

Kinetics and Mechanism of Oxidative Transformation of Some Amino Acid by Pyridiniumdichromate in DMF-Water Medium

Shilpa Rathor¹, B. K. Dangarh²

¹Research Scholar, Pacific academy of Higher Education and Research University, Udaipur (India)

²Assistant Professor of Chemistry, Govt. P. G. College, Neemuch, M.P. (India)

Abstract: The present paper describes the comparative study of the kinetics and mechanism of oxidation of DL-alanine and Glycine by Pyridiniumdichromate by Spectrophotometrically in the presence of perchloric acid in DMF-H₂O (v/v) medium at 40 °C. The reaction is first order with respect to oxidant, substrate and [H⁺]. The reaction rate increased with increasing volume percentage of DMF in reaction mixture, suggesting the involvement of an ion and neutral molecule in the rate determining step. The reaction rates were studied at different temperatures [25, 30, 35, 40, 45, 50 °C] and the activation parameters have been evaluated.

Keywords: Kinetics, Amino acid, Oxidation, PDC, Spectrophotometrically

1. Introduction

Amino acids serve important functions in biological systems and play significant role in metabolism. 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(NH₂)COOH undergo chemical transformations while hydrocarbon moiety remains intact. Mahanti and Banerji¹ have reviewed the synthetic and mechanistic aspect of the use of chromium (VI) halo chromates as mild and selective reagents in synthetic organic chemistry.

Hiran et al. reported the oxidation of glycine² and tyrosine³ by pyridiniumbromochromate in aqueous acetic acid in presence of perchloric acid. Kinetics of oxidation of methionine⁴ oximes⁵ unsaturated acids⁶ cysteine⁷, alcohols⁸ by pyridiniumchlorochromate were reported.

Dangarh et al. studied the oxidation of α-amino acids by pyridiniumdichromate (PDC) indicated an inhibition of the rate of oxidation with increasing H⁺ ion concentration⁹⁻¹¹. These observations, together with the products of oxidation, were inconsistent with the observation of Karim and Mahanti¹²⁻¹⁴ in the oxidation of α-amino acids by PBC. We have tried to correlate the structure and reactivity in these oxidations.

2. Materials and Method

Pyridiniumdichromate was prepared by the method described in the literature¹⁵ and its purity was checked by iodometrically and by IR spectrum.
I.R. = ν_{max} (KBr) = 3250, 1660, 1500, 1340, 1110, 950, 870, 770 cm⁻¹

DL-Alanine and Glycine (A.R. grade) were used as supplied. Doubly distilled water was used throughout the investigation. All other reagents used were of "AnalaR" grade. The rate

measurements were carried out at 40 ± 0.1 °C in 2M HClO₄ under the condition [amino acid] >> [PDC], in the solvent system of 30 % (v/v) DMF-H₂O. 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.

3. 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 (0.5-4.0) × 10⁻³ mol/dm⁻³ at 313K.

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 (1 × 10⁻² M to 3 × 10⁻² M). The results of the effect of substrate concentration on the rate constant are summarized in (Table - 1). A plot of log k_{obs} 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 versus 1/[substrate] is a 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 amino acid. A similar phenomenon has been observed in the oxidation of α-amino acids by pyridiniumbromochromate¹⁶. The variation of the rate of oxidation of DL-alanine and glycine with PDC can be expressed as

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

Effect of $[H^+]$ Ion:

In order to study the effect of $[H^+]$ on the rate of reaction, kinetic runs were carried out keeping the concentration of all other reactants are constant and varying the $[H^+]$ with $HClO_4$. From an inspection of the data present in [Table 1], it may be seen that the rate of the reaction increase with increase in hydrogen ion concentration. When the logarithms of k_{obs} values were plotted against logarithms of the corresponding $[H^+]$, a linear plot with a positive slope was obtained and indicate the first order reaction with respect to the hydrogen ion concentration.

This is similar to the results obtained by Karim and Mahanti¹²⁻¹⁴ who observed first order with H^+ in the oxidation of amino acids by quinoliniumdichromate and cyanide as a product. 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 pyridiniumbromochromate¹⁶. The results are summarized in Table-1.

Effect of Solvent composition

Effect of solvent was studied by changing proportion of Dimethylformamide and water; varied from 10 to 50 % DMF v/v. The reaction rate increased with an increase in the percentage of DMF, suggesting that a low dielectric medium favors the oxidation (Table-1). A plot of log k_{obs} 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 step¹⁷⁻¹⁹. Wieberg and Evans²⁰ have made a similar approximation with regard to the same binary solvent system.

Effect of temperature

Rate of reactions were determined at different temperature (298 to 323 K). Rate of oxidation increases with increase in temperature. 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 54 to 58 kJ mol⁻¹. The entropy values are all negative and high suggesting 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]=1 X 10⁻³ M T = 313 K

[Substrate] X 10 ⁻² M	[HClO ₄] X M	DMF % v/v	$K_{obs} \times 10^3, sec^{-1}$	
			DL-Alanine	Glycine
1	2	30	20.07	26.29
1.5	2	30	24.98	29.05
2	2	30	27.71	32.16
2.5	2	30	30.24	34.62
3	2	30	34.54	35.81
1	1	30	4.64	7.25
1	1.5	30	10.82	19.99
1	2	30	20.07	26.29
1	2.5	30	40.91	46.13
1	3	30	52.89	56.11
1	2	10	9.51	11.51
1	2	20	12.09	17.08
1	2	30	20.07	26.29
1	2	40	36.65	47.40
1	2	50	49.32	69.16

Table 2: [Substrate]=1 X 10⁻² M [HClO₄]=2M
[PDC]=1 X 10⁻³ M [DMF]=30% v/v

Temp. (K)	$K_{obs} \times 10^5, sec^{-1}$	
	DL-Alanine	Glycine
298	9.78	10.09
303	10.01	16.54
308	16.46	20.22
313	20.07	26.29
318	33.66	41.53
323	49.43	69.74

Table 3: Thermodynamic Parameters

Amino acid	Log A	Energy of activation ΔE^\ddagger kJ mol ⁻¹	Entropy of activation ΔS^\ddagger J mol ⁻¹ K ⁻¹	Free energy of activation ΔG^\ddagger kJ mol ⁻¹	Enthalpy of activation ΔH^\ddagger kJ mol ⁻¹
DL-Alanine	7.04	54.17	-114.06	87.27	51.56
Glycine	7.69	57.39	-101.51	86.56	54.79

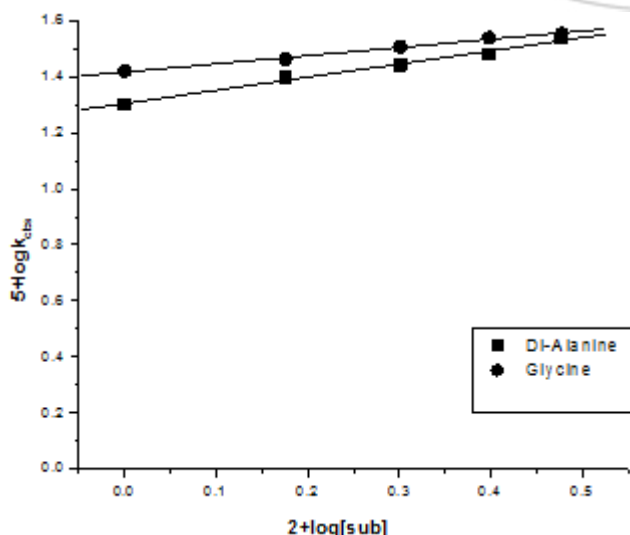


Figure 1: Effect of Substrate Concentration

4. Conclusion

Oxidative transformation of DL-Alanine and Glycine is first order with respect to substrate oxidant and $[H^+]$. At low temperature the reaction between amino acid and PDC is very slow in the low perchloric acid concentration in DMF-water medium. The reaction was studied at different temperatures. In the temperature range of 298-323K, Arrhenius equation is valid. The negative value of entropy indicates that the complex is more ordered than reactant.

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