

STUDIES ON OXIDATION OF TYROSINE BY PYRIDINIUM BROMOCHROMATE IN ACETIC ACID-WATER MEDIUM

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ABSTRACT

Kinetics of oxidation of tyrosine by pyridinium bromochromate [PBC] has been studied in aqueous acetic acid in presence of perchloric acid. The reaction shows first order dependence on PBC, inverse first order with H^+ ions and Michaelis –Menten type kinetics with respect to tyrosine. The rate of oxidation decreases with increase in dielectric constant of solvent indicating ion–dipole interaction. The products are ammonia, carbon dioxide and aldehyde. Activation parameters have been evaluated and mechanism involving a complex formation between neutral amino acid and PBC has been proposed.

Key words : Kinetics, Oxidation, Tyrosine, Pyridinium bromochromate

INTRODUCTION

Mahanti and Banerji¹ have reviewed synthetic, kinetic and mechanistic aspect of complexed Cr (VI) compounds. Pyridinium bromochromate² (PBC) is very effective, selective and mild oxidizing and brominating agent. It is used as an oxidant for oxidation of alcohols³, aliphatic aldehydes⁴, thio acids^{5, 6} and glycine⁷, etc. Karim and Mahanti⁸ studied oxidation of several α -amino acids by quinolinium dichromate (QDC) in DMF – aqueous sulphuric acid. They proposed that oxidation of amino acids is catalyzed by hydrogen ions but our studies show contradictory results. The present investigation reports oxidation of amino acid (tyrosine) by PBC in acetic acid–water medium.

EXPERIMENTAL

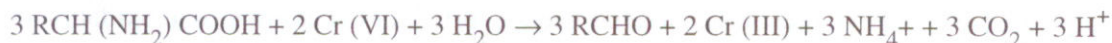
All the chemicals used were of Analar grade. Purity of tyrosine [p -OH- $C_6H_4CH_2CH(NH_2)COOH$, mol.wt. = 181] was checked by m.p. Pyridinium bromochromate [PBC, $O_2Cr(Br)O^+PyH^+$] mol.wt = 259.98] was prepared by reported method² and its purity checked iodometrically and m.p. (428 K). Refluxing over CrO_3 for six hours and followed by distillation, gave purified acetic acid. The reaction was carried out under pseudo first order conditions in water–acetic acid containing perchloric acid. The course of reaction was followed

iodometrically. The rate constants computed from the linear plots of log (hypo) against time by least square method were reproducible within $\pm 4\%$.

Pyridinium bromochromate is soluble in large number of solvents like water, acetone, dimethylformamide, dimethylsulfoxide, dichloromethane, acetonitrile, acetic acid, nitrobenzene and many other organic solvents. Spectra were taken in water, acetic acid and mixtures of acetic acid–water–perchloric acid. PBC solutions in the above solvents obey Beer–Lambert's law in dilute solutions ($\lambda_{\text{max}} = 356 \text{ nm}$). No change in optical density and spectra were observed on long standing (15 days) and heating (438 K). This proved stability of the reagent (PBC) and inertness to solvents used in the experiments.

The qualitative product study was made under kinetic conditions i.e. with an excess of substrate over the oxidant. The product of oxidation was corresponding aldehyde i.e. *p*-hydroxyphenyl acetaldehyde and was identified by their 2,4–D.N.P. derivatives. Mahanti and Karim⁸ obtained cyanide as product of oxidation of amino acid by quinolinium dichromate. Nessler's reagent and lime water test was used to detect ammonium ion and carbon dioxide, respectively.

The Stoichiometric equation is



RESULTS AND DISCUSSION

The rate constants were measured by varying concentration of oxidant, substrate, solvent composition, perchloric acid, pyridine, ionic strength and temperature.

Effect of PBC: At constant $[\text{H}^+]$ and temperature, with tyrosine in excess (>10 times PBC), plot of log [PBC] against time is linear indicating first order in [PBC]. The observed rate constant (Table 1) is independent of the initial concentration of [PBC].

Effect of substrate: The rate of oxidation was found to increase on increasing the concentration of amino acid (tyrosine) (Table 1). The plot of $1/k_{\text{obs}}$ vs. $1/[\text{tyrosine}]$ is linear and makes a positive intercept on Y-axis, which indicates that there is kinetic evidence for the formation of a complex. This shows that Michaelis–Menten type kinetics is followed with respect to tyrosine. Michaelis – Menten constant (K_m) was evaluated (5.75×10^{-3}). This is a measure of stability constant of complex formed between tyrosine and PBC.

Effect of perchloric acid: Increase of $[\text{HClO}_4]$ at constant ionic strength was found to decrease the rate of oxidation (Table 1). This suggests that H^+ ion reacts with amino acid (tyrosine) forming a non-reactive species. Further it indicates that simple neutral amino acid reacts to form a complex. The protonated amino acid can not form a coordinate bond between Cr and nitrogen, as lone pair of amino group is not available for coordination,

Hence, it has been proposed that simple species (neutral) of amino acid exists in the reaction and forms a complex, which subsequently breaks down (Scheme 1) to form the products. Karim and Mahanti⁸ suggested protonated amino acid as a reactive species in oxidation of amino acids by QDC. The plot of $\log k_{\text{obs}}$ vs. $\log [\text{H}^+]$ is a straight line with a negative slope, which indicates inverse order w.r.t. hydrogen ion.

Effect of solvent composition: The rate of oxidation of tyrosine was affected considerably by changing solvent composition of acetic acid– water mixture (Table 1). The rate of oxidation increases with increase in volume percentage of acetic acid. The rate of oxidation depends upon the polarity of medium, at a constant ionic strength and $[\text{H}^+]$. The rate of oxidation of tyrosine with PBC increases with decrease in the polarity of solvent. The plot of $\log k_{\text{obs}}$ vs. inverse of dielectric constant is linear with a positive slope = 65, which suggests interaction between an ion and a dipole⁹. Further, decrease in rate with increase in dielectric constant also shows the polar character of transition state as compared to the reactants.

Effect of ionic strength: Rate of oxidation does not change by the addition of sodium sulphate. No change in rate of reaction has been reported for the chromic acid oxidation of benzyl alcohol in aqueous acetic acid by pyridinium chlorochromate¹⁰ and by PFC¹¹ and aryl alkanes in aqueous acetic acid¹² by PFC.

Effect of temperature: The rate of reaction increases with increase in temperature (Table 1). The plot of $\log k_{\text{obs}}$ vs. $1/T$ is a straight line in the temperature range 300–318 K. From the Arrhenius plot; activation parameters were calculated and summarized in Table 1. The entropy of activation is negative as expected for a bimolecular reaction. The negative value also suggests the formation of a cyclic intermediate from non–cyclic reactants in the rate–determining step¹³. The complex formation is proved by plot of inverse of rate constant against inverse of substrate concentration (tyrosine). Glasstone¹⁴ has pointed out that if entropy of activation is large and positive, the reaction will be normal and fast, but if it is negative, the reaction will be slow. The observed negative entropy of activation also supports the mechanism as the charge separation takes place. The charged ends become highly solvated, this results in immobilization of large number of solvent molecules, which is reflected in the loss of entropy.

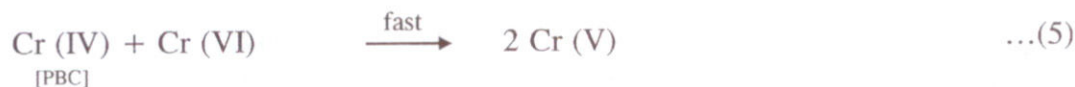
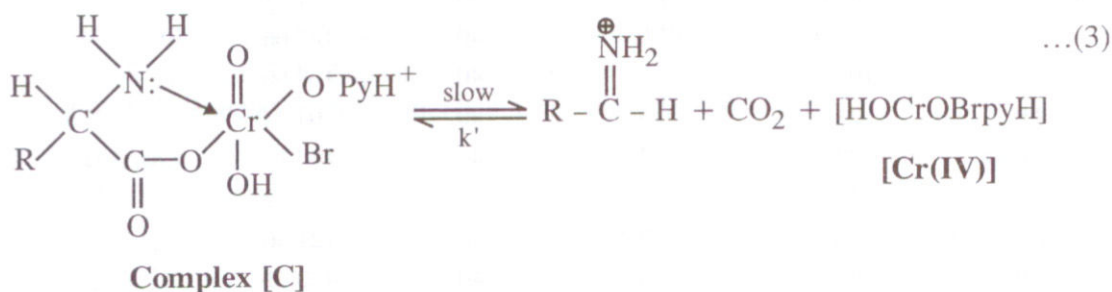
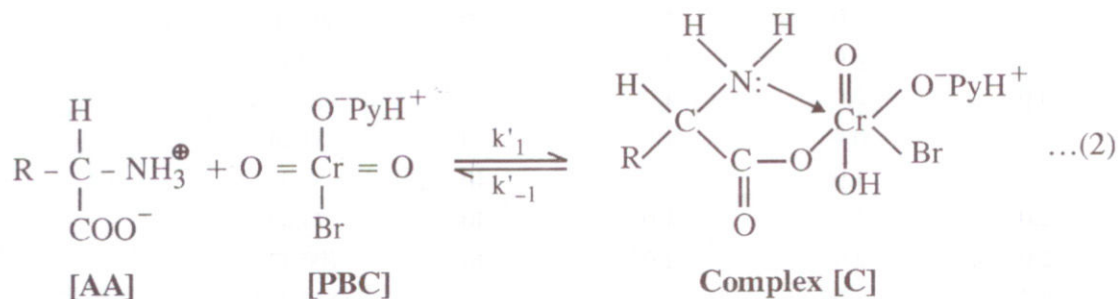
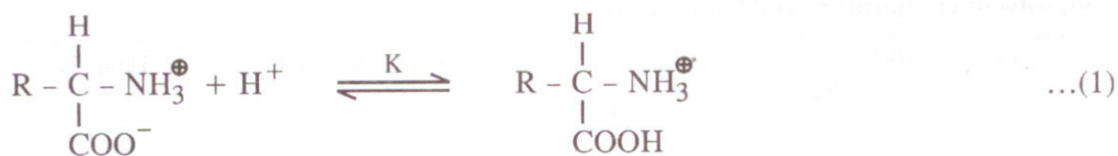
Involvement of radical mechanism is ruled out, as the reaction does not induce polymerization of acrylonitrile under nitrogen atmosphere. Rate of reaction does not change on addition of pyridine indicating thereby the stability of PBC i.e. PBC is not hydrolyzed.

Table 1: Variation of rate with oxidant concentration, substrate concentration, perchloric acid, solvent composition and temperature

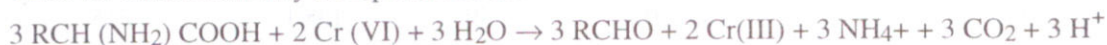
$10^3[\text{PBC}]$ mol dm^{-3}	$10^2[\text{substrate}]$ mol dm^{-3}	$[\text{H}^+]$ mol dm^{-3}	AcOH v/v %	$k_{\text{obs}} \times 10^5 \text{ s}^{-1}$	Temp. K
0.5	2.0	1.0	40	97.65	303
1.0	2.0	1.0	40	96.95	
1.43	2.0	1.0	40	99.80	
2.0	2.0	1.0	40	100.15	
4.0	2.0	1.0	40	100.16	
2.0	0.49	1.0	40	51.24	303
2.0	1.00	1.0	40	57.92	
2.0	1.36	1.0	40	74.02	
2.0	2.00	1.0	40	100.47	
2.0	3.00	1.0	40	126.24	
2.0	4.00	1.0	40	141.21	303
2.0	4.50	1.0	40	147.66	
2.0	10.0	1.0	40	168.66	
2.0	2.0	0.5	40	204.21	
2.0	2.0	0.7	40	164.15	
2.0	2.0	0.8	40	136.82	303
2.0	2.0	0.9	40	121.96	
2.0	2.0	1.0	40	100.41	
2.0	2.0	1.5	40	72.32	
2.0	2.0	1.0	25	51.21	
2.0	2.0	1.0	30	63.12	303
2.0	2.0	1.0	35	78.61	
2.0	2.0	1.0	40	100.42	
2.0	2.0	1.0	45	146.21	
2.0	2.0	1.0	50	195.45	
2.0	2.0	1.0	55	269.35	300
2.0	2.0	1.0	40	89.32	
2.0	2.0	1.0	40	100.4	
2.0	2.0	1.0	40	113.85	
2.0	2.0	1.0	40	138.17	
2.0	2.0	1.0	40	151.3	318

$$\Delta E^\ddagger = 23.2 \pm 1.0 \text{ kJ mol}^{-1}, \Delta S^\ddagger = -186.0 \pm 6.8 \text{ J mol}^{-1} \text{K}^{-1} \Delta F^\ddagger = 57.32 \pm 2.6 \text{ kJ mol}^{-1}$$

Following reaction scheme explains all the observed experimental results.



The over all reaction may be represented as:



Where R represents the group $p\text{-OH-C}_6\text{H}_4\text{-CH}_2\text{—}$

The rate law, derived on the basis of above mechanism, is as follows:

$$\text{Rate of reaction } \frac{d[C]}{dt} \propto [C] = k' [C]$$

Concentration of complex [C] can be evaluated by applying steady state concept:

Rate of formation of complex = Rate of disappearance of complex

$$k_1' = [AA] [PBC]_{eq} = k_{-1}' [C] + k' [C]$$

Where [AA] is equilibrium concentration of the amino acid.

$$\text{Since } [PBC]_{total} = [PBC]_{eq} + [C]$$

$$\text{Therefore } [PBC]_{eq} = [PBC]_t - [C]$$

$$\text{Hence } k_{-1}' [AA] ([PBC]_t - [C]) = [k_{-1}' + k'] [C]$$

$$k_{-1}' [AA] [PBC]_t - k_{-1}' [AA] [C] = [k_{-1}' + k'] [C]$$

$$\text{Therefore, } \{k_{-1}' + k' + k_{-1}' [AA]\} [C] = k_{-1}' [AA] [PBC]_t$$

$$\text{Hence } [C] = \frac{k_{-1}' [AA] [PBC]_t}{k_{-1}' + k' + k_{-1}' [AA]}$$

$$= \frac{[AA] [PBC]_t}{\frac{k_{-1}' + k'}{k_{-1}'} + [AA]}$$

$$= \frac{[AA][PBC]_t}{K_m + [AA]}$$

$$\text{Since Rate} = k' [C]$$

$$= k' \frac{[AA][PBC]_t}{K_m + [AA]}$$

$$= k_1 [PBC]_t = k_{obs} [PBC]_t$$

$$\text{Where } k_1 = k_{obs} = \frac{k' [AA]}{K_m + [AA]}$$

Therefore, K_m can be calculated by slope /intercept of plot $1/k_{obs}$ vs. $1/[AA]$.

This rate law explains all the observed results. Decrease in the rate of reaction with increase in amino acid can be explained on the basis of equation (1) i.e. neutral amino acid concentration will decrease as H^+ concentration increases and hence, a decrease in rate of reaction.

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