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A KINETIC AND MECHANISTIC STUDY OF THE OXIDATION OF 2-AMINO BUTYRIC ACID BY PYRIDINIUM CHLOROCHROMATE IN AQUEOUS DMF MEDIUM

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Abstract:
The kinetics of oxidation of 2-Amino butyric acid by pyridinium chlorochromate in DMF-water mixture containing perchloric acid has been studied at 40ºC. The rate of reaction was found to be of first order dependence on [PCC], [2-Amino butyric acid] and [H^+]. The increase in the rate of oxidation with increase in acidity indicates the involvement of a protonated chromium(VI) species in the rate-determining step. The product of oxidation has been identified as butyraldehyde. The rate of reaction decreased with increase in the polarity (dielectric constant of medium) of solvent, which indicates that there is involvement of an ion-dipole type of interaction in the rate-determining step. On the basis of the experimental findings, a suitable mechanism has been proposed.
Keywords: kinetics, oxidation, DMF (N, N-dimethylformamide), 2-Amino butyric acid, PCC.

1. Introduction

A large variety of compounds containing chromium(VI) have proved to be versatile reagent capable of oxidising almost every oxidisable functional group[1,2]. Pyridinium chlorochromate (PCC) is one of the most versatile available oxidising agents[3]. A number of reports on the oxidation of several substrates by pyridinium chlorochromate are available in literature[4-8]. Literature survey reveals that, there is no report on the oxidation of 2-Amino butyric acid by PCC in the DMF-water containing perchloric acidic media.

The study on kinetics of oxidation of amino acids is an area of active experimentation due to their biological importance. Amino acids play a significant role in a number of metabolic reactions. A special metabolic role of amino acids includes the biosynthesis of polypeptides, proteins and the synthesis of nucleotides. Thus, the mechanism of analogous non-enzymatic chemical processes in the oxidation of amino acids is a potential area for intensive investigations. We report herein the kinetics of oxidation of 2-Amino butyric acid by PCC in the DMF-H_2O acidic media.

2. Experimental

Pyridinium chlorochromate was prepared by the method described in literature[9], and its purity was checked iodometrically and by the UV-vis spectra. 2-Amino butyric acid Analar grade (SRL) was used as supplied (purity was checked by its melting point 233°C) and all other reagents were of Analar grade.

The reaction was carried out under pseudo-first order conditions in the DMF-water (70% (v/v) DMF) solvent system at 313 K. The reaction was initiated by mixing thermally equilibrated solution of PCC and 2-Amino butyric acid which also contained the required quantities of perchloric acid. The reaction was followed by monitoring the decrease in the absorbance of PCC at 354 nm in 1cm cell placed in the thermostated compartment of JASCO model 7800 UV/vis. spectrophotometer.

The kinetic runs were followed for more than 70% completion of reaction and good first order kinetics was observed. Pseudo-first order rate constants, k_{obs}, were obtained from the slope of the plot of log(absorbance) versus time.

3. Result and Discussion

3.1 Stoichiometry and product analysis:

Reaction mixture containing known slight excess of PCC over 2-Amino butyric acid containing 0.3 mol/dm^3[$HClO_4$] in 70 vol. % DMF, 30 vol. % water mixture (v/v), were allowed to stand at 40ºC. When the reaction was completed, the PCC concentration was assayed by measuring the absorbance at 354 nm. The results indicated that 2 mol of PCC react with 3 mol of 2-Amino butyric acid, as shown in equation (1). The qualitative product study was made under kinetic conditions. The main reaction product was identified as Butyraldehyde by its 2,4-D.N.P. derivative. The Nessler reagent test and lime water test were used to detect the ammonium ion and carbon dioxide, respectively, and Cr(III) was confirmed by the visible spectra of the reaction solution after completion of the reaction. The observed stoichiometry may be represented as follows:

$$3RCH(NH_2)COOH + 2Cr(VI) + 3H_2O \rightarrow 3RCHO + 2Cr(III) + 3NH_4^+ + 3H^+ + 3CO_2 \quad (1)$$

3.2 Effect of PCC:

At constant [$HClO_4$], temperature and [2-Amino butyric acid] ([2-Amino butyric acid] >> [PCC]), plot of lg[PCC] against time was linear indicating first order dependence of the rate on PCC. The observed rate constant k was not affected by the change in PCC initial concentration (Table 1).

Table 1. Variation of rate with PCC, 2-Amino butyric acid, perchloric acid concentrations, DMF:H_2O and temperature

[PCC] $\times 10^3$ (mol dm^{-3})	[AA] $\times 10^2$ (mol dm^{-3})	$[H^+] \times 10$ (mol dm^{-3})	Temp. (K)	DMF: H_2O (%)	$k_{obs} \times 10^5$ (s^{-1})
2.5	2.0	3.0	313	70:30	25.34
2.25	2.0	3.0	313	70:30	25.15
2.0	2.0	3.0	313	70:30	25.25
1.75	2.0	3.0	313	70:30	25.71
1.5	2.0	3.0	313	70:30	25.25
1.0	2.0	3.0	313	70:30	25.25
2.0	1.2	3.0	313	70:30	16.53
2.0	1.43	3.0	313	70:30	19.75
2.0	1.6	3.0	313	70:30	21.25
2.0	2.0	3.0	313	70:30	25.25
2.0	2.4	3.0	313	70:30	30.77
2.0	2.8	3.0	313	70:30	36.18
2.0	3.66	3.0	313	70:30	45.65
2.0	5.0	3.0	313	70:30	60.25
2.0	2.0	1	313	70:30	09.2
2.0	2.0	2.5	313	70:30	21.28
2.0	2.0	3.0	313	70:30	25.09
2.0	2.0	3.5	313	70:30	40.37
2.0	2.0	5.0	313	70:30	59.4
2.0	2.0	7.0	313	70:30	94.09
2.0	2.0	3.0	298	70:30	8.51
2.0	2.0	3.0	303	70:30	12.04
2.0	2.0	3.0	308	70:30	19.41
2.0	2.0	3.0	313	70:30	25.39
2.0	2.0	3.0	318	70:30	32.61
2.0	2.0	3.0	323	70:30	47.37
2.0	2.0	3.0	313	70:30	25.25
2.0	2.0	3.0	313	60:40	20.30
2.0	2.0	3.0	313	55:45	10.25
2.0	2.0	3.0	313	50:50	4.91
2.0	2.0	3.0	313	40:60	2.60
2.0	2.0	3.0	313	30:70	1.10
Activation parameters: E_a= 52.37 kJ mol^{-1} ; ΔH^* = 49.767 kJ mol^{-1}; ΔS^* = -96.2 J K^{-1} mol^{-1}; ΔF^* = 79.87 kJ mol^{-1}					

3.3 Effect of substrate:

At constant PCC concentration, $[H^+]$ and temperature, the reaction rate increased with an increase in the concentration of 2-Amino butyric acid from 1.2×10^{-2} to 5.0×10^{-2} mol/dm^3 (Table 1). The plot of lgk_{obs} versus lg [2-Amino butyric acid] (Fig. 1) was linear with positive slope indicating first order dependence of the rate on [2-Amino butyric acid]. The plot of 1/k_{obs} versus 1/[2-Amino butyric acid] (Fig. 2) ia a straight line with positive intercept, which indicates that the Michaelis–Menten type kinetics is followed with respect to 2-Amino butyric acid. Although the intercept value is very small, it indicates formation of a complex which may be highly reactive so concentration will be very small at any time. A similar phenomenon has been observed in the oxidation of α-amino acid **by Cr(VI)**[10,11]**.**

Fig. 1**. Variation of rate with 2-Amino butyric acid concentration**

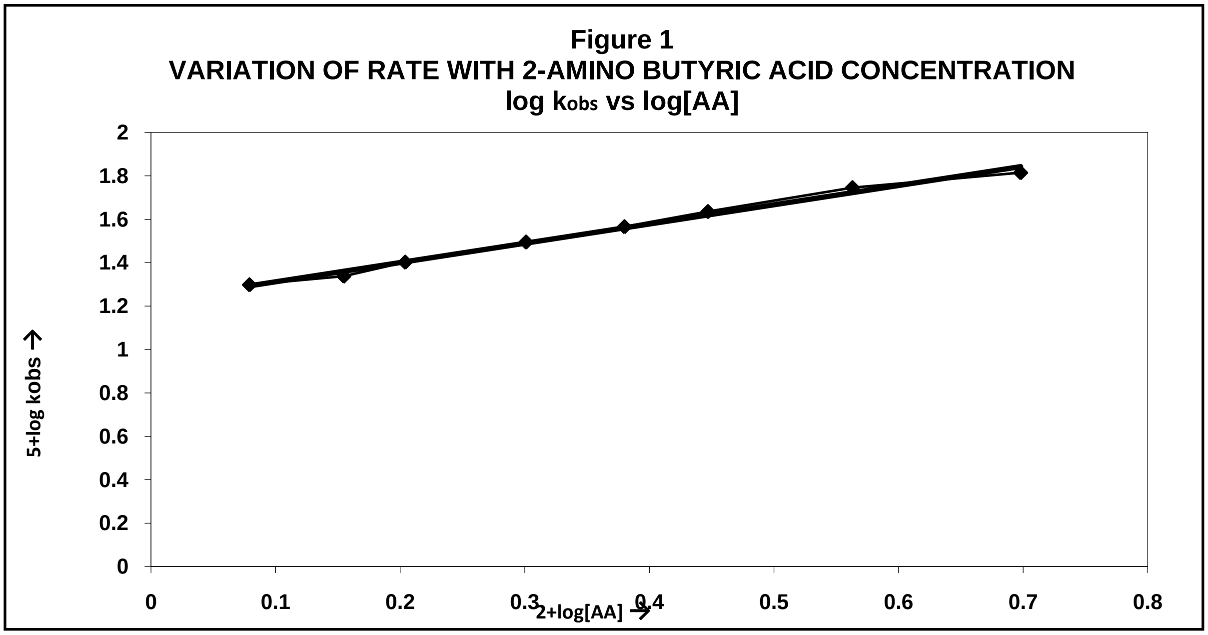
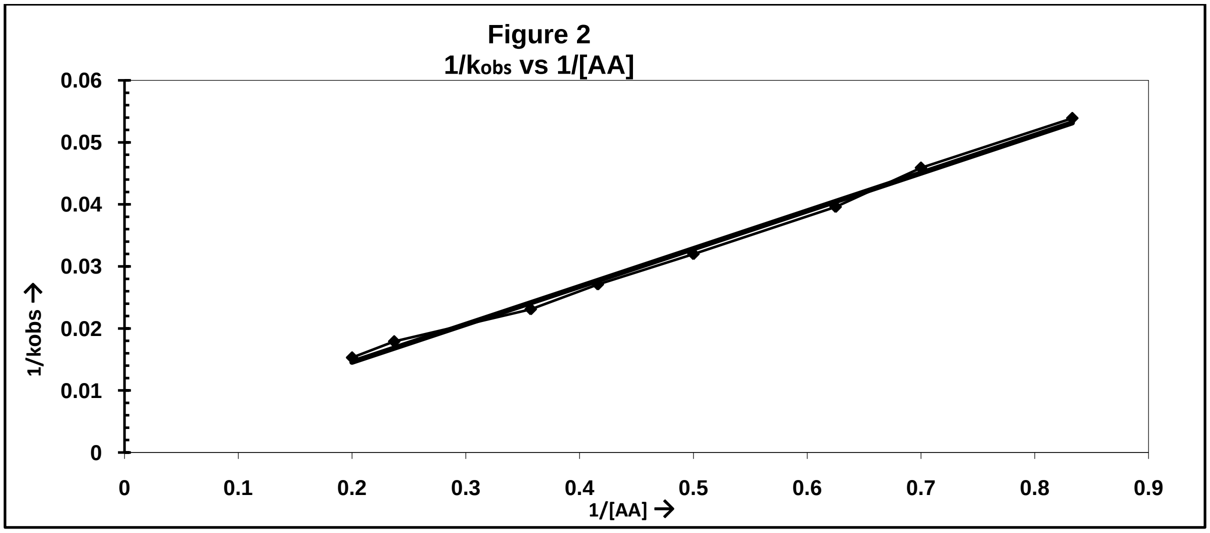


Fig. 2.1/k_{obs} versus 1/[2-Amino butyric acid]



3.4 Effect of ionic strength:

The effect of ionic strength was studied by varying sodium sulphate concentration. The ionic strength in the reaction medium was varied from 1.0 to 11.0 × 10^{-3} mol dm^{-3} (Table 2) at constant concentration of 2-Amino butyric acid, PCC, $HClO_4$ and with other conditions remaining constant. It has been observed that there was no significant effect of ionic strength on the rate. This indicates that the reaction may be between an ion and a neutral molecule or between neutral molecules[12].

Table 2. Variation of rate with sodium sulphate concentration.

[2-Amino butyric acid] = 2.0 ×10^{-2} mol dm^{-3}; [$HClO_4$] = 0.3 mol dm^{-3};

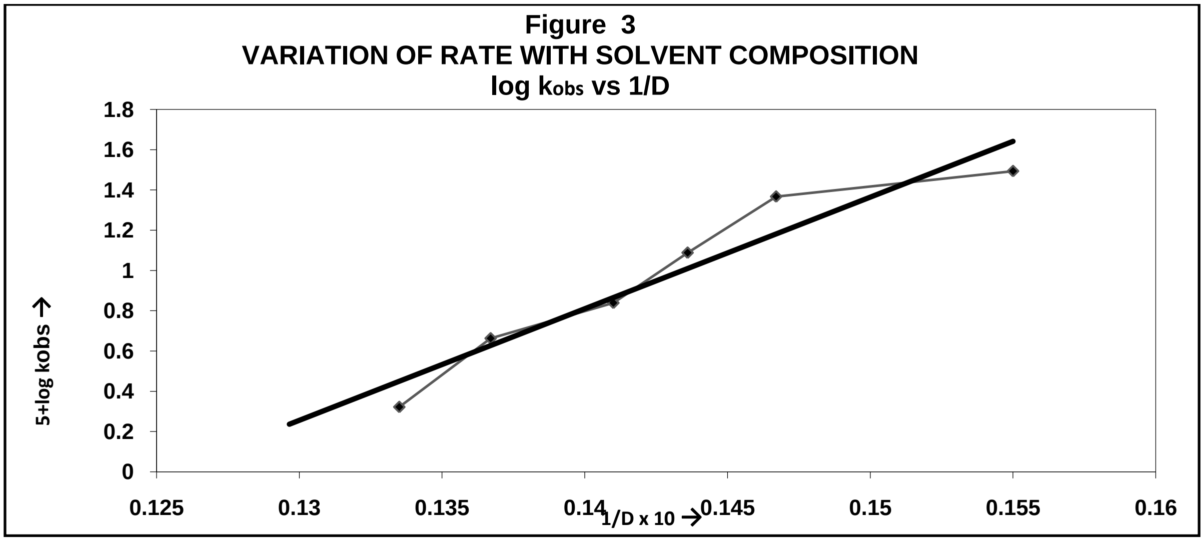
[PCC] = 2.0 ×10^{-3} mol dm^{-3}; DMF = 70 %(v/v)

[Na_2SO_4] × 10^3 (mol dm^{-3})	1.0	3.0	5.0	7.0	9.0	11.0
k_{obs} × 10^5 (s^{-1})	25.25	25.34	24.70	25.01	24.80	24.70

3.5 Effect of solvent composition:

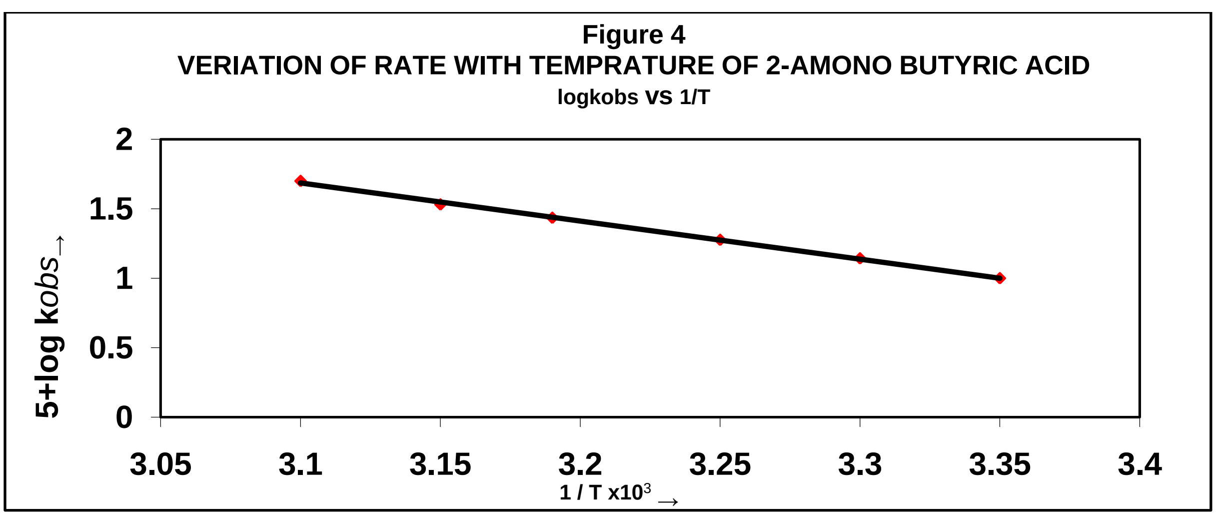
It was observed that the change in solvent composition by varying DMF (% v/v) in the reaction mixture, keeping other conditions remaining constant, affected significantly the reaction rate. The rate of reaction increased with an increase in volume percentage of DMF (Table 1). Many theories have been put forward to give a quantitative explanation[13,14] for the effect of dielectric constant (*D*) of the medium on the kinetics of liquid phase reactions. For the limiting case of a zero angle of approach between two dipoles or ion-dipole system, Amis[15] had shown that in the linear plot of lgk_{obs} versus 1/*D* a positive slope indicates a positive ion-dipole reaction, while a negative one indicates the involvement of two dipoles or a negative ion-dipole reaction. In the present investigation a plot of lgk_{obs} versus 1/*D* (Fig. 3) gives a straight line with a positive slope, clearly supporting that there is an involvement of positive ion-dipole in the rate determining step.

Fig. 3. Variation of rate with solvent composition.



3.6 Effect of temperature:

The rate constant of the reaction was found to increase with an increase in temperature (Table 1). The energy of activation was obtained by the plot of lg *k* versus 1/*T* (Fig. 4), from which the activation parameters were calculated (Table 1). The entropy of activation is negative as expected for bimolecular reaction. The negative value also suggests the formation of a cyclic intermediate from non-cyclic reactants in the rate-determining step[16]. The complex formation is proved by the plot of inverse of rate constant against inverse of substrate concentration [2-Amino butyric acid]. It has been pointed out[17] that if entropy of activation is negative and small the reaction will be slow.

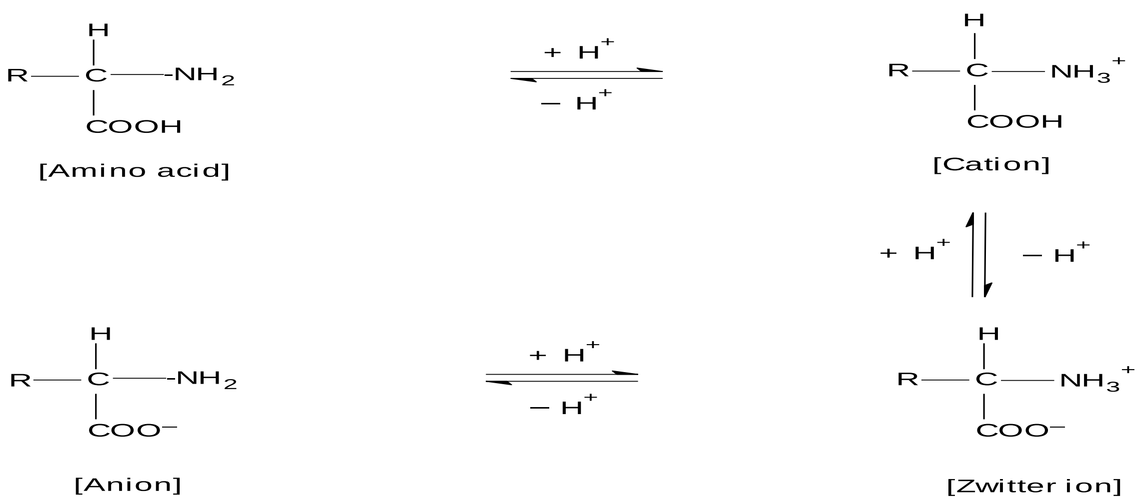


3.7 Effect of perchloric acid:

At fixed concentration of 2-Amino butyric acid and PCC and with other conditions remaining constant, the rate was found to increase with an increase in the perchloric acid concentration (Table1). A plot of lgk_{obs} versus log[$HClO_4$] (Fig. 5) is a straight line with a positive slope ≈1. This shows that reaction is of first order with respect to the hydrogen ion concentration.

Under the present experimental conditions, the concentration of anion form will be very low and hence the possible species may be either the cation form of 2-Amino butyric acid or zwitterion. With cation as the active species, the rate law predicts a second order dependence of the rate on [H^+], which is contrary to experimental results. Protonated 2-Amino butyric acid is not involved in the reaction sequence and the zwitterion is the active species in this reaction.

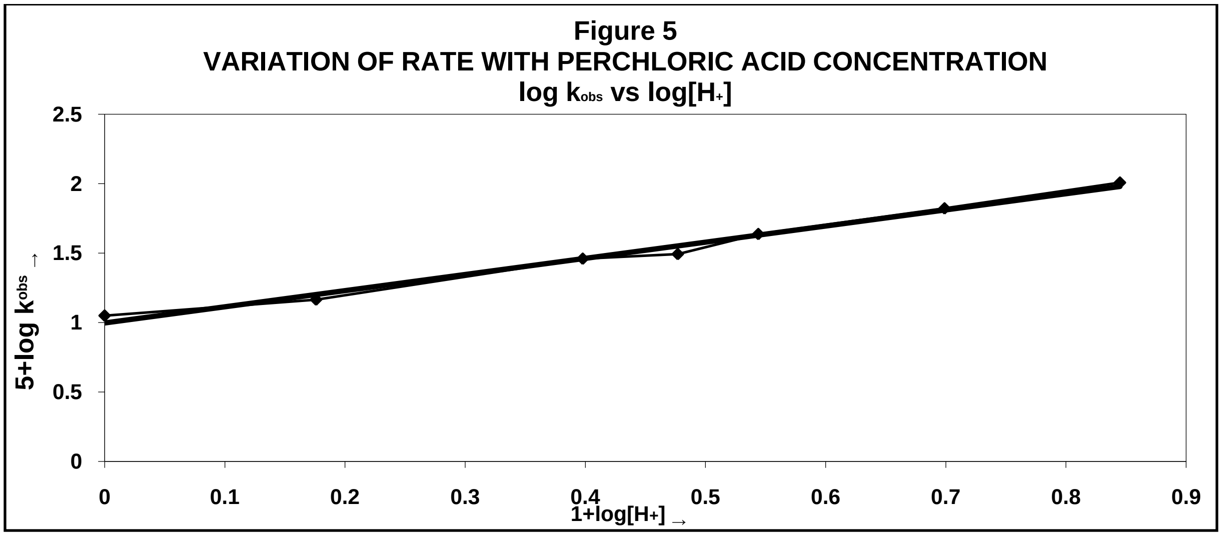
An amino acid is known to exist in the following equilibria:



The acid catalysis may well be attributed to a protonation of PCC (equation (2)) to yield a stronger oxidant and an electrophile both with the protonated and unprotonated forms being reactive. The formation of a protonated species of PCC has been also reported[18-20].

$$PyHOCrO_2Cl + H^+ \rightleftharpoons PyHOCr^+(OH)OCl \quad \text{------------- (2)}$$

Fig. 5. Variation of rate with perchloric acid concentration

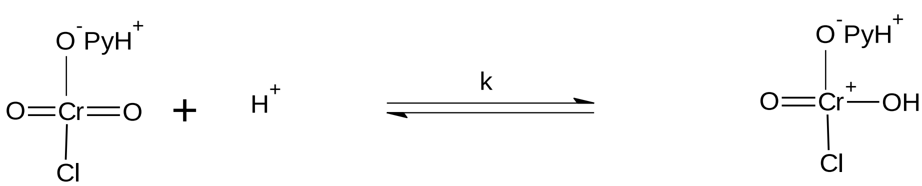


3.8 Effect of acrylonitrile:

Involvement of radical mechanism is ruled out, as there is neither any decrease in rate in the presence of stabiliser free acrylonitrile nor milky appearance under kinetic conditions. The rate of reaction dose not change on addition of pyridine indicating thereby, the stability of PCC, i.e. PCC is not hydrolysed under the conditions under study.

4. **Mechanism:**

On the basis of above experimental results the following possible mechanism has been proposed for the oxidation 2-Amino Butyric acid:



[PCC] **[Protonated PCC]**

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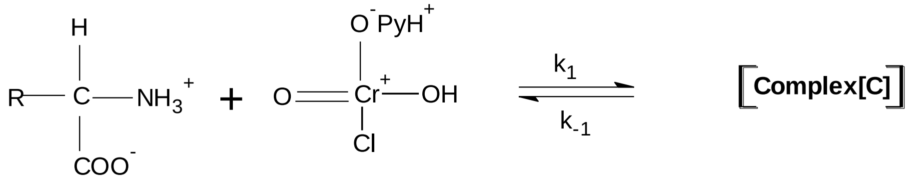
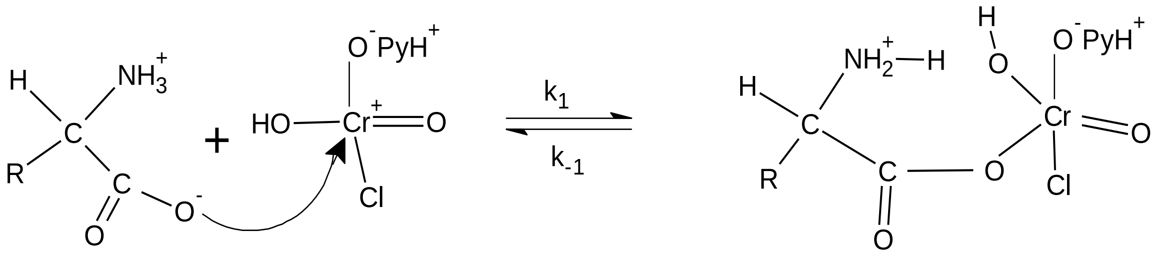
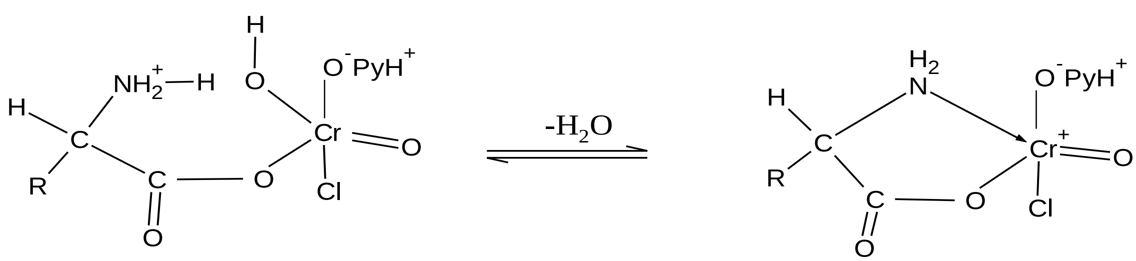


[Amino Acid] **[Protonated PCC]**

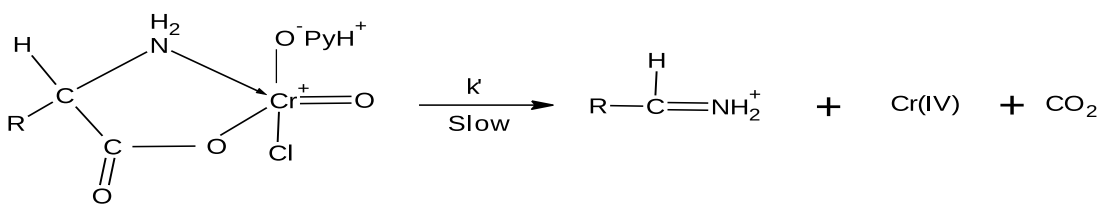
The formation of a complex between amino acid and protonated PCC may be represented as:

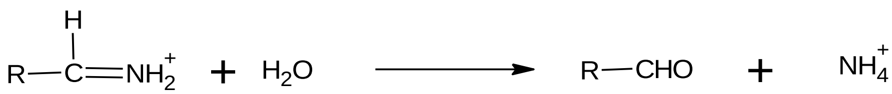


[Amino acid] [Protonated PCC]



Complex[C]





$$\underset{[PCC]}{Cr(VI)} + Cr(IV) \xrightarrow{Fast} 2Cr(V)$$

$$\underset{[PCC]}{2Cr(V)} + \underset{[Amino\ acid]}{2RCH(NH_2)COOH} + 2H_2O \xrightarrow{Fast} 2RCHO + 2CO_2 + 2NH_4^+ + 2Cr(III) + 2H^+$$

The overall reaction may be represented as:

$$2Cr(VI) + 3RCH(NH_2)COOH + 3H_2O \longrightarrow 3RCHO + 2Cr(III) + 3NH_4^+ + 3CO_2 + 3H^+$$

5. Rate Law

On the basis of above mechanism, the rate law can be expressed as:

Rate of reaction $= -\frac{d[C]}{dt} \alpha [C]$

$= k^{`}[C]$ 1

Concentration of complex, [C] can be calculated by applying steady state concept.

Rate of formation of complex = Rate of disappearance of complex

$k_1 [AA] [PCC]_{prot.} = k_{-1} [C] + k^{`} [C]$ 2

Since

$[PCC]_{total} = [PCC]_{prot.} + [C]$

Therefor

$[PCC]_{prot.} = [PCC]_{total} - [C]$ . . ..……………... 3

Hence

$k_1 [AA] \{[PCC]_{total} - [C]\} = (k_{-1} + k^`) [C]$

$k_1 [AA] [PCC]_{total} - k_1 [AA] [C] = (k_{-1} + k^`) [C]$

$k_1 [AA] [PCC]_{total} = k_1 [AA] [C] + (k_{-1} + k^`) [C]$

$k_1 [AA] [PCC]_{total} = \{k_{-1} + k^` + k_1 [AA]\} [C]$

$$[C] = \frac{k_1 [AA] [PCC]_{total}}{k_{-1} + k^` + k_1 [AA]}$$

$$= \frac{[AA] [PCC]_{total}}{\frac{k_{-1} + k^`}{k_1} + [AA]}$$

$$= \frac{[AA] [PCC]_{total}}{k_m + [AA]}$$

Hence

$$Rate = k^` [C]$$

$$= k^` \frac{[AA] [PCC]_{total}}{k_m + [AA]}$$

$= k [PCC]_{total} = k_{obs} [PCC]_{total}$ (when [AA] = constant)

Where

$$k_{obs} = k` \frac{[AA]}{k_m + [AA]}$$

$$\frac{1}{k_{obs}} = \frac{k_m}{k`} \frac{1}{[AA]} + \frac{1}{k`}$$

There for k_m can be calculated by intercept of plot 1/ k_{obs} versus 1/ [AA].

6. CONCLUSIONS

The study on the oxidation of 2-Amino butyric acid by pyridinium chlorochromate in DMF-water medium in the presence of perchloric acid reveals that the neutral amino acid takes part in the reaction, and the protonated amino acid is not involved in the reaction. The reaction was carried out at different temperatures. In the temperature range of 298-323 K, the Arrhenius equation is valid. The thermodynamic parameters indicate that the reaction is entropy-controlled.

The overall mechanistic sequence described here is consistent with the product analysis and kinetic and mechanistic data.

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