green catalytic process by use of environmentally friendly oxidant or green catalysts. In present paper we explored the kinetics of oxidation of Phenylalanine[1-4] with oxidant, Dibromo Dimethyl hydantoin[5-8] because it is an eco friendly, cheap, easily synthesized in chemical laboratories, available in the market. Phenylalanine is an α-amino acid that is used in the biosynthesis of proteins. It contains an α-amino group, an α-carboxylic acid group. In the present work, the kinetics of oxidation of phenylalanine with Dibromo Dimethyl hydantoin in acid in presence of Ir(III)chloride has been studied with a view to elucidate the mechanism of the reaction and to identify the reactive species of oxidant in acetic acid-water medium.

MATERIALS AND METHODS

The oxidant Dibromo Dimethyl hydantoin (Aldrich sample), Phenylalanine (sigma chemicals) were used and purified by the literature procedure[9]. The standard solution of 2-phenylethylamine (sigma chemicals sample) was prepared in acetic acid. Double distilled water employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of Dibromo Dimethyl hydantoin was stored in an amber colored bottle and its strength was checked iodometrically[9] using 1 % solution of freshly prepared starch as an indicator.

Kinetic measurements*:* All kinetic measurements made under pseudo first-order conditions, by keeping large excess of phenylalanine over oxidant Dibromo Dimethyl hydantoin. Mixture containing requisite amount of solutions of Dibromo Dimethyl hydantoin, and Ir(III)chloride in 40 % acetic acid equilibrated at 308K. To this mixture added a measured amount of pre-equilibrated at 308 K., standard solution of Dibromo Dimethyl hydantoin. To maintain the desired temperature (within ± 0.1^{o}C) the reaction mixture was kept in a thermo stated water bath and the progress of the reaction was monitored iodometrically by withdrawing aliquots of the reaction mixture at regular time of intervals.

RESULTS 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 [Phenylalanine]. Plot of k_1 versus [Phenylalanine] 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 phenylalanine and oxidant (Dibromo Dimethyl hydantoin) and appeared before the slow step (Fig.1).

Effect of [Ir(III)]: **Reaction** rate increases with increase the concentration of Ir(III) ions. 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).

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).

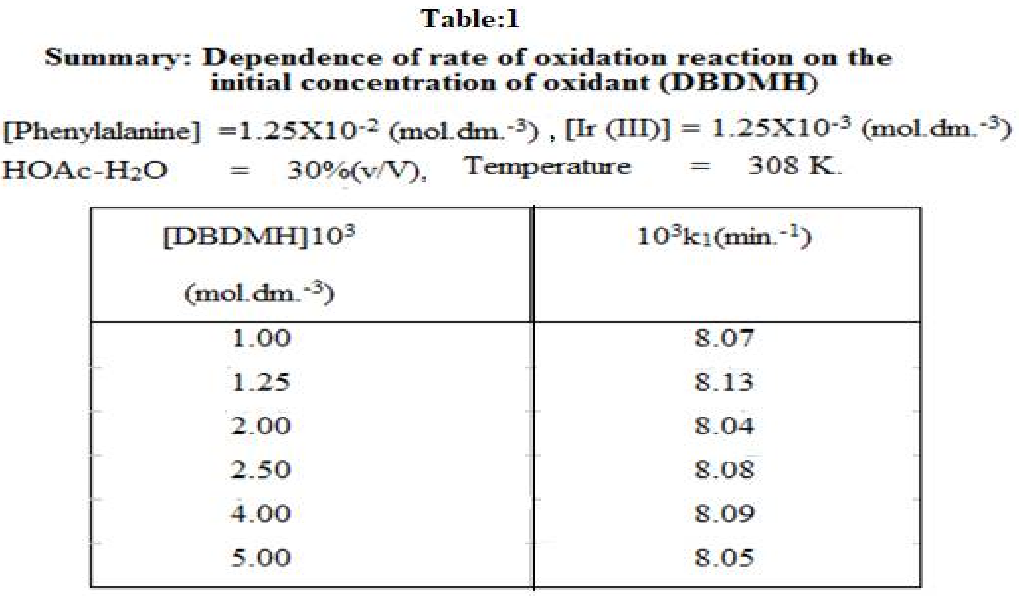


Table:1

Summary: Dependence of rate of oxidation reaction on the initial concentration of oxidant (DBDMH)

[Phenylalanine] $=1.25X10^{-2}$ (mol.dm.$^{-3}$) , [Ir (III)] = $1.25X10^{-3}$ (mol.dm.$^{-3}$)

$HOAc-H_2O$ = 30%(v/V), Temperature = 308 K.

$[DBDMH]10^3$ (mol.dm.$^{-3}$)	10^3k_1(min.$^{-1}$)
1.00	8.07
1.25	8.13
2.00	8.04
2.50	8.08
4.00	8.09
5.00	8.05

Table:2

Dependence of rate on varying in the solvent composition and dielectric constant of the medium and solvent polarity

[DBDMH]=2.50X10^{-3} , [Phenylalanine]=1.25X10^{-2},
[Ir(III)]=1.25X10^{-3}; Temp. =308K

HOAc-H_2O % (v/V)	$\frac{1}{D^*}$	$10^3 k_1$(min.$^{-1}$)
20	17.17	7.99
30	19.15	**8.08**
40	21.98	8.90
50	25.64	9.85
60	30.36	10.49

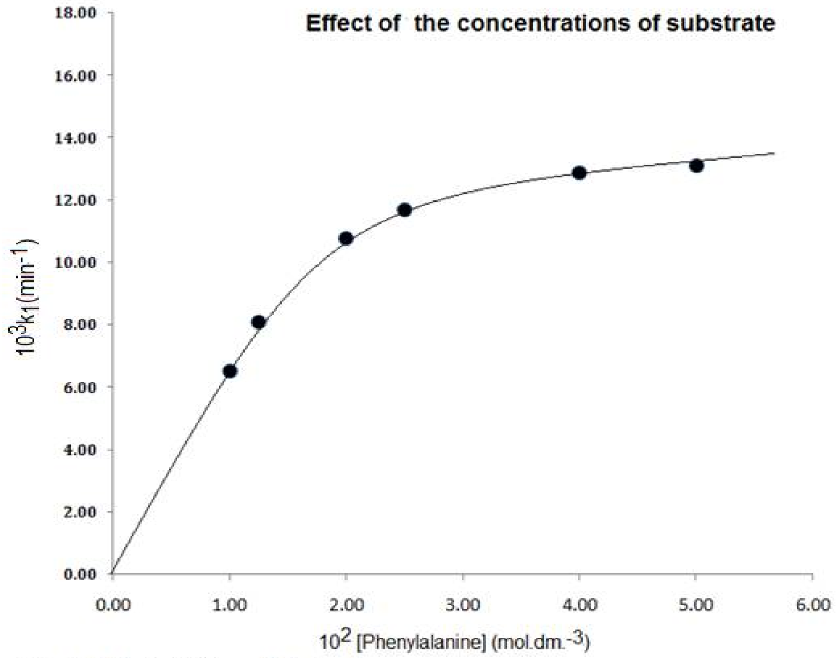


Fig.1 Effect of [Phenylalanine]

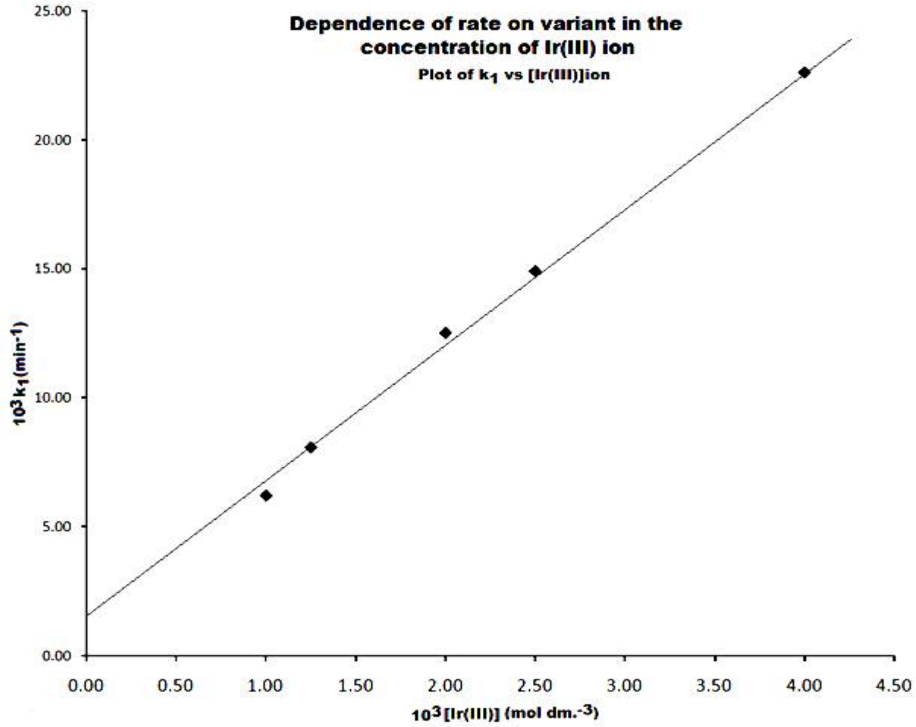
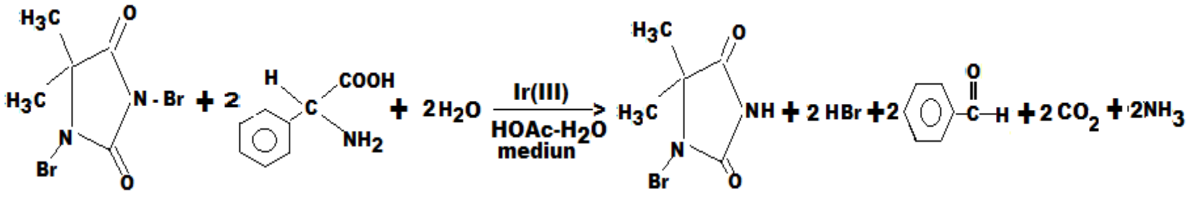


Fig. 2 Effect of [Ir(III)]Ion

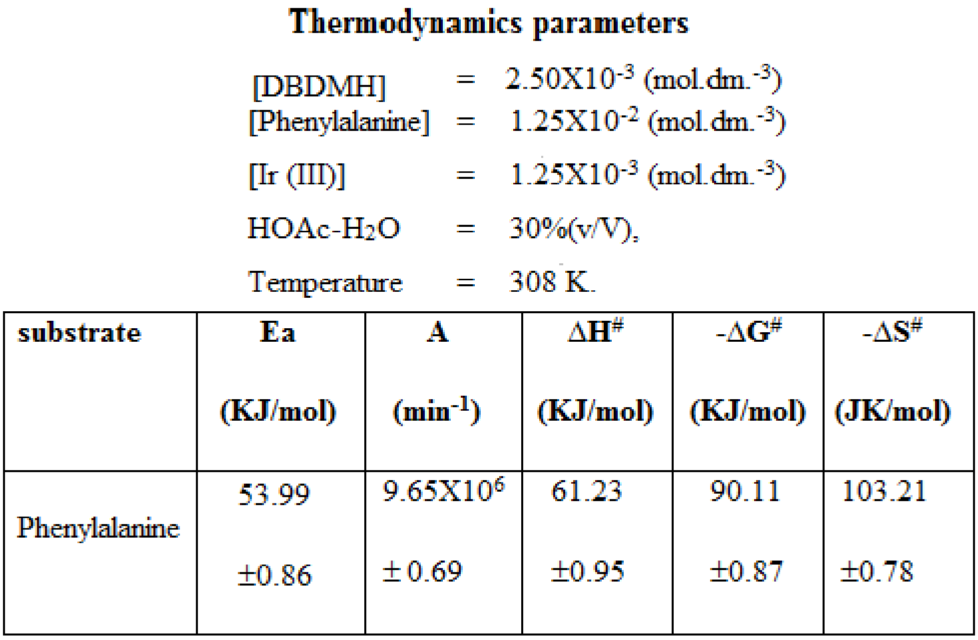
Benzaldehyde was formed as the end-product of oxidation of phenylalanine, which was identified by the determination of melting points of 2, 4-dinitrophenylhydrazone derivatives (mp.239°C) of oxidation products and existing conventional methods.



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 phenylalanine –DBDMH system and according to the reaction mechanism, rate equation and order of reaction have been discussed(Table:3).

Table: 3



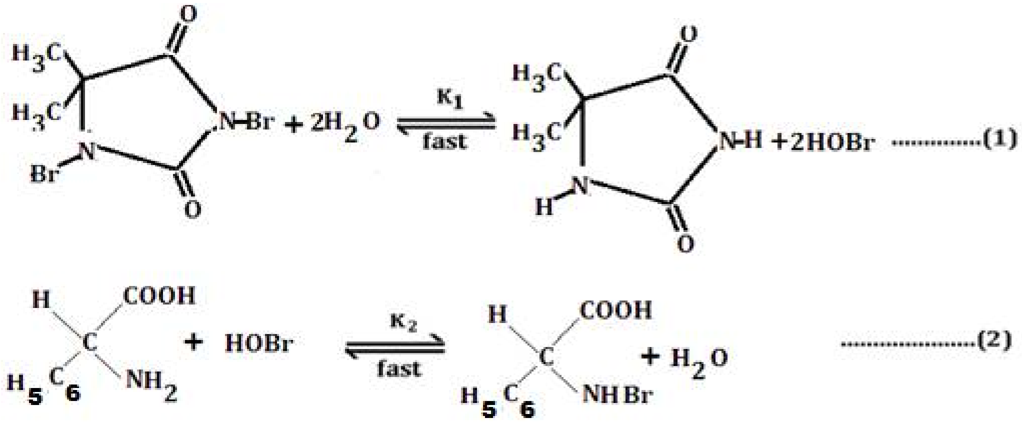
Thermodynamics parameters

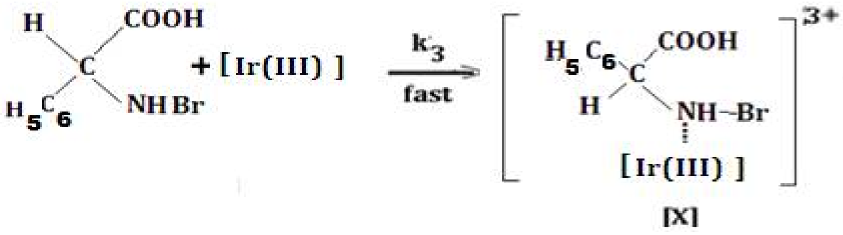
[DBDMH] = 2.50×10^{-3} (mol.dm.$^{-3}$)
[Phenylalanine] = 1.25×10^{-2} (mol.dm.$^{-3}$)
[Ir (III)] = 1.25×10^{-3} (mol.dm.$^{-3}$)
HOAc-H_2O = 30%(v/V),
Temperature = 308 K.

substrate	Ea (KJ/mol)	A (min^{-1})	$\Delta H^{\#}$ (KJ/mol)	$-\Delta G^{\#}$ (KJ/mol)	$-\Delta S^{\#}$ (JK/mol)
Phenylalanine	53.99 ±0.86	9.65×10^{6} ±0.69	61.23 ±0.95	90.11 ±0.87	103.21 ±0.78

MECHANISM

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





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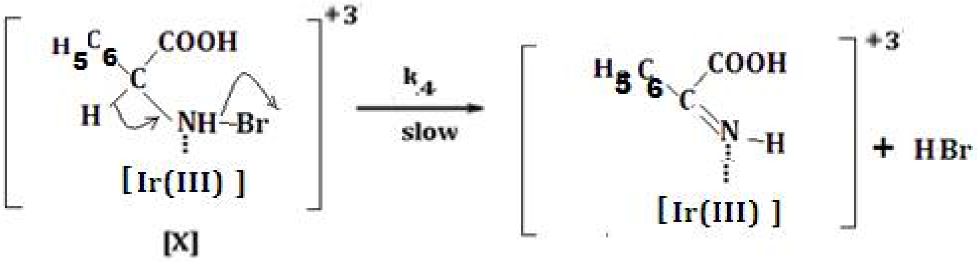

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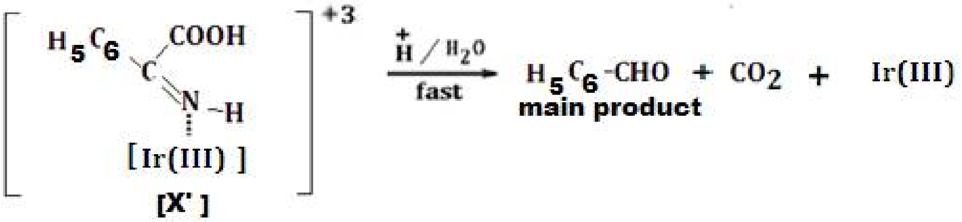

....(5)

Derived Rate law:

$$k_{obs} = \frac{K_3 K_1 K_2 [S] \quad [DBDMH]t \ [Ir(III)]}{\{1 + K_1\} + \{K_1 K_2 [S]\}}$$

Above rate Equation is in good agreement with the observed experimental data and results

CONCLUSIONS

Kinetic studies utilizing DBDM H 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 Dibromo Dimethyl Hydantoin 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[12-17].

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