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Kinetics and Mechanism of Oxidative Transformation of α-amino acid by pyridiniumdichromate in partial aqueous medium

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Abstract

The comparative study of oxidation of alanine and phenyl alanine by pyridiniumdichromate has been studied spectrophotometrically in the presence of perchloric acid in acetic acid-aquo (v/v) medium. The reaction is first order with respect to oxidant and inverse first order in $[H^+]$. The rate of reaction increases with a decrease in the polarity of solvent indicating an ion–dipole interaction in the slow step. The reactions exhibit no primary kinetic isotope effect. The activation parameters have been evaluated. The reaction mechanism involving the formation of chromate-ester between unprotonated PDC and unprotonated amino acid followed by C–C bond fission in the slow step has been suggested.

Key words: Kinetics, Amino acid, Oxidation, PDC.

Introduction

The chemical oxidations of amino acids using various oxidizing reagents may not always follow the routes for biochemical oxidations viz., Amino acid → Keto acid → Carboxylic acid. Generally only the amino and carboxyl functionality in RCH (NH_2) COOH undergo chemical transformations while hydrocarbon moiety remains intact. Mahanti and Banerji[2] have reviewed the synthetic and mechanistic aspect of the use of chromium (VI) halochromates as mild and selective reagents in synthetic organic chemistry.

Hiran *et al*. reported the oxidation of

glycine[3] and tyrosine[4] by pyridiniumbromochromate in aqueous acetic acid in presence of perchloric acid. Kinetics of oxidation of methionine[5] oximes[6] unsaturated acids[7] cysteine[8], alcohols[9] by pyridiniumchlorochromate were reported. Our previous studies on the oxidation of α-amino acids by pyridiniumdichromate(PDC) indicated an inhibition of the rate of oxidation with increasing H^+ ion concentration[10-11]. These observations, together with the products of oxidation, were inconsistent with the observation of Karim and Mahanti[12-14] in the oxidation of α-amino acids by PBC. We have tried to correlate the structure and reactivity in these oxidations.

Materials and Method

Pyridiniumdichromate was prepared by the method describe in the literature[15] and its purity was checked by iodometrically and by IR spectrum.

I R. = nmax (KBr) = 3250,1660,1500,1340, 110,950,870,770 cm^{-1}

Alanine and phenyl alanine (A.R.grade) were used as supplied. Acetic acid was purified by distillation over CrO_3, and fractional distillation in the presence of acetic anhydride and fraction was collected over 491 K. Double distilled water was used throughout the investigation. All other reagents used were of "AnalaR" grade.

The rate measurements were carried out at 35 ± 0.1 ^oC in 1M $HClO_4$ under the condition [amino acid] >> [PDC], in the solvent system of 30 % (v/v) acetic acid-H_2O. The reaction was initiated by mixing a calculated amount of thermostattedpyridini-umdichromate in to the reaction mixture. The progress of the reaction was followed by measuring the absorbance of PDC in one cm cell placed in the compartment of Systronics VISISCAN-167 spectrophotometer.

Results and Discussion

Effect of oxidant:

When substrates were in excess, the rate at which PDC disappears followed the first-order rate law. The first-order rate constants are independent of the initial concentration of the PDC when varied in the range (1–3) $\times 10^{-3}$ mol/dm^{-3} at 308 K

Effect of Substrate:

At constant [PDC], the rate constants for oxidation calculated at different initial concentration of substrates found to increase linearly with the increase in concentration of substrates ($2x10^{-2}$M to $5x10^{-2}$M). The results of the effect of substrate concentration on the rate constant are summarized in (Table - 1). A plot of log k_1 against log [substrate] gives a straight line in both cases. This revealed that the rate of oxidation is first order with respect to amino acids. It has been found that plot of $[1/k_1]$ versus (1/[substrate]) is straight line with an intercept on the rate ordinate, indicating the oxidation of amino acids follows Michaelis–Menten type kinetics and proceeds through the formation of a complex between the oxidant and the α -amino acid. A similar phenomenon has been observed in the oxidation of α-amino acids by pyridiniumbromochromate[16].

The variation of the rate of oxidation of glycine and alanine with PDC can be expressed as

$$\frac{d[PDC]}{dt} = \frac{k[amino\ acid][PDC]}{K_m + [amino\ acid]}$$

Effect of H^+ Ion :

The rate of oxidation was studied from [H+] = 0.2 M to 1.5 M. It was observed that rate constant decreases with increase in hydrogen ion concentration. This suggests that reactive species in oxidation of amino acid is simple molecular amino acid. By increasing H^+ ion concentration protonation of amino acid will increase, which does not take part in oxidation process. Since protonated species cannot form coordinate bond with oxidant i.e. no complex formation and hence rate decreases. (fig-1)This is contrary to the results obtained by Karim and Mahanti[12-14] who observed first order with H^+ in the oxidation of amino acids by quinoliniumdichromate and cyanide as a product.

There is no direct reaction of PDC with amino acids. The reaction starts when protons are added. This indicates that the reaction of PDC with amino acid is a reaction not of a zwitterion or protonated amino acid as the reaction is retarded by the further addition of protons; thus, a chelate formation is a necessary condition in the oxidation of amino acids as protonated nitrogen (donor of electron pair). Hence, the mode of mechanism with amino acid follows a different path than that adopted by other substrates, hence, the difference in the rate dependence on H^+ ion concentration. Log k versus log [H^+] is a straight line in all the acids with slopes nearly one. The observations are similar to oxidation of amino acids by pyridinium bromochromate[16]. The results are summarized in Table-1.

Effect of Solvent composition :

Effect of solvent was studied by changing proportion of acetic acid and water; varied from 20 to 60 % acetic acid v/v. The reaction rate increased with an increase in the percentage of acetic acid, suggesting that a low dielectric medium favors the oxidation (Table-1). A plot of log k_1 against 1/D (dielectric constant) is linear with a positive slope for the amino acids under study. This indicates an ion–dipole type of interaction in the rate-determining step[17-19]. Wieberg and Evans[20] have made a similar approximation with regard to the same binary solvent system.

Effect of temperature :

Rate of oxidation increases with increase in temperature. Rate of reactions were determined at different temperature (303 to 323 K). In all the cases, a plot of log k_{obs} versus 1/T (inverse of absolute temperature) is a straight line. This shows that Arrhenius equation is valid for this oxidation.

The energy of activation ranges between 66 to 74 kJ mol^{-1}. The entropy values are all negative and highsuggesting that the transition state is more rigid and extensively solvated than the reactants. The negative entropy also suggests the formation of cyclic intermediate from acyclic species. (Table 2 &3).

Table 1. Effect of [Substrate], [H^+] and Solvent

[PDC] = 2 x 10^{-3}M T = 308 K

[Substrate] x 10^2M	[$HClO_4$] x 10M	Acetic acid % v/v	k_1 x 10^5, sec^{-1}	
			DL-Alanine	Phenyl Alanine
1.25	10.0	30	6.15	6.89
1.66	10.0	30	8.05	7.44
2.0	10.0	30	9.04	7.99
3.30	10.0	30	13.45	9.15
5.0	10.0	30	17.45	11.28
2.0	2.0	30	32.92	20.93
2.0	3.5	30	23.68	16.56
2.0	5.0	30	15.16	12.03
2.0	7.0	30	10.67	8.53
2.0	10.0	30	9.04	7.99
2.0	15.0	30	6.12	5.02
2.0	10.0	20	7.07	7.03
2.0	10.0	30	9.04	7.99
2.0	10.0	40	10.5	8.7
2.0	10.0	50	14.16	9.72
2.0	10.0	60	19.98	12.7

Table 2

[Substrate] = 2 x 10^{-2} M [$HClO_4$] = 1 M

[PDC] = 2 x 10^{-3}M [CH_3COOH] = 30 % v/v

Temp (K)	k_1 x 10^5, sec^{-1}	
	DL-Alanine	Phenyl Alanine
303	4.94	4.92
308	9.04	7.99
313	14.39	13.14
318	18.44	18.27
323	34.45	25.82

Table 3. THERMODYNAMIC PARAMETERS

Amino Acids	log A	Energy of activation $\Delta E^{\#}$ kJ mol^{-1}	Entropy of activation $\Delta S^{\#}$ $Jmol^{-1}K^{-1}$	Free energy of activation $\Delta G^{\#}$ kJ mol^{-1}	Enthalpy of activation ΔH kJ mol^{-1}
DL-Alanine	10.279	74.44	-51.75	87.80	71.87
Phenyl Alanine	8.807	66.13	-80.26	88.36	63.56

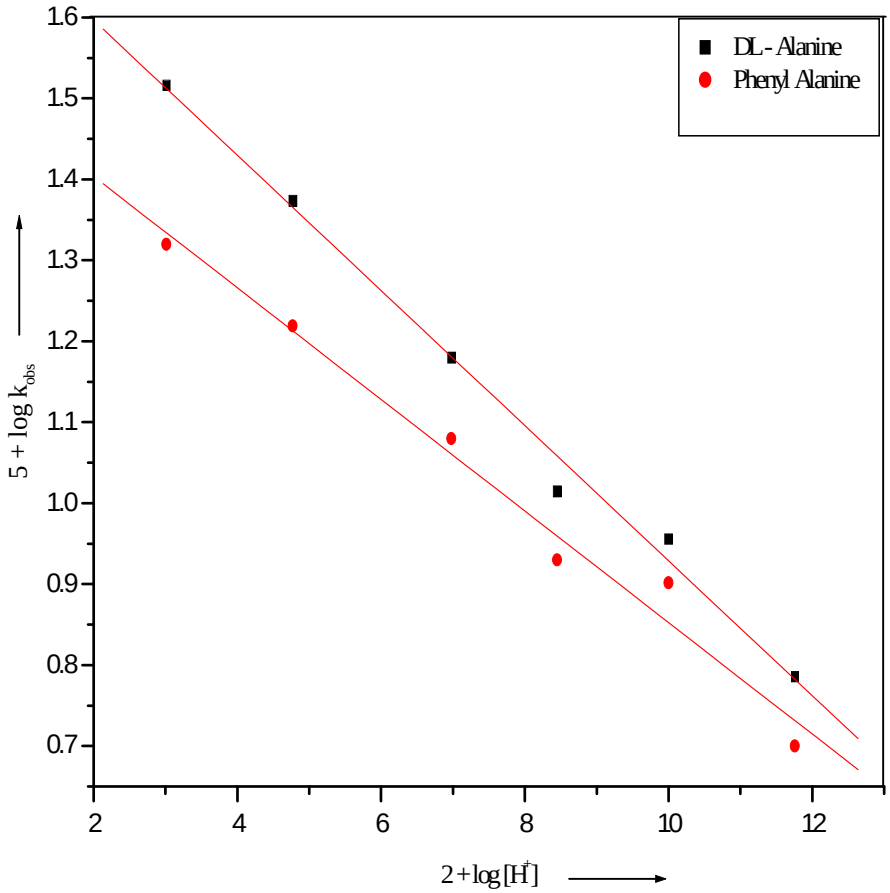

Figure –1

VARIATION OF RATE WITH ACID CONCENTRATION

DL-Alanine & Phenyl Alanine

Conclusion

Oxidative transformation of DL-Alanine and Phenyl alanine is first order with respect to oxidant and inverse first order in $[H^+]$. There is no direct reaction of PDC with amino acids. The reaction starts when protons are added. This indicates that the reaction of PDC with amino acid is a reaction not of a zwitterion or protonated amino acid as the reaction is retarded by the further addition of protons; thus, a chelate formation is a necessary condition in the oxidation of amino acids as protonated nitrogen (donor of electron pair). Hence, the mode of mechanism with amino acid follows a different path than that adopted by other substrates, hence, the difference in the rate dependence on H^+ ion concentration.

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