

RESEARCH ARTICLE

KINETIC AND MECHANISTIC STUDY OF PALLADIUM (II) CATALYZED OXIDATION, DEAMINATION AND DECARBOXYLATION OF GLYCINE BY ALKALINE PERMANGANATE.

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Abstract

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Key words:-Glycine, Manganese(VII), Oxidation, Mechanism, Catalyst, Pd(II). Kinetics of oxidation of glycine by permanganate in presence of Palladium(II) catalyst was studied spectrophotometrically. It was found that the reaction exhibits first order dependence on [catalyst] & [oxidant] and less than unit order in [glycine] and [alkali]. The data suggests that oxidation proceeds via formation of a complex between the substrate and the catalyst, which than reacts with one mole of permanganate in a slow step to form a glycine free radical followed by a fast step to yield the products. The activation parameters of the rate determining step were computed and are discussed. The reaction constants involved in the mechanism were calculated and there is good agreement between observed and calculated rate constants under different experimental conditions.

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Introduction:-

The kinetic investigations on the oxidation of amino acids are important because of their biological significance and a precise understanding of the mechanism of such biological redox reactions helps in the synthesis of reaction products. Amino acids acts as building blocks in protein synthesis and also play a significant role in metabolism. Presently large numbers of oxidation studies on α -amino acids are being carried out using various oxidants. Glycine, is a non-essential, simplest amino acid and mild reductant, requires drastic conditions or powerful oxidants for studying its kinetic behavior. The oxidation of glycine has been studied from mechanistic point of view with potassium permanganate in aqueous phosphate buffers by Joaquin et al [1], where the reaction is auto catalyzed by one of the products, colloidal manganese dioxide. The uncatalyzed and the surfactant catalyzed oxidation of glycine by acidic permanganate [2] have been studied in which the reaction followed first order dependence in both glycine and permanganate. Amino acids have been are oxidized by number of reagents [3]. The oxidations of amino acids are of interest as they produce different oxidation products for different oxidants [4, 5]

Permanganate is one such powerful multi-electron oxidant which can exist in various oxidation states, among which +7 is its highest oxidation state, which occurs in the oxocompounds like MnO_4^- , Mn_2O_7 , MnO_3F . Out of which MnO_4^- is the most commonly used well known oxidant species to carry out kinetic studies in acidic, neutral and alkaline media. Oxidation by permanganate ion is used in organic synthesis especially in phase transfer catalysis [6-12].

Palladium (II) is known to catalyze various reactions [10]. Most studies using Palladium (II) as catalyst have been used in the form of Palladium (II) chloride [11] and the nature of its active form in such reaction remains obscure. Hence the effect of chloride on the reactions was studied in order to study the active species of palladium in chloride medium. The uncatalysed reaction of glycine and permanganate has been reported earlier [13]. Here we have described the results of the title reaction in order to know the active species of oxidant, reductant and catalyst in such media and to interpret the possible mechanism.

Results and Discussion:-

Reaction Order:-

As theoxidation of glycine by permanganate in alkaline medium proceeded with a measurable rate in the absence of Pd(II) catalyst, the catalysed reaction is understood to occur in parallel paths. The reaction orders were determined from the slops of logk_cversus (concentration) plots by varying the concentrations of oxidant, reductant, alkali and catalyst, while keeping other parameters constant.

Effect of oxidant, Substrate and Catalyst:-

The oxidant permanganate was varied in the range of 0.5-5.0 $\times 10^{-4}$ mol dm⁻³ and the linearity of the plot of log [MnO₄] versus Time indicates the order in [MnO₄] is unity. This was also confirmed by varying [MnO₄], which did not show any change in pseudo-first order rate constants k_c (Table 1). The dependence of rate on substrate [glycine] was studied by varying the concentration of glycine in the range of $1.0 - 6.0 \times 10^{-3}$ mol dm⁻³ keeping the concentrations of all the other reactants constant at three different temperatures 298, 303 and308K. The rate increased with increase in [glycine] (Table-1) and the order with respect to [glycine] was found to be fractional. Further, the plots of [Pd(II)] / k' vs 1/ [glycine] (Fig.1) are linear with positive intercepts on rate axis indicating that the reaction obeys Michelis-Menton behavior. The concentration of Palladium(II) catalyst effect was studied by varying the concentration in the range of $(0.2 \text{ to } 2.0 \text{ })10^{-6} \text{ mol dm}^{-3}$ and it was found that rate constants increased with increase [Pd(II)]. The order in [Pd(II)] was found to be unity.



Fig 1:- Effect of concentration of glycine on Palladium (II) catalyzed oxidation of glycineby permanganate in alkaline medium

Effect of alkali:-

The effect of alkali on the rate of the reaction was studied at constant concentrations of glycine, permanganate, Pd(II) and ionic strength at 30^{0} C. The rate constants obtained were found to increase with increase in [alkali] (Table 1) and the order with respect to alkali is found to be fractional order.



Fig 2:- Effect of [OH⁻] on the pseudo first order rate constant, k['] on Palladium (II) catalyzedoxidation of glycine by permanganate in alkaline medium.

Effect of ionic strength:-

The effect of ionic strength on the reaction rate was studied by varying the concentration of sodium perchlorate in the reaction mixture in the range of 0.2- 0.7 mol dm^{-3} at constant [glycine], [permanganate], [Pd(II)] and [alkali]. The rate constants obtained were found to be constant (Table 1) which shows that the ionic strength has negligible effect on the rate of the reaction.

Effect of the product:-

The effect of the product, manganese(VI) on the reaction rate, was studied by carrying out kinetic runs keeping the concentrations of all other reactants constant and varying the concentration of manganese(VI) from $(0.25-2.5) \times 10^{-4}$. The pseudo-first order rate constants thus obtained are found to remain practically constant indicating that manganese (VI), one of the products does not have any significant effect on the rate of the reaction (Table 1).

Table 1:- Effect of [Glycine], [MnO₄⁻], [OH⁻] and Pd(II) catalyzed oxidation of Glycine by permanganate in aqueous alkaline medium at 25° C (I = 0.5mol dm⁻³).

1.1					
$[Gly] \ge 10^3$	$[MnO_4] \ge 10^4$	[OH ⁻]	$[Pd(II) \times 10^5]$	k _{obs}	$k_{cat}10^4 (s^{-1})$
mol dm ⁻³	mol dm ⁻³	mol dm ⁻³	mol dm ⁻³	$10^4 (s^{-1})$	
0.5	2.0	3.0	1.0	2.22	2.27
1.0	2.0	3.0	1.0	2.85	2.83
2.0	2.0	3.0	1.0	3.57	3.62
3.0	2.0	3.0	1.0	4.76	4.80
5.0	2.0	3.0	1.0	5.55	5.6
2.0	0.5	3.0	1.0	6.24	6.22
2.0	1.0	3.0	1.0	6.34	6.21
2.0	2.0	3.0	1.0	6.22	6.20
2.0	3.0	3.0	1.0	6.15	6.23
2.0	5.0	3.0	1.0	6.28	6.25
2.0	2.0	1.0	1.0	5.23	5.15
2.0	2.0	2.0	1.0	6.45	6.38
2.0	2.0	3.0	1.0	7.64	7.52
2.0	2.0	4.0	1.0	8.67	8.51
2.0	2.0	5.0	1.0	9.89	9.58
2.0	2.0	3.0	0.2	3.26	3.21
2.0	2.0	3.0	0.6	6.6	6.18
2.0	2.0	3.0	1.0	6.87	6.79
2.0	2.0	3.0	1.5	7.57	7.58
2.0	2.0	3.0	2.0	8.32	8.21

Test for free radical:-

The free radical test has been carried out by taking glycine, sodium hydroxide in a thumberg tube and acrylonitrile and permanganate in the bent tube. After evacuating the system the solutions were mixed by tilting the tube. The reaction mixture was kept aside and after 24 hours a soft precipitate was observed which indicates the formation of free radical.

Effect of Temperature:-

The influence of temperature on the rate of reaction was studied for the reaction at 25, 30, 35 and 40°C. With varying [OH] by keeping other conditions constant. The rate was found to be increased with increase in temperature. The rate constants, k, for the slow step of Scheme 1 were obtained from the slopes and the intercept of the plots [Pd(II)]/k versus 1/[OH] and were used to calculate activation parameters. The values of k (dm³ mol⁻¹ s⁻¹) were 5.2 x 10⁴, 6.2 x 10⁴, 7.5 x 10⁴ and 8.32 x 10⁴ at 25, 30, 35 and 40°C respectively. The activation parameters for the rate determining step were obtained by the least square method of plot of log k versus 1/T are given in Table 3 and are good agreement with uncatalysed reaction.

Table 2:- Thermodynomic activation parameters for the Pd(II) catalysed oxidation of glycine by alkaline permanganate at 25^{0} C (I = 0.20 mol dm⁻³).

	Values			
Parameters	Uncatalyzed	Catalyzed		
Ea (kJmol ⁻¹)	28.49±0.02	26.62±0.5		
$\Delta H (kJmol^{-1})$	25.93±0.05	24.14±0.04		
$\Delta G (kJmol^{-1})$	117.18±0.4	109.22±0.23		
$\Delta S (kJmol^{-1})$	-306.23±1.62	-285.45±1.45		

Discussion:-

Glycine, an optically inactive non-essential amino acid exists in the form of zwitter ion(gly) $H_3N-CH_2 -COO^-$ in neutral medium, in the form of the cationic species H_3N-CH_2-COOH in acid medium and in the form of anionic species (gly-) $H_2N-CH_2 - COO^-$ in alkaline medium. pH metric method using computer augmented programs SCPHD and MINIQUAD75[18] has been used to determine the pKa values of glycine for carboxylic acid and amino groups. Glycine exists predominantly in the anionic form, $H_2N-CH_2 - COO^-$ (gly-), under the experimental conditions employed, in presence of alkali.

It is interesting to note that the probable species of Pd(II) chloride in alkaline medium. It is noted that the reaction is not influenced by chloride ions, which is usually expected in Pd(II) catalysed reactions [19]. In alkaline solutions Pd(II) is mostly presented as hydroxilated species, [Pd(OH) (Cl)], represented by Pd(II)[#] in **scheme 1**, which is in accordance with earlier work[20] and not as its chloride complex as in the other works[19].

Permanganate acts as powerful oxidant in acid as well as alkaline media. Its oxidation reactions are very interesting because of the several oxidation states to which it can be reduced. The stable reduction product of manganese is largely determined by the pH of the medium.

In solutions of low alkali and in neutral media, manganese (VII) is reduced to manganese (IV) [21, 22]. $MnO_4^- + 2 H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-E^\circ = +1.23 V$

In strongly alkaline medium (pH > 12.5) permanganate is usually reduced to manganese (VI). MnO_4^{-2} = 0.558 ± 0.002 V

Most of the oxidations by permanganate in neutral and alkaline media proceed through intermediate complex formation between oxidant and substrate [23, 24]. In alkaline medium, MnO_4^- is the only active species of permanganate known to exist. Though oxidations by permanganate involve multi electron changes in neutral and acidic media but in strong alkaline media (pH >12.5) they involve only one electron change, forming manganese (VI). In the present investigation in the presence of pd(II) catalyst the stoichiometry of the reaction indicates that permanganate is reduced to manganese(VI) state only and no evidence is obtained for further reduction of manganese(VI) by glycine to manganese(IV).

The results suggest that first alkali combines with permanganate to form an alkali permanganate species in an equilibrium step which is also supported by the fractional order of [OH⁻] and reciprocal of Michalis-Menton plot,

which is linear with positive slope (Figure.2). Glycine reacts with Pd(II) species to form complex. The complex further reacts with alkali permanganate in a slow step to form glycine free radical, which further reacts with another permanganate species in a fast step to form the products. Based on these observations the following mechanism has been proposed.



SCHEME-1

The spectral evidence for such complex is obtained from the UV-Visible spectra of pd(II) and mixture of Pd(II) and glycine. A bathochromic shift Amax 4 nm from 220-224 nm and hyperchromicity at Amax 224-380 was observed. Thus the above scheme leads to rate law given as

 $Rate = -\underline{d[MnO_4^-]} = KK_1K_2[gly][MnO_4^-][Pd(II)][OH^-]$ (2) (1+K₁)[OH⁻] (1+K2 (gly)(1+K₁ MnO₄⁻)(1+K₂[Pd (II)]

$$Rate = \underline{d[MnO_{4}^{-}]} = \frac{KK_{1}K_{2} [gly] [MnO_{4}^{-}][OH] [Pd(II)]}{1 + K_{1}[OH] + K_{2} [gly]}$$

$$\underline{Rate} = K_{obs} = \frac{KK_{1}K_{2}[gly][OH^{-}] [Pd(II)]}{1 + K_{1} [OH^{-}] + K_{2} [gly] + K_{1}K_{2}[gly][OH^{-}]}$$
(3)
$$\underline{Pd (II)}_{K_{obs}} = \frac{1}{KK_{1}K_{2}[gly] [OH^{-}]} + \frac{1}{KK_{2}[gly]} + \frac{1}{KK_{2}[gly]} + \frac{1}{KK_{1} [OH^{-}]} + \frac{1}{K} - \dots - (4)$$

Rate Law

Further equation (4) predicts the plots of [Pd(II)]/k versus 1/[glycine] and [Pd(II)]/k versus 1/[OH⁻] (Fig.1,2) is a linear with a positive intercept supports the Pd(II) - Glycine complex, which is reported earlier [25]. Experimentally observed plots are the one similar predicted from the rate equation thus supporting the proposed mechanism. Also the rate constants of the rate determining step, k, are determined from the intercepts of the plots of of [Pd(II) /k / versus 1/ [glycine] at three different temperatures (25, 30 & 35° C) and the activation parameters Ea and Δ S# are computed using linear least square method and were found to 24.36 ± 0.03 KJ⁻¹ mol⁻¹ and -266.13± 2.62 JK⁻¹ mol⁻¹ respectively. A high negative value of entropy indicates that the transition state is rigid in nature. This type of radical intermediate has been observed in earlier work [26] on alkaline –permanganate oxidation of amino acids.

Conclusion:-

The observations in the present study reveal that anionic form of glycine, $H_2N-CH_2-COO^{-}(gly-)$ and MnO_4^{-} are the reactive species in alkaline medium and formaldehyde is the product of oxidation. It is interesting to note that the oxidant species [MnO_4^{-}] requires a pH>12 otherwise the system becomes disturbed and the reaction proceeds further to give reduced product of the oxidant as manganese (IV). Pd (II) catalyst is known to catalyze various reactions, especially in alkaline medium. Which catalysis the reaction in a measurable velocity at a concentration of 1.0×10^{-6} Mol dm⁻³. The active species of the catalyst was found to be PdCl.

Experimental:-

Materials and Methods:-

A stock solution of glycine (E.Merck) was prepared afresh by dissolving in required volume of water and its strength is determined by the acetuous-perchloric acid method [14].

A stock solution of permanganate is prepared by dissolving potassium permanganate in double distilled water. The solution is boiled gently for 15-30 minutes, cooled and filtered through a sintered glass crucible. It is standardized by titrating with sodium oxalate [15].

A stock solution of manganese(VI) is prepared by heating potassium permanganate in 8.0 mol dm⁻³ sodium hydroxide until a clear green color is produced and is standardized spectrophotometrically[16] at 610 nm using a molar absorbance value of 1530 dm³ mol⁻¹ cm⁻¹. All the chemicals used in this investigation were of analytical grade. Double distilled water is used throughout the investigation. NaOH and NaClO₄ were used to provide required alkalinity and ionic strength respectively.

A palladium(II) stock solution was prepared by dissolving a known weight of palladium(II) chloride (S.D. Fine Chem.) in 0.20 mol dm⁻³HCl and standardized against EDTA [17]. For some kinetic runs in the absence of chloride, the chloride ion in the palladium(II) stock solution was precipitated with AgNO₃ and removed by repeated centrifugation. The resulting clear palladium(II) solution contained less than 5.0×10^{-5} mol dm⁻³ of Cl⁻ and Ag⁺. Such extremely low concentrations of Cl⁻ and Ag⁺ were found to have no significant effect on the reaction. The chloride concentration was maintained between 2.0×10^{-5} mol dm⁻³ with KCl.

Kinetic measurements:-

Kinetic measurements were carried out at $30 \pm 0.1^{\circ}$ C in alkaline medium under the conditions [glycine] is tenfold excess over permanganate ion at constant ionic strength. The reaction was initiated by mixing the thermostated solutions of MnO₄, palladium(II) and gylcine, which also contained the required amount of NaOH and NaClO₄ to maintained requisite alkalinity and ionic strength respectively. The progress of the reaction was followed by measuring the absorbance of permanganate at 526 nm using Milton Roy 1201 UV–VIS Spectrophotometer with 1cm path length glass cells. As no other species except manganese(VII) has any significant absorbance at this wave length under the conditions employed, the absorbance of the solution is taken as the residual concentration of manganese(VII) at time 't'. The plots of log (absorbance) versus time are found to be linear up to 85% completion of the reaction and the rate constants were reproducible within $\pm 5\%$.

The effect of carbonate on the rate of reaction was studied and it is found that added carbonate has no effect on the rate of reaction. The effect of dissolved oxygen on the rate was also studied in the presence of N_2 . No significant result was observed in the presence of N_2 and air. However fresh solutions were used while conducting the experiments.

Stoichiometry and product Analysis:-

In order to identify the products formed, different sets of reaction mixtures containing different reactant concentrations at constant ionic strength and alkali were kept to react at 30 $^{\circ}$ C. After 24 hours the residual permanganate in each case was determined spectrophotometrically at 526nm. The sresults showed that 2 mole of permanganate consumed 1 mole of glycine according to the equation (1).

 $H_2C (H_2N) COOH + 2 Mn (VII) + 2OH \longrightarrow HCHO + NH_3 + CO_2 + 2Mn (VI) + H_2O$

The main product formaldehyde is identified by chromo tropic acid test [6] in which, a drop of the reaction mixture is mixed with 2ml of sulphuric acid (72% solution) in a test tube and a little of solid chromo tropic acid is added. The test tube is heated for 10 minutes in a water bath at 30° C. A bright violet colour appeared in the test tube confirming the presence of formaldehyde as the main product along with ammonia and carbon dioxide, which are identified by Nessler's reagent and lime water respectively and manganate by its visible spectrum. The main product aldehydic was also confirmed by its IR spectrum, which shows a band at 2845-2019 cm⁻¹ due to aldehydic stretching and was found that it does not undergo further oxidation. The concentration of catalyst, Pd(II), remained unchanged at the end of reaction, as found by estimating the palladium as azide complex [17]at 315 nm ($\epsilon = 12000$ dm³ mol⁻¹ cm⁻¹ ± 10 %).

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