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ORIGINAL ARTICLE

Oxidation of phenyl alanine by pyridinium chlorochromate in acidic DMF–water medium: A kinetic study

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Abstract The kinetics of oxidation of phenyl alanine by pyridinium chlorochromate in DMF–water (70:30%) mixture in presence of perchloric acid leads to the formation of corresponding aldehyde. The reaction is of first order each in [PCC], [HClO₄] and [AA]. Michaelis–Menten type kinetics was observed with phenyl alanine. The reaction rates were determined at different temperatures [25, 30, 35, 40, 45, 50 °C] and the activation parameters were calculated. The reaction does not induce polymerization of acrylonitrile. With an increase in the amount of DMF in its aqueous mixture, the rate increases. A suitable mechanism for the reaction was postulated.

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1. Introduction

Pyridinium chlorochromate being one of the most versatile available oxidizing agent (Mahanti and Banerji, 2004). A number of reports on the oxidation of several substrates by pyridinium chlorochromate (PCC) are available in the literature like methionine (Sharma et al., 1997), benzhydrol (Venkataraman et al., 1978), unsaturated acids (Kumbhat and Sharma, 2004), cysteine (Adari et al., 2006), alcohols (Hiran et al., 2009). There seems to be no report on the oxidation of phenyl alanine by pyridinium chlorochromate.

Our literature survey reveals that the oxidation of phenyl alanine by different oxidants has received a limited attention so we are particularly interested to see the mechanism of the oxidation of phenyl alanine by pyridinium chlorochromate in acidic DMF–water media.

2. Experimental

2.1. Materials

In the present work, phenyl alanine analytical grade (SRL) was used as supplied (purity was checked by its melting point) and double distilled water was used for preparing the solutions.

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Perchloric acid was prepared by diluting known volume of acid in water. The solution so prepared was standardized by titration with previously standardized sodium hydroxide using phenolphthalein as an indicator. Doubly distilled analytical grade DMF (SRL) was used as a source of solvent. And all other reagents used were of analytical grade with 99.9% purity.

2.2. Preparation of pyridinium chlorochromate

Pyridinium chlorochromate was prepared in the lab by the method described in the literature (Core and Suggs, 1975). To 184 ml of 6 M hydrochloric acid (1.1 mol) was added 100 g (1.0 mol) of CrO_3 rapidly with stirring. After 5 min the homogeneous solution was cooled to 0 °C and 79.1 g (1.0 mol) of pyridine was carefully added over 10 min recooling to 0 °C gave a yellow orange solid which was collected on a sintered glass funnel and dried for 1 h in vacuum; yield 172.9 g (80%). The solid is not appreciably hygroscopic and can be stored for extended periods at room temperature without change. The purity was checked by iodometrically and by the UV–Vis, IR spectral analysis [λ_{max} = 354 nm; ν_{max} (KBr) = 3066, 2033, 1898, 1599, 1533, 1485, 1033, 949, 750 cm^{-1}].

Chlorochromic Acid   Pyridinium Chlorochromate
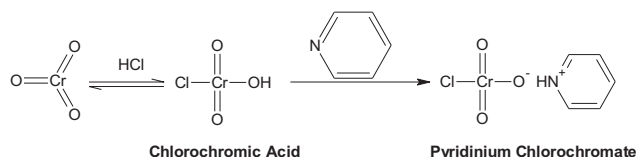
2.3. Method

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 phenyl alanine 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 1 cm cell placed in the thermostatted 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.

2.4. Stoichiometry and product analysis

The stoichiometry of the reaction was determined by performing the experiment at 313 K, under the condition of [PCC] > [phenyl alanine], containing 0.3 mol/dm^3 [$HClO_4$] in 70% vol. DMF, 30% vol. water mixture (v/v) were allowed to stand at 40 °C. When the reaction was completed, the PCC concentration was assayed by measuring the absorbance at 354 nm. The qualitative product study was made under kinetic conditions. The main reaction product was identified as aldehyde by its 2,4-dinitrophenylhydrazine derivative. Nesseler's reagent test and lime water test were used to detect the ammonium ion and carbon dioxide, respectively, and Cr(III) was confirmed by the UV–Visible spectra of the reaction solu-

tion after completion of the reaction. The observed stoichiometry may be represented as:

$$3RCH(NH_2)COOH + 2Cr(VI) + 3H_2O$$
$$\rightarrow 3RCHO + 2Cr(III) + 3NH_4^+ + 3H^+ \quad (A)$$
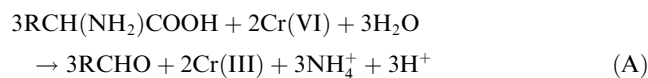
3. Results and discussion

3.1. Stability of pyridinium chlorochromate

The solution of PCC in DMF–water (70% (v/v) DMF) obeys Beer–Lambert's Law at λ = 354 nm. There was no change in optical density and spectra of PCC solution, without substrate in DMF–water (70% (v/v) DMF) on long standing or heating up to 335–345 K.

3.2. Effect of PCC

At constant [$HClO_4$], temperature and [amino acid] ([phenyl alanine] $\gg$ [PCC]), plot of log[PCC] against time was linear indicating first-order dependence of the rate on PCC. The observed rate constant k_{obs} was not affected by a change in initial concentration of PCC (Table 1).

3.3. Effect of substrate

At constant PCC concentration, [H$^+$] and temperature, the reaction rate increased with an increase in the concentration of phenyl alanine from 1.2×10^{-2} to 5.0×10^{-2} mol/dm^3 (Table 1). The plot of $\log k_{obs}$ versus log[phenyl alanine] (Fig. 1) was linear with positive slope equals to 0.8592 indicating first-order dependence of the rate on [phenyl alanine]. The plot of $1/k_{obs}$ vs. 1/[phenyl alanine], (Fig. 2) gives straight line with positive intercept, which indicates that Michaelis–Menten type kinetics is followed with respect to phenyl alanine. Although the intercept value [K_m = 0.004] is very small but the value

Table 1 Variation of rate with PCC, phenyl alanine, and perchloric acid concentrations.

$10^3 \times$ [PCC] mol/dm^3	$10^2 \times$ [Amino acid] mol/dm^3	$10 \times$ [H$^+$] mol/dm^3	$k_{obs} \times 10^5$ s^{-1}
2.5	2.0	3.0	24.94
2.25	2.0	3.0	25.26
2.0	2.0	3.0	25.28
1.75	2.0	3.0	25.91
1.5	2.0	3.0	25.91
1.0	2.0	3.0	25.28
2.0	1.2	3.0	15.67
2.0	1.6	3.0	21.87
2.0	2.0	3.0	25.71
2.0	2.4	3.0	29.75
2.0	2.8	3.0	34.54
2.0	3.66	3.0	41.07
2.0	2.0	1	6.52
2.0	2.0	2.5	19.57
2.0	2.0	3.0	25.71
2.0	2.0	3.5	31.47
2.0	2.0	5.0	47.21
2.0	2.0	7.0	80.61

T = 313 K DMF = 70% (v/v).

VERIATION OF RATE WITH PHENYL ALANINE CONCENTRATION

logk$_{obs}$ vs log[phenyl alanine]

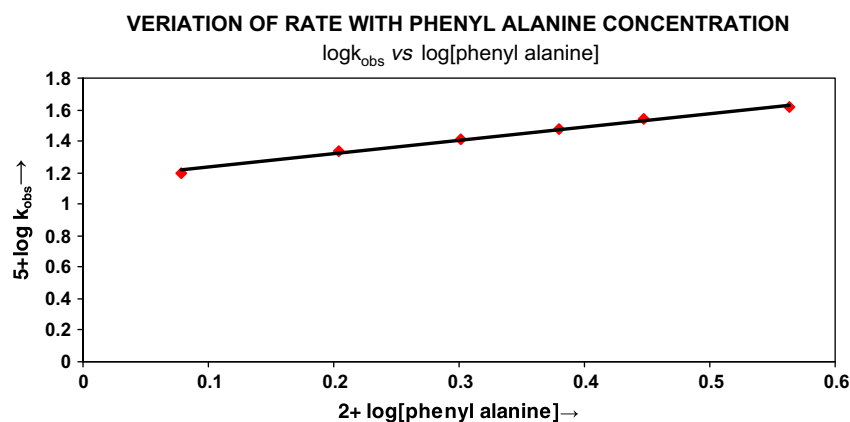**Figure 1**   Veriation of rate with phenyl alanine concentration $\log k_{obs}$ vs log[phenyl alanine].
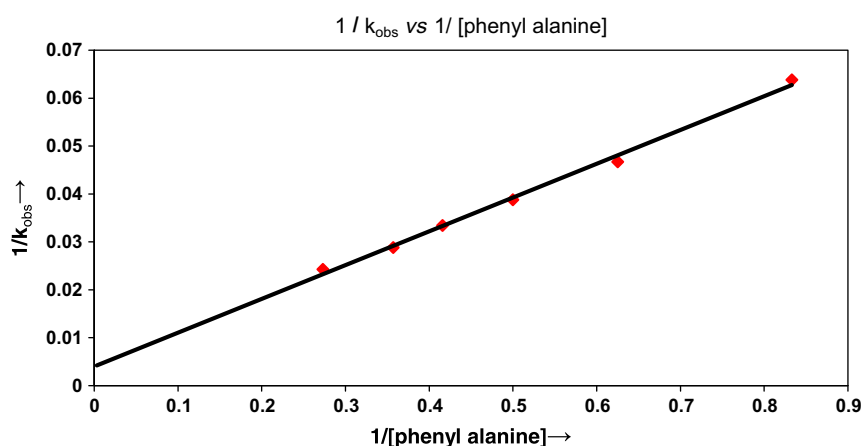
1 / k$_{obs}$ vs 1/ [phenyl alanine]

Figure 2 $1/k_{obs}$ vs 1/[phenyl alanine].

Table 2   Variation of rate with sodium sulfate concentration of phenyl alanine at 313 K.

$[Na_2SO_4] \times 10^3$ mol/dm^3	1.0	3.0	5.0	7.0	11.0
$10^5\ k_{obs}$ (s^{-1})	25.26	24.95	25.42	26.38	25.42

[Phenyl alanine] $= 2.0 \times 10^{-2}$ mol/dm^3; [HClO$_4$] $= 0.3$ mol/dm^3; [PCC] $= 2.0 \times 10^{-3}$ mol/dm^3; DMF $= 70\%$ (v/v).

indicate formation of 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) (Hiran et al., 2004; Nandibewoor et al., 2008).

3.4. Effect of ionic strength

The effect of ionic strength was studied by varying the sodium sulfate 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 phenyl alanine, 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 (Kabilan and Ganapathy, 1989).

3.5. Effect of solvent composition

It was observed that a change in solvent composition by varying DMF (% v/v) in the reaction mixture, keeping other conditions constant, and the reaction rate was affected considerably. The rate of reaction increased with an increase in volume percentage of DMF (Table 3). Many theories have been put forward to give a quantitative explanation (Amis, 1967; Entelis and Tiger, 1976) 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 (1953) had

Table 3   Variation of rate with solvent composition.

DMF:H$_2$O	$k_{obs} \times 10^5$ s^{-1}
70:30	25.91
60:40	14.43
50:50	8.005
40:60	6.14
30:70	5.015
20:80	2.21

[Phenyl alanine] $= 2.0 \times 10^{-2}$ mol/dm^3; [HClO$_4$] $= 0.3$ mol/dm^3; [PCC] $= 2.0 \times 10^{-3}$ mol/dm^3; $T = 313$ K

VARIATION OF RATE WITH DIELECTRIC CONSTANT
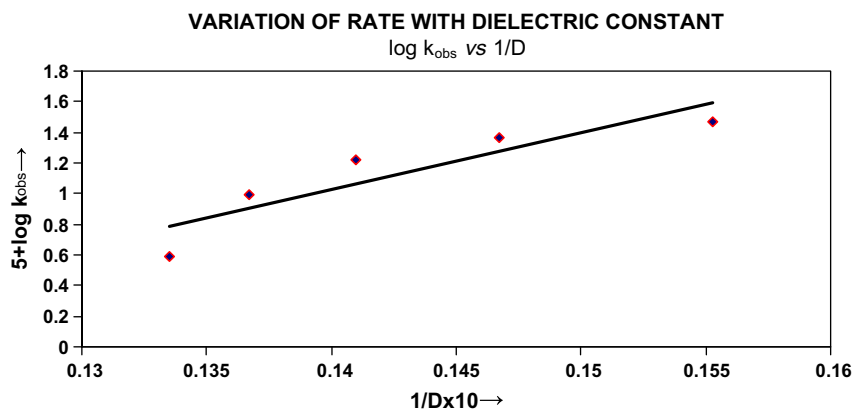log k$_{obs}$ *vs* 1/D

Figure 3   Variation of rate with dielectric constant $\log k_{obs}$ vs $1/D$.

Table 4   Variation of rate with temperature.

Temperature (k)	298	303	308	313	318	323
$k_{obs} \times 10^5 \text{ s}^{-1}$	8.76	12.66	16.83	25.71	31.15	43.79

[Phenyl alanine] mol/dm^3;   [HClO$_4$] = 0.3 mol/dm^3; [PCC] = 2.0×10^{-3} mol/dm^3; DMF = 70% (v/v).

Table 5   Activation parameters.

Parameters	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (kJ mol^{-1})	$\Delta F^{\neq}$ (Jk^{-1} mol^{-1})
Values	53.61	51.01	−93.75	80.35

shown that in a linear plot of $\log k_{obs}$ vs. $1/D$ a positive slope indicates a positive ion–dipole reaction, while a negative slope indicates the involvement of two dipoles or a negative ion–dipole reaction. In the present investigation a plot of $\log k_{obs}$ vs. $1/D$ (Fig. 3) gives a straight line with a positive slope equals to $+43.432$, clearly supporting that there is an involvement of positive ion–dipole in the rate determining step.

3.6. Effect of temperature

The rate constant of the reaction was found to increase with an increase in temperature (Table 4). The energy of activation was obtained by the plot of $\log k$ versus $1/T$ (Fig. 4), from which the activation parameters were calculated (Table 5). The entropy of activation is negative as expected for bimolecular reaction. The negative value also suggests the formation of a cyclic intermediate from a non-cyclic reactants in the rate determining step (Bhattacharjee and Bhattacharjee, 1990).

The complex formation is proved by the plot of inverse of the rate constant against inverse of the substrate concentration [phenyl alanine]. It has been pointed out (Glasstone et al., 1941) that if entropy of activation is negative and small, the reaction will be slow.

3.7. Effect of acrylonitrile and pyridine

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

3.8. Effect of perchloric acid

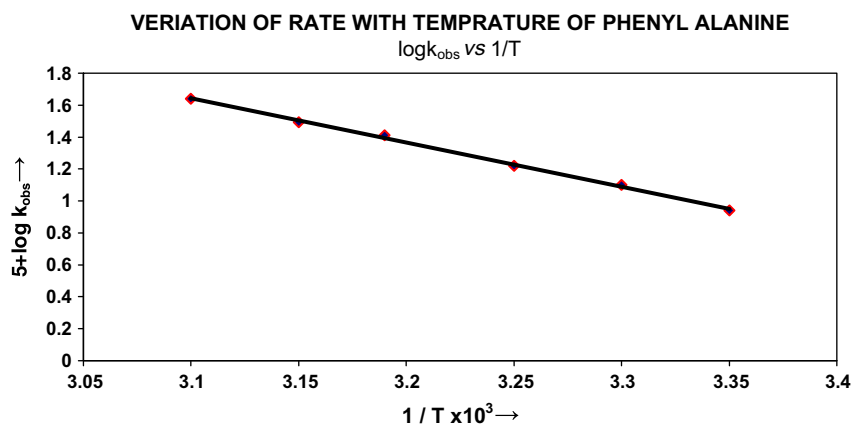At fixed concentration of phenyl alanine and PCC and with other conditions remaining constant, the rate was found to

VERIATION OF RATE WITH TEMPRATURE OF PHENYL ALANINE
logk$_{obs}$ *vs* 1/T

Figure 4   Veriation of rate with temprature of phenyl alanine $\log k_{obs}$ vs $1/T$.

VERIATION OF RATE WITH HYDROGEN ION OF PHENYL ALANINE

log k_{obs} vs log[H$^+$]

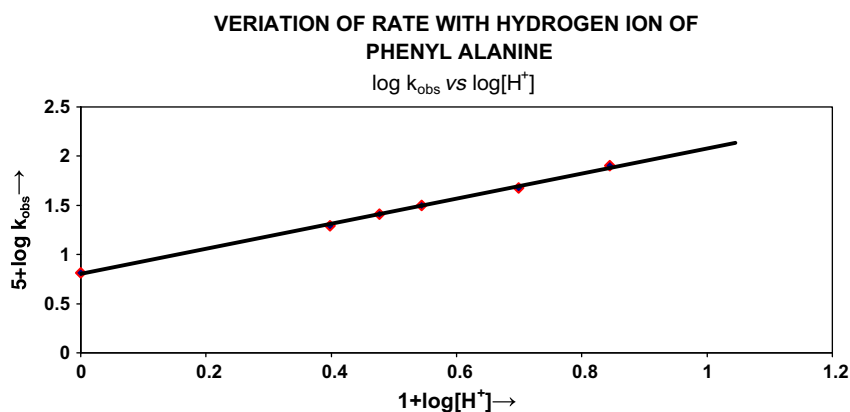**Figure 5**   Veriation of rate with hydrogen ion of phenyl alanine $\log k_{obs}$ vs log[H +].

increase with an increase in the perchloric acid concentration (Table 1). A plot of $\log k_{obs}$ vs. $\log[HClO_4]$ (Fig. 5) is a straight line with a positive slope ≈ 1 (1.277). 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 phenyl alanine or Zwitter ion. 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 phenyl alanine is not involved in the reaction sequence and the Zwitter ion is the active species in this reaction.

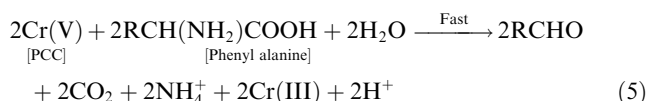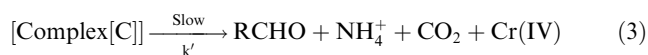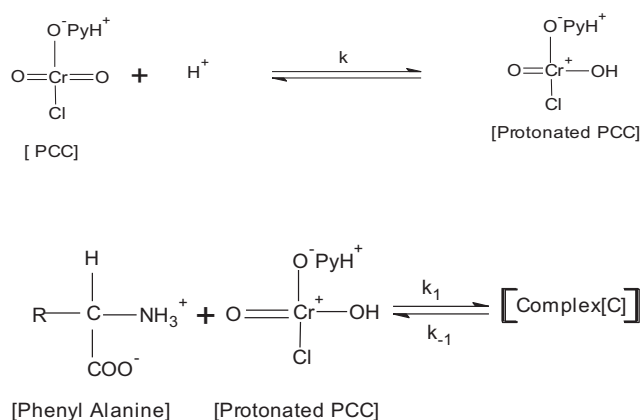An amino acid is known to exist in the following equilibria:
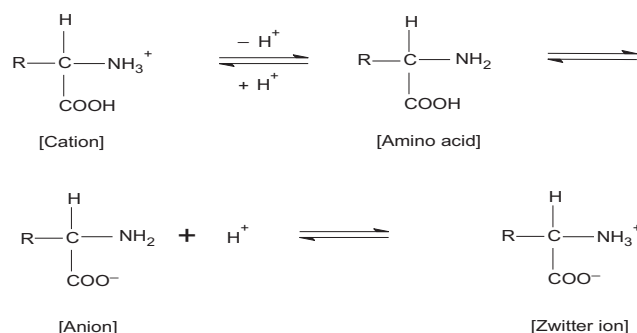
The acid catalysis may be well attributed to a protonation of PCC [Eq. (B)] to yield a stronger oxidant and an electrophile with both the protonated and unprotonated forms being reactive. The formation of a protonated species of PCC has been also reported (Seth et al., 1990; Sharma and Banerji, 1997; Kumbhat and Sharma, 2004).
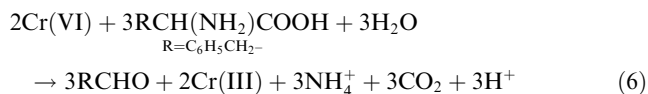
$$PyHOCrO_2Cl + H^+ \rightleftharpoons PyHOCr^+(OH)OCl \qquad (B)$$

4. Mechanism

On the basis of above experimental results, a suitable mechanism is given below:

$$[Complex[C]] \xrightarrow[k']{Slow} RCHO + NH_4^+ + CO_2 + Cr(IV) \qquad (3)$$

$$\underset{[PCC]}{Cr(VI)} + Cr(IV) \xrightarrow{Fast} 2Cr(V) \qquad (4)$$

$$2\underset{[PCC]}{Cr(V)} + 2\underset{[Phenyl alanine]}{RCH(NH_2)COOH} + 2H_2O \xrightarrow{Fast} 2RCHO$$
$$+ 2CO_2 + 2NH_4^+ + 2Cr(III) + 2H^+ \qquad (5)$$

The overall reaction may be represented as:

$$2Cr(VI) + 3\underset{R=C_6H_5CH_2-}{RCH(NH_2)COOH} + 3H_2O$$
$$\rightarrow 3RCHO + 2Cr(III) + 3NH_4^+ + 3CO_2 + 3H^+ \qquad (6)$$

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

$$-d[PCC]/dt \alpha [PCC][phenyl\ alanine][H^+].$$

5. Conclusion

The study on the oxidation of phenyl alanine by pyridinium chlorochromate in DMF–water media in the presence of

perchloric acid reveals that the neutral amino acid takes part in the reaction, 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, Arrhenius equation is valid.

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

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