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A kinetics and mechanistic study of the oxidation of alanine by chromium(VI) in DMF-water medium

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ABSTRACT

The oxidation of Alanine by Pyridinium chlorochromate has been studied by spectrophotometrically in the presence of perchloric acid in DMF-H_2O medium. The reaction is first order with respect to PCC and fractional order with respect to [H^+] and Alanine. Michaelis-Menten type kinetics was observed with alanine. The reaction rates were studied at different temperatures [25, 30, 35, 40, 45, 50 °C] and the activation parameters were computed. 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 main reaction product were identified as chromium(III) and acetaldehyde. A suitable mechanism for the reaction was postulated.

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INTRODUCTION

Chromium(VI) is well known oxidant in acidic media. The kinetics and mechanism of oxidation by chromium(VI) have been well studied, Pyridinium chlorochromate being one of the most versatile available oxidizing agent[1]. Kinetics of oxidation of methionine[2], oximes[3], unsaturated acids[4],cysteine[5], alcohols[6] by pyridinium chlorochromate were reported. There seems to be no reports on the oxidation of alanine by PCC.

Our literature survey reveals that the oxidation of Alanine by different oxidants has received limited attention; we are particularly interested to see the mechanism of the oxidation of alanine by PCC in acidic DMF-Water media.

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MATERIALS AND METHODS

Pyridinium chlorochromate was prepared by the method describe in the literature[7], and its purity was checked by iodometrically and melting point. Glycine (A.R.grade) (SRL) were used as supplied and purity was cheked by its melting point. All other chemicals used in this investigation were of analytical reagent grade. Double distilled water was used throughout in the investigation.

The rate measurements were carried out at 40 ± 0.1 ºC in 0.3 mole dm^{-3} $HClO_4$ under the condition [alanine] $\gg$ [PCC], in the solvent system of 70-30 % (v/v) DMF-H_2O. The reaction was initiated by mixing a calculated amount of thermostatted pyridinium chlorochromate in to the reaction mixture. The progress of the reaction was followed by measuring the absorbance of PCC at 354 nm in one cm cell placed in the thermostatted compartment of JASCO model 7800 UV/VIS spectrophotometer.

The kinetics run were followed for more than 60-70% completion of the reaction and good first order kinetics were observed. Pseudo-first order rate constant k_{obs} were obtained from the slope of the plot of log (absorbance) versus time.
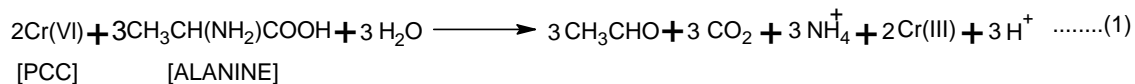
RESULTS AND DISCUSSION

Stoichiometry and product analysis
To determine the stoichiometry of reaction a known slight excess of pyridinium chlorochromate was added to a known amount of alanine, by keeping all other condition of reaction is constant and after 12 hours the residual pyridinium chlorochromate was determined spectrophotometrically at 354 nm. The Stoichiometry of the reaction was found to correspond to the equation.

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. acetaldehyde and was identified by its 2,4-dinitro phenyl hydrazine. derivative. Nesseler's reagent and lime water test were used to detect ammonium ion and carbon dioxide respectively.

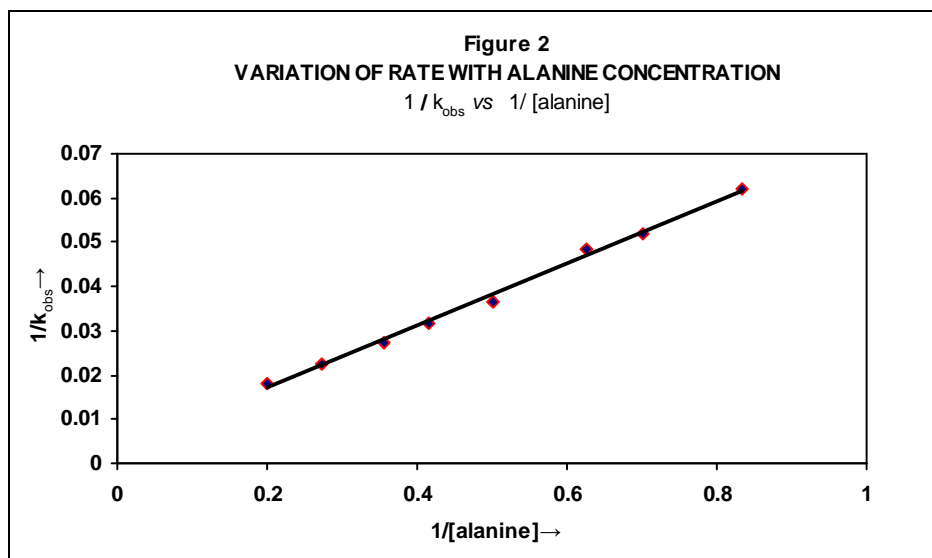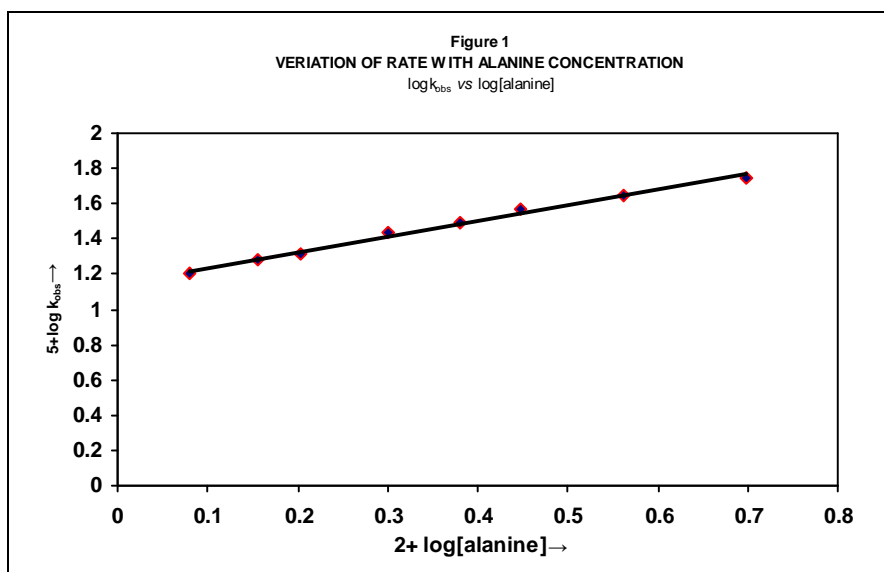The stoichiometry of the reaction was found to correspond to the equation.

$$2\,Cr(VI) + 3\,CH_3CH(NH_2)COOH + 3\,H_2O \longrightarrow 3\,CH_3CHO + 3\,CO_2 + 3\,NH_4^+ + 2\,Cr(III) + 3\,H^+ \quad \text{........(1)}$$

$$\text{[PCC]} \qquad \text{[ALANINE]}$$

Effect of PCC
Under pseudo-first order conditions of [alanine] $\gg$ [PCC] at constant [alanine], [$HClO_4$], DMF % and temperature, plots of log[PCC] versus time was linear indicating first order reaction and rate is depend on [PCC]. Furthermore, the rate constant did not change with change in concentration of pyridinium chlorochromate **[Table 1]**, confirming first order dependence on [PCC].

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Table 1. Variation of rate with PCC, Alanine and perchloric acid concentrations
Temp. = 313 K   DMF = 70 % (v/v)

10^3 x [PCC] mol dm^{-3}	10^2 x [alanine] mol dm^{-3}	10 x [H$^+$] mol dm^{-3}	k_{obs} x 10^5 s^{-1}
2.5	2.0	3.0	27.50
2.25	2.0	3.0	27.50
2.0	2.0	3.0	27.18
1.75	2.0	3.0	27.18
1.5	2.0	3.0	27.50
1.0	2.0	3.0	27.30
2.0	1.2	3.0	16.31
2.0	1.43	3.0	19.21
2.0	1.6	3.0	20.72
2.0	2.0	3.0	27.25
2.0	2.4	3.0	31.47
2.0	2.8	3.0	36.85
2.0	3.66	3.0	44.53
2.0	5.0	3.0	55.27
2.0	2.0	1	9.27
2.0	2.0	2.5	22.39
2.0	2.0	3.0	27.18
2.0	2.0	3.5	33.90
2.0	2.0	5.0	54.05
2.0	2.0	7.0	75.80

Effect of substrate

The effect of alanine concentration on the reaction rate was studied at constant [PCC], [HClO$_4$], temperature and DMF % **[table 1]**. The reaction rate is increased with increasing of alanine concentrations. When the logarithms of k$_{obs}$ values were plotted against the logarithms of the [alanine], (**Figure 1)** a linear plot with a slop of **0.8811** was obtained. Its indicating the order with respect to alanine to be fractional. The plot of 1/k$_{obs}$ versus 1/[alanine], (**Figure 2)** was found to be linear with small positive intercept, indicates that Michaelis–Menten type kinetics is followed with respect to alanine but the value of intercept is very small indicates that intermediate complex may be highly reactive so concentration will be very small at any time. A similar observation have been found in the oxidation of α-amino acid by Cr(VI) [8,9].

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Figure 1
VERIATION OF RATE WITH ALANINE CONCENTRATION
log k_{obs} *vs* log[alanine]

Figure 2
VARIATION OF RATE WITH ALANINE CONCENTRATION
1 / k_{obs} *vs* 1/ [alanine]

Effect of ionic strength and Dielectric constant

At constant concentration of reactants and with other constant conditions, the ionic strength was varied between 1.0 and 11.0 mol dm^{-3} using sodium sulfate solution **[Table 2]**. The result indicates that the negligible effect of ionic strength on the rate of reaction. This shows that the reaction may be between an ion and a neutral molecule or between neutral molecules.

The influence of variation of dielectric constant of the medium was carried out by the changing DMF (% v/v) in the reaction medium, keeping other conditions remaining constants and the reaction rate was affected considerably. The rate of reaction increased with an increasing volume percentage of DMF [**Table 3**]. A lot of theories have been given to quantitative explanation [10,11] for the effect of dielectric constant (D) of the reaction medium on the kinetics of liquid phase reaction. For the limiting case of a zero angle of approach between two dipoles or ion-dipole system, Amis[12] had shown that in a linear plot of logk_{obs} vs. 1/D. The positive slope

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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. $1/D$ **[Figure 3]** shows a straight line with a positive slope, clearly supporting that there is involvement of positive ion-dipole in the rate determining step.

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

$[Na_2SO_4] \times 10^3$ mol dm^{-3}	1.0	3.0	5.0	7.0	11.0
$10^5 \, k_{obs} \, (s^{-1})$	27.35	27.82	27.34	27.82	27.82

[Glycine] = 2.0 x10^{-2} mol dm^{-3}   *[HClO$_4$] = 0.3 mol dm^{-3}*
[PCC] = 2.0 x10^{-3} mol dm^{-3}   *DMF = 70 %(v/v)*

Table 3 variation of rate with solvent composition at 313 K
[Alanine] = 2.0 x10^{-2} mol dm^{-3}   *[HClO$_4$] = 0.3 mol dm^{-3}*
[PCC] = 2.0 x10^{-3} mol dm^{-3}   *DMF = 70 %(v/v)*

DMF : H$_2$O	$k_{obs} \times 10^5$ sec^{-1}
70 : 30	27.50
60 : 40	12.66
50 : 50	8.636
40 : 60	5.29
30 : 70	2.96

Figure 3
VARIATION OF RATE WITH DMF PERCENTAGE
log k$_{obs}$ *vs* 1/D
[alanine]
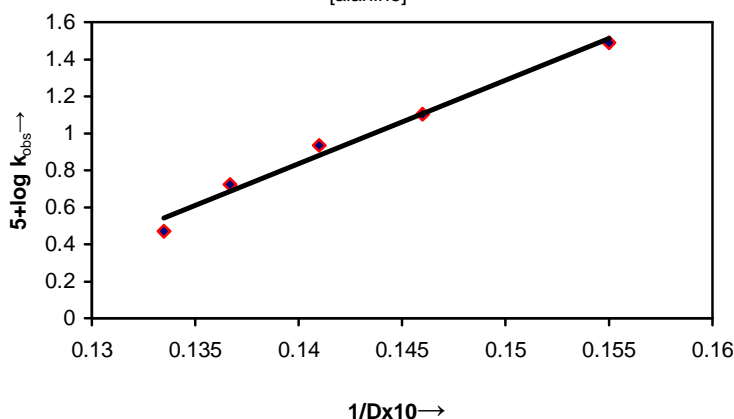
Effect of temperature

The reaction was studied at different temperatures (298-323 K), keeping other experimental conditions constant. The rate constant of the reaction was found to increase with increaseing temperature **[Table 4].** From the Arrhenius plot of $\log k_{obs}$ versus $1/T$ **[Figure 4],** activation energy and other thermodynamic parameters were calculated **[Table 5]**. The entropy of activation is negative as expected for bimolecular reaction. The negative value also suggests the

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formation of a cyclic intermediate from non-cyclic reactants in the rate determining step[13]. The complex formation is proved by the plot of $1/k_{obs}$ against $1/[alanine]$. It has been pointed out[14] that if entropy of activation is negative and small the reaction will be slow.

Table 4 variation of rate with temperature

Temperature (k)	298	303	308	313	318	323
k_{obs} x 10^5 s^{-1}	9.98	13.82	18.80	27.25	34.16	50.28

[Glycine] = 2.0 x10^{-2} mol dm^{-3}   *[HClO$_4$] = 0.3 mol dm^{-3}*
[PCC] = 2.0 x10^{-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	55.26	52.65	-87.98	80.2

Figure 4
VERIATION OF RATE WITH TEMPRATURE OF ALANINE
logk$_{obs}$ *vs* 1/T
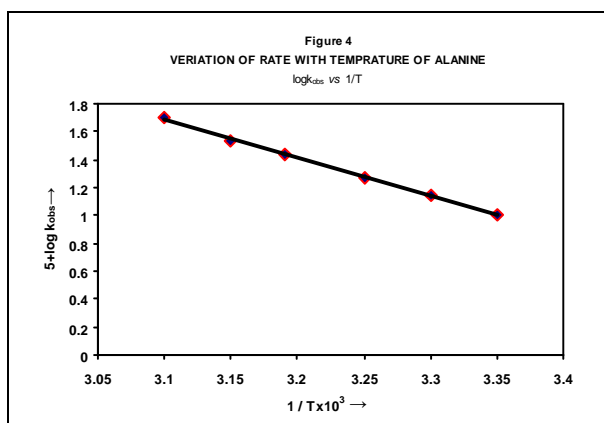
Test for free radicals
To test for free radicals, the reaction mixture containing stabilizer free acrylonitrile was kept for 24 hours in an inert atmosphere. On diluting the reaction mixture by methanol and no precipitate was observed. Its indicating that there is no intervention of free radicals in the reaction.

Effect of pyridine
It has been observed that there no effect of addition of pyridine on rate of reaction, indicating that PCC is not hydrolyzed in the reaction. Further this shows stability of PCC in the conditions understudy.

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Effect of perchloric acid

In order to study the effect of $[H^+]$ on the rate the of reaction, kinetic runs were carried out keeping the concentrations 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 increases with increase in $[H^+]$. When the logarithms of k_{obs} values were plotted against logarithms of the corresponding $[H^+]$ **[Figure 5]**, a linear plot with a positive slope of **1.098** was obtained and indicate that first order reaction with respect to the hydrogen ion concentration.

Figure 5
VERIATION OF RATE WITH HYDROGEN ION
log k_{obs} *vs* log$[H^+]$
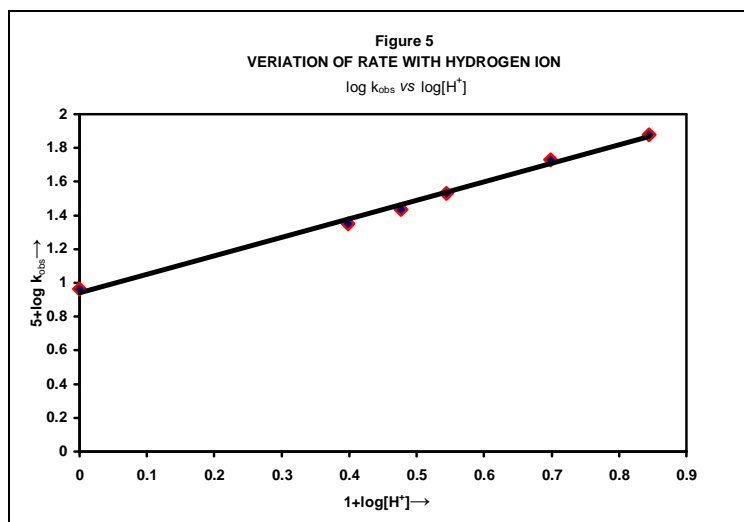
Under the present experimental conditions, the concentration of anion form will be very low and hence the possible species may be either the cation form of glycine or zwitter ion. With cation as the active species, the rate law predicts a second-order dependence of the rate on $[H^+]$, which is contrary to experimental results. Protonated alanine is not involved in the reaction sequence and the zwitter ion is the active species in this reaction.

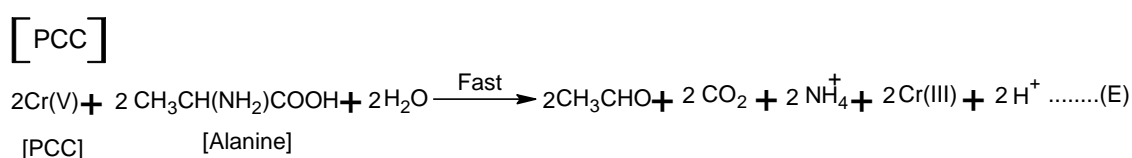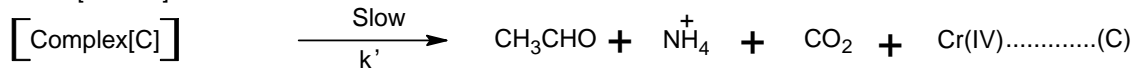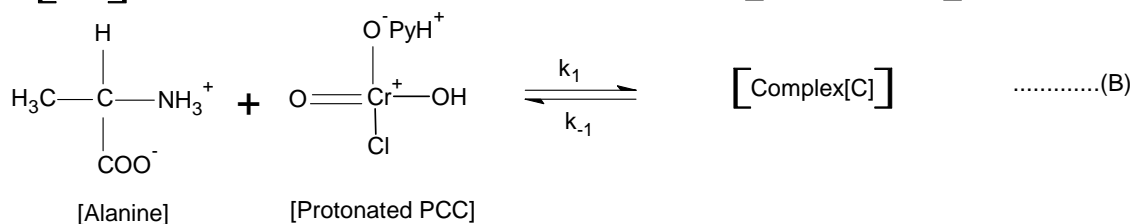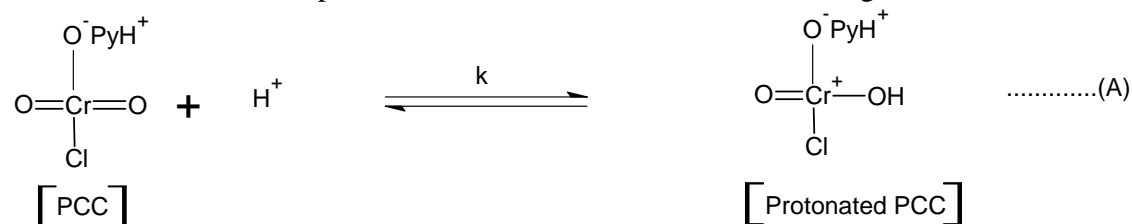An amino acid is known to exist in the following equilibria
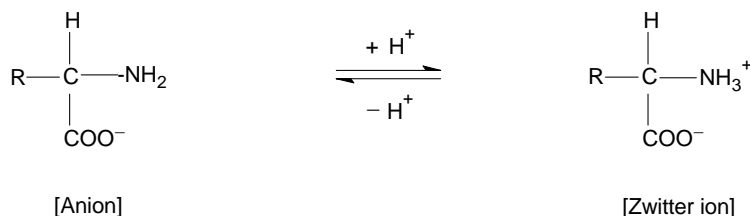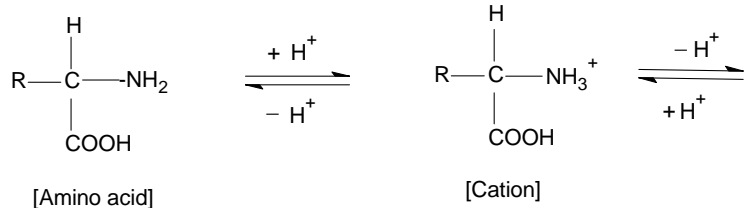
The acid catalysis may well be attributed to a protonation of PCC **[eq.2]** to yield a stronger oxidant and an electrophile with both the protonated and unprotonated forms being reactive.

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Under the present experimental conditions (0.1-0.7 mol dm^{-3} [H$^+$]), the protonated chromium(VI) is presumed to be the reactive species since the rate increases with increase in [H$^+$]. The formation of a protonated species of PCC has been also reported[15-17].
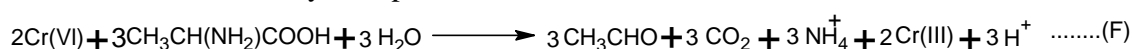

Equation (1): [PCC] + H$^+$ $\rightleftharpoons$ [Protonated PCC]
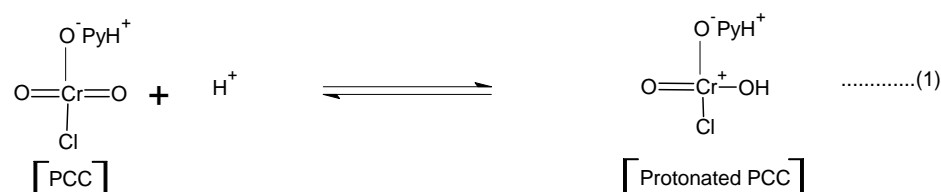
Mechanism

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

[PCC] + H$^+$ $\xrightarrow{k}$ [Protonated PCC] ....(A)

[Alanine] + [Protonated PCC] $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ [Complex[C]] ....(B)

$$[\text{Complex[C]}] \xrightarrow[k']{\text{Slow}} CH_3CHO + \overset{+}{N}H_4 + CO_2 + Cr(IV) ....(C)$$

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

$$2Cr(V) + 2\,CH_3CH(NH_2)COOH + 2\,H_2O \xrightarrow{\text{Fast}} 2CH_3CHO + 2\,CO_2 + 2\,\overset{+}{N}H_4 + 2\,Cr(III) + 2\,H^+ ....(E)$$
[PCC]   [Alanine]

The overall reaction may be represented as:

$$2Cr(VI) + 3CH_3CH(NH_2)COOH + 3\,H_2O \longrightarrow 3\,CH_3CHO + 3\,CO_2 + 3\,\overset{+}{N}H_4 + 2\,Cr(III) + 3\,H^+ ....(F)$$

On the basis of above mechanism the rate law can be expressed as:
$-d[PCC]/dt \ \alpha \ [PCC]\,[Alanine]\,[H^+]$

CONCLUSION

At room temperature the reaction between alanine and PCC is very slow in the low perchloric acid concentration in DMF-water medium. The oxidation of alanine by PCC is first order with respect to [PCC], [Alanine] and [HClO$_4$].The Zwitterionic form of alanine is oxidized to give acetaldehyde. The reaction was studied at different temperatures. In the temperature range of 298-323 K, Arrhenius equation is valid. The negative value of entropy indicates that the complex C is more ordered than reactant. The description of the mechanism is consistent with all experimental evidence.

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REFERENCES

[1] M. K. Mahanti, K. K. Banerji, *J. Indian Chem. Soc*., **2002,** 79,31.

[2] V. Sharma, P. K. Sharma, K.K. Banerji: *J. Indian Chem. Soc*., **1997,** 74 (8), 607**.**

[3] A. Bhandari, P. K. Sharma, K.K. Banerji, *Indian J.   Chem*., **2001,** 40(A), 470.

[4] R. Kumbhat, V. Sharma, *J. Indian Chem. Soc.,* **2004,** 81, 745.

[5] K. K. Adari, A. Nowduri, P. Vani, *J Trans. Metal Chem.,* **2006,** 31(6), 745.

[6] B. L. Hiran, S. Jain, C. V. Bhatt, *E J Chem*., **2009,** 6(1), 237.

[7] E.J. Core, W.T. Suggs, *Tetrahedron Lett*., **1975,** 31, 2647.

[8] B.L. Hiran, V. Joshi, J. Choudhary, N. Shorgar, P. Verma; *Int. J. Chem. Sci.,* **2004,** 2(2), 164.

[9] S. T. Nandibewoor, P .N. Naik, S. A. Chimitadar; *Transition Met. Chem.,* **2008,** 33, 405.

[10] S. amis, "Solvent effects on Reaction Rates and Mechanisms" *Academic Press, new York*,1966.

[11] G. Entelis, R. P. Tiger, "Reaction in Liquid Phase" *Wiley, New York,* 1976.

[12] E. S. Amis, *J. Chem. Educ.*, **1953**, 30, 351.

[13] U. Bhattacharjee, A. K. Bhattacharjee; *Indian J. Chem.,* **1990,** 29(A), 1187.

[14] S. Glasstone, K. J. Laidler, H. Eyring, 'Theory of rate process ' *Megraw-Hill, New york*. Chepter (III) and (IV), 1941.

[15] A. Seth, A.Mathur, K. K. Banerji, *Bull. Chem. Soc. Jpn.,* **1990,** 63, 3640.

[16] P. K. sharma, K. K. Banerji, *J. Indian Chem. Soc.,* **1997,** 74, 607.

[17] R. Kumbhatand, V. Sharma; *J. Indian Chem. Soc.,* **2004,** 81, 745.