THE KINETIC AND MECHANISTIC INVESTIGATION OF L – PHENYLALANINE BY N – BROMOACETAMIDE IN PRESENCE OF Pd(II) CATALYST IN ACIDIC MEDIUM

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Abstract:-

The kinetic investigation of Pd (II) catalyzed oxidation of L – phenylalanine by N – bromoacetamide (NBA) in $HClo_4$ in presence of mercuric acetate as a bromide ion scavenger have been carried out . The reaction follows a first order kinetics with respects with respect to each N – bromoacetamide, L – Phenylalanine and Pd (II). While a negative effect was observed in $[H^+]$ and $[Cl^-]$ variation. The influence of mercuric acetate and ionic strength is insignificant. A suitable mechanistic steps in conformity with the kinetic observation is proposed.

Introduction

The kinetics of redox reactions catalyzed by certain transition – metal ions viz. Os(VIII) , [1] Ru(III), [2 – 4] and Ir (III)[5-6] as homogenous catalyst have been extensively investigated several papers have been devoted to the kinetics and mechanism of uncatalysed oxidation of alcohols [7] , Ketones[8-9] and DMSO[10] by NBA which has been earlier used has halogenating and oxidizing agent in estimation of several compounds. Although some work has been reported taking Pd(II) as catalyst in alkaline medium [11-12]. So far, no one has attempted to probe the role of Pd(II) chloride in oxidation of L-phenylalanine by N-bromoacetamide. Therefore in present paper an attempt has been made to investigate the kinetic and mechanistic studies of Pd(II) catalysis in N-bromoacetamide oxidation of L-phenylalanine.

Experimental

Material & Method:-

N- Bromoacetamide (S.Merck,Germany)and amino acid (E.Merck) were used as supplied. Pd (II) chloride solution was prepared by dissolving 1.0g of sample (Johnson & Mathey) in 500mL of 0.1M HCL and then diluted it hundred times. All other reagents such as $HClO_4$, $Hg(0\ Ac)_2$, KCl, $NaClO_4$ were prepared in doubly distilled water. Aqueous solution of NBA was prepared afresh each day by direct weighing and its strength was checked by iodometric titrations of active bromine. $HClO_4$ was used as a source of H^+ ion.

A theromstated water bath was used to maintain the desired temperature. Requisite volumes of ($90cm^3$) of all reagents except NBA were introduced into a reaction vessel (which was blanckend to avoid any photo chemical reactions) and equilibrated at 35^0C. A measured volume ($10cm^3$) of NBA solutions equilibrated separately at same temperature was mixed into the reaction vessel. An aliquot of 5ml mixture was taken out and poured into the potassium iodide solution. The librated iodine was titrated with standard solution of sodium thiosulphate using starch as indicator. After 5 or 10 minutes the estimation of unconsumed NBA was carried out by iodometric titration up to completion of 70 – 80% of the reaction. The order of reaction with respect to NBA is obtained by plotting a graph between unconsumed [NBA] against time. The order of the reaction with respect to other reactants say amino acid Pd(II), KCl, mercuric acetate and $HClO_4$ is computed by repeating the experiment at different initial concentration of the reagents.

Result and Discussion:

The results of experiments performed for the oxidation of L-phenylalanine in given in Table 1. Findings of experiment showed first order kinetics with respect to N- bromoacetamide, Pd(II) and L- phenylalanine. The reaction showed a negative effect of $[H^+]$ on reaction rate. Zero effect on variation of ionic strength of the medium (Not shown) was observed during the course of reaction. Addition of mercuric acetated and potassium chloride showed negligible and negative effect on the rates of reaction respectively (Not given in Table)

Pd(II) chloride in hydrochloric acid exists as $[Pdcl_4]^{2-}$, N–bromoacetamide and

L - Phenylalanine (PA) are present in protonated form in acidic medium as $(NBAH)^+$ and (PAH^+) respectively .

In acidic medium NBA exists following eqilibria-

$$CH_3CONHBr + H_3O^+ \rightleftharpoons (CH_3CONH_2Br)^+ + H_2O$$

NBA $(NBAH)^+$

$$(CH_3CONH_2Br)^+ + H_2O \rightleftharpoons CH_3CONH_2 + (H_2OBr)^+$$

Taking $(NBAH)^+$ and $(PdCl_4)^{2-}$ as active species of oxidant and catalyst a suitable mechanistic steps have been suggested,

$$NBAH^+ \overset{K1}{\rightleftharpoons} NBA + H^+ \quad \text{---------- 1}$$

$$[PdCl_4]^{2-} + NBA \overset{K2}{\rightleftharpoons} [PdCl_3(NBA)]^- + Cl^- \quad \text{----------2}$$

$[PdCl_3(NBA)]^- + PAH^+ \xrightarrow[\text{Slow}]{k} [PdCl_2(NBA)PA] + Cl^- + H^+$ ----------3

$[PdCl2(NBA)PA] + 2H2O \longrightarrow NHA + \underset{HOOC}{\overset{R}{C=NH}} + [PdCl2(OH)2]2- + HBr$ ----------4

$HOOC\text{—}\underset{}{\overset{R}{C=NH}} + H_2O \xrightarrow{Fast} RCHO + NH_3 + CO_2$ ----------5

$[PdCl_2(OH)_2]^{2-} + 2Cl^- \xrightarrow{Fast} [PdCl_4]^{2-} + 2OH^-$ ----------6

$2OH^- + 2H^+ \longrightarrow 2H_2O$ ---------7

Considering above mechanistic steps (1- 3) the rate law given in terms of loss of [NBA] as by equation (a).

$$\frac{-d[NBA]}{dt} = \frac{k.\,K_1 K_2[NBA][\text{L-Phenylalanine}]\,[Pd(II)]}{K_1[Cl^-]+[H^+][Cl^-]+ K_1 K_2[Pd(II)]}$$

At constant [Pd(II)]

$$\frac{-d[NBA]}{dt} = \frac{k.\,K_1 K_2[NBA][\text{L-Phenylalanine}]\,[Pd(II)]}{K_1[Cl^-]+[H^+][Cl^-]+ C}$$ ----------**(a)**

Where $C = K_1 K_2[Pd(II)]$ = Constant.

The rate law **(a)** obtained is in agreement with kinetic data, hence proposed mechanism is valid.

Table 1 : **Effect of variation of [NBA], [L - Phenylalanine] and [Pd(II)] on the rate constant .**

[KCl] = 4.00X10^{-4}M, Hg(OAC)$_2$ = 3.34X10^{-3}M, Ionic strength = 2.00X10^{-2}M

Temp = 35^{0}C

NBAX10^4M	L – Phenylalanine X 10^2M	Pd(II)X10^6M	[H^+]X10^2M	kX10^7.S^{-1}
8.00	2.50	4.82	2.00	7.53
10.00	2.50	4.82	2.00	6.63
12.50	2.50	4.82	2.00	6.88
16.67	2.50	4.82	2.00	6.22
20.00	2.50	4.82	2.00	7.04
25.00	2.50	4.82	2.00	6.60
10.00	2.00	4.82	2.00	7.88
10.00	2.50	4.82	2.00	8.14
10.00	3.33	4.82	2.00	7.06
10.00	5.00	4.82	2.00	8.42
10.00	10.00	4.82	2.00	8.35
10.00	2.50	1.92	2.00	6.85
10.00	2.50	3.86	2.00	7.20
10.00	2.50	4.82	2.00	7.30
10.00	2.50	5.72	2.00	6.92
10.00	2.50	7.71	2.00	7.35

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