KINETICS AND MECHANISM OF OXIDATION OF PHENYLALANINE BY CHROMIC ACID IN PRESENCE OF SULPHURIC ACID

Shaikh Ishrat Bano Ibrahim[1], B.K.Mishra[2] & Mohit Aggarwal[3]

[1]*Department of Chemistry, S,V,S's.Arts & Science College Dondaicha, Dhule-425408 (India)*

[2,3]*Research Centre, Department of Chemistry, Saifia Science College, Bhopal-462001 (India)*

ABSTRACT

The present paper describes the kinetics and mechanism of oxidation of L-Phenylalanine by Cr (VI) in presence of Sulphuric Acid. The products are Phenylacetic Acid, Ammonia and Carbon dioxide. Reaction is catalysis by H^+ has been noticed. The results show that the logarithm of the rate constants of oxidation increases with the increase in the concentration of Sulphuric Acid. Kinetics of oxidation of L - Phenylalanine by Chromic Acid shows first order reaction, order of the reaction is also one in presence of Sulphuric Acid. Kinetic data and spectrophotometric results show the formation of intermediate (VI) – Phenylalanine. The complex finally decomposes to give reaction product. A mechanism consistent with the observed kinetic data has been proposed. The kinetic parameters such as catalytic constant, dielectric constant and temperature coefficient are calculated.

I INTRODUCTION

A large no of investigations have been directed towards understanding the mechanism of Chromic Acid oxidation of organic substrates. All available information indicates that Chromium (VI) is a very strong oxidant which will react very rapidly with any other reducing reagent..Chromic Acid principally made by adding Chromium trioxide to water. Chromic Acid has long been used as an oxidizing agent in preparative organic chemistry; it is only in comparatively past years that kinetic or mechanistic investigations have been conducted. Since the first kinetic studies performed by Novick & Westheimer.F. H.[10]on the Chromic Acid oxidation of isopropyl alcohol, investigations have been carried out on the mechanism of oxidation of hydrocarbons, aldehydes, ketones, carboxylic acids, ethers, olefins and glycols as well as alcohols. Oxidation of a variety of organic compounds by Chromic Acid has been extensively studied. G.V. Bakore & S. Narain [2] have studied the oxidation of a number of α hydroxyl acids (Lactic Acid, Malic Acid and Mandelic Acid), Sahu [16] have studied the oxidation of a number of amino acids (Glycine, Anthranilic Acid and Nicotinic Acid) in presence of mineral acids and explained the mechanism on the basis of the H. Kwart & P. S Francis [4] scheme, which is a minor variation of the well known F.H.Westheimer[6] mechanism.L-Phenylalanine, is biologically converted into L-Tyrosine one of the DNA-encoded amino acid.Tyrosine is converted into L-DOPA, which is further converted into dopamine, norepinephrine and epinephrine. This essential amino acid is classified as non polar because of the hydrophobic nature of the benzyl side chain However, no kinetic data for the oxidation of L-Phenylalanine by Chromic Acid in presence of Sulphuric Acid are known.

II MATERIALS AND METHODS

All chemicals were commercially available and used as received from the manufacturer. They were of AR grade, L-Phenylalanine (Sun Chem) Chromium trioxide (Qualigens) . Sulphuric Acid (B.D.H.). All the solutions were prepared in doubly distilled water. Cr (VI) was prepared by dissolving known amount in double distilled water and its concentration was checked iodometrically. Solutions of the oxidant and reaction mixture containing known quantities of the substrate L-Phenylalanine, Chromic Acid, Sulphuric Acid and other necessary solutions were separately thermostated (± 0.1^0C).The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture, monitored by following the rate of disappearance of Cr (VI) by spectro photometrically. In order to investigate the effect of Sulphuric Acid on the oxidation of L-Phenylalanine by Chromic Acid, a series of kinetic runs were performed by keeping the concentrations of Chromic Acid, L-Phenylalanine constant at 7.5 x 10^{-3} M and 1.25 x10^{-3} M respectively, while the concentration of Sulphuric Acid had varied from 0.25 M to 2.00 M. The rate constant and others kinetic data of various reaction mixtures at 29^0C are recorded below in the table No 01 & 02.

Table No.01

RATE CONSTANT, pH VALUE & H^+ ION CONCENTRATION

S.No.	Concentration of Sulphuric Acid (M)	pH value at 29^0C	Rate Constant k x 10^{-3} min^{-1}	Hydrogen ion Concentration x 10^{-2}
1	0.00 M	1.99	1.0423	0.1023
2	0.25 M	1.82	2.7273	0.1514
3	0.50M	1.71	3.2920	0.1950
4	0.75 M	1.62	3.8050	0.2399
5	1.00 M	1.51	4.3527	0.3090
6	1.25 M	1.47	4.9871	0.3388
7	1.50 M	1.42	5.4005	0.3802
8	1.75 M	1.34	6.0018	0.4571
9	2.00 M	1.31	6.6482	0.4898

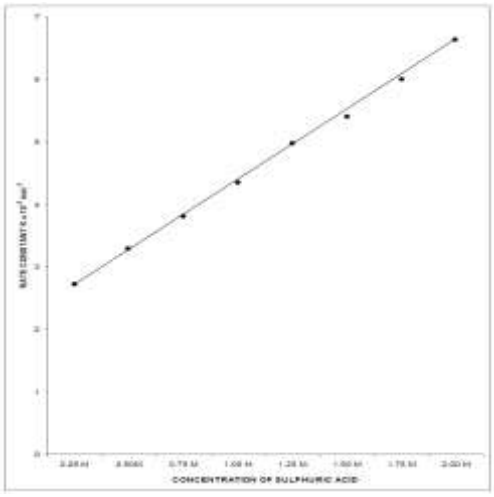


Fig. 01

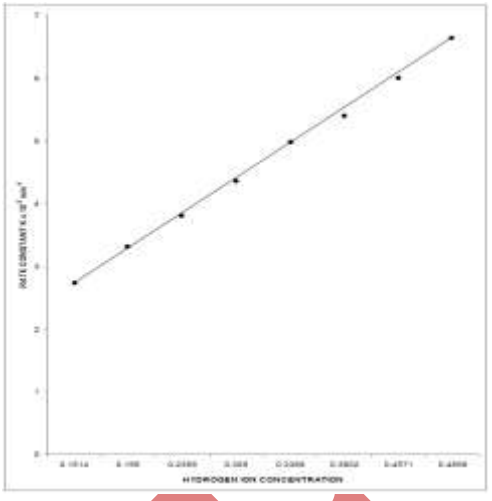


Fig. 02

Fig. 01 : Variation of Rate Constant with the Concentration of H_2so_4 Cf Table – 01

Fig. 02 : Variation of Rate Constant with the Hydrogen Ion Concentration of H_2so_4cf Table - 01

Table No.02

CATALYTIC CONSTANT & DIELECTRIC CONSTANTAT29⁰C

S. No.	Concentration of H_2SO_4	Catalytic Constant $K_H^+ \times 10^{-1}$	Dielectric Constant
1	0.00 M	-	1.589*
2	0.25 M	11.1248	1.569
3	0.50M	11.5333	1.567
4	0.75 M	11.5131	1.566
6	1.25 M	11.6413	1.563
7	1.50 M	11.4621	1.562
8	1.75 M	10.8499	1.560
9	2.00 M	11,4552	1.559
Average Value = 11.2863 x 10^{-1}			**1.560**

Not included in the average

Table No.03

RATE CONSTANT AT DIFFERENT TEMPERATURES

S. No.	Concentration of H_2SO_4	Rate constant K x 10^{-3} min^{-1}		
		29^0C	39^0C	49^0C
1	0.00 M	1.0423	2.0430	4.0238
2	0.25 M	2.7273	5.3690	10.4638
3	0.50M	3.2920	6.3854	12.2585
4	0.75 M	3.8050	7.3890	14.7615
5	1.00 M	4.3527	8.4875	16.6350
6	1.25 M	4.9871	9.8238	19.2570
7	1.50 M	5.4005	10.6392	20.5405
8	1.75 M	6.0018	1351.64	22.3560
9	2.00 M	6.6482	13.0935	25.5380

Table No. 04

TEMPERATURE COEFFICIENT

S. No.	Concentration of H_2SO_4	Temperature Coefficient	
		K_{39} / K_{29}	K_{49} / K_{39}
1	0.00 M	1.96	1.97
2	0.25 M	1.97	1.95
3	0.50M	1.94	1.92
4	0.75 M	1.94	2.00
5	1.00 M	1.95	1.96

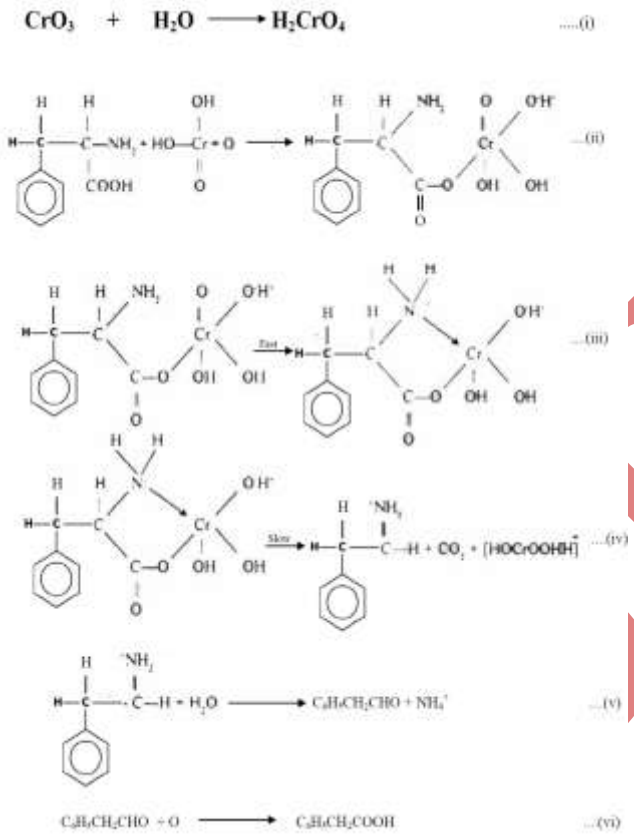
6	1.25 M	1.97	1.96
7	1.50 M	1.97	1.93
8	1.75 M	1.94	1.92
9	2.00 M	1.97	1.95

III RESULTS AND DISCUSSION

In the oxidation of L-Phenylalanine by Chromic Acid the kinetic behavior of the reaction is the same in the presence of Sulphuric Acid as in its absence as shown in the observation (Table No. 01).The reaction rate however increases with the increase in the concentration of Sulphuric Acid in the system. A graph obtained between rate constant and concentration of Sulphuric Acid (Fig. No. 01) suggest that the rate is linear function of the concentration of Sulphuric Acid. A graph obtained (Fig. No. 02) between rate constant and Hydrogen ion concentration also suggest that oxidation reaction is first order with respect to Hydrogen ion concentration.

Reaction mixture containing L-Phenylalanine and Chromic Acid was stirred in water at 29^{o}C for 48 hours. The solvent removed using a rotator evaporator under reduced pressure. The residue was extracted using diethyl ether in separator funnel. The organic layer was concentrated with a rotator evaporator. The products, Phenyl acetic Acid, Ammonia and Carbon dioxide identified by its spot test. Phenyl acetic Acid is also confirmed by its melting point. The actual melting point is 77^{0}C while the observed melting point was 75^{0}C. The evolution of Carbon dioxide was tested by a conventional lime water test. The pH value decreases quite naturally with the increase in the Sulphuric Acid concentration. No significant change in the values of dielectric constant and catalytic constant of the system is observed by the concentration of the added Sulphuric Acid. To test the presence of free radical in the reaction 20% acryl amide solution was added to reaction mixture containing the substrate and the Cr VI solution and was placed in an inert atmosphere for 24 hours. On further addition of methanol, it was found that there is no precipitate in the reaction mixture. This clearly shows that there is no formation of free radicals in the redox reactions under experiments. Finally, the oxidation reaction was studied at three different temperatures, i.e., 29^{0}C, 39^{0}C and 49^{0}C keeping all other experimental conditions constant. Values of rate constants and temperature coefficient are given in Table No-03 and - 04. As the value of temperature coefficient is equal to two, hence no unusual effect of temperature has been observed. As the rate of the reaction is altered in presence of Sulphuric Acid, hence reaction is catalyzed. The rate of reaction does not depend on the concentration of Hydrogen ion only. Thus the acid effect is not due to specific acid catalysis, it seems to be due to general acid catalysis. The catalyzed oxidation of L-Phenylalanine can be explained by considering the Rocek[8] mechanism which considers the formation of a ternary complex of Cr (VI) involving L-Phenylalanine and the decomposition of the mixed ligand complex through a 3e-transfer step at the rate determining step.

IV MECHANISM OF THE REACTION



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