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Oxidation of Leucine by Pyridinium Chlorochromate in Acidic DMF–Water Medium: Kinetic Mechanistic Studies

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ABSTRACT

Oxidation of Leucine by pyridinium chlorochromate in aqueous DMF medium, containing perchloric acid has been studied at 40ºC. The rate of reaction was found to be of first order dependence on [PCC], [Leucine] 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 2-methylbutanal. The rate of reaction decreased with increase in the polarity (dielectric constant of medium) of solvent, which indicates that there is involvement of an iron–dipole type of interaction in the rate-determining step. The activation parameters have been evaluated. On the basis of the experimental findings, a suitable mechanism has been proposed.

Keywords: Kinetics, Oxidation, DMF (N, N-Dimethylformamide), Leucine, PCC (Pyridinium Chlorochromate).

INTRODUCTION

Due to the direct or indirect impact on life and industry, systematic analysis of the kinetics and mechanistic studies of the oxidation of organic compounds has always been a subject of considerable importance. Amino acids were oxidized by a variety of oxidizing agents[1, 2]. It acts not only as a building block in protein synthesis but also plays a significant role in metabolism. Oxidation study of amino acids is of great interest because of their biological significance and selectivity toward the oxidant to yield different products [3-6].

Pyridinium chlorochromate being one of the most versatile available oxidizing agents [7]. A number of reports on the oxidation of several substrates by pyridinium chlorochromate (PCC) are available in the literature like methionine [8], oximes [9], unsaturated acids [10], cysteine [11], alcohols [12] Glycine [13], Alanine, Phenyl Alanine. There seems to be no report on the oxidation of Leucine by pyridinium chlorochromate.

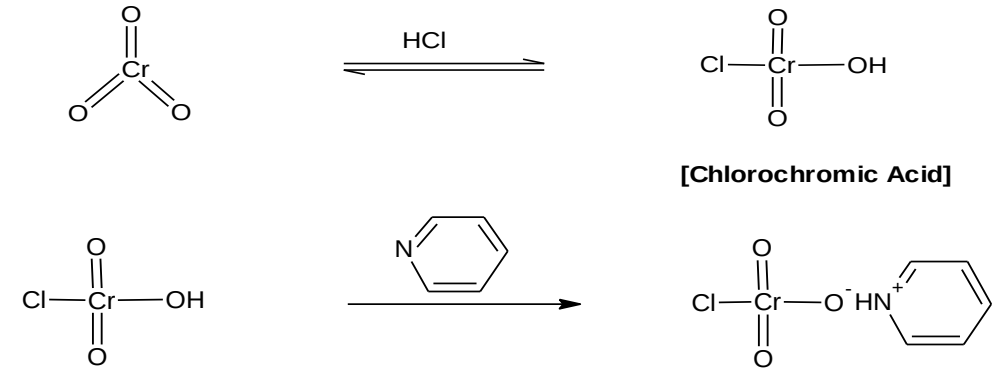
Our literature survey reveals that the oxidation of Leucine by different oxidants has received a limited attention so we are particularly interested to see the mechanism of the oxidation of Leucine by pyridinium chlorochromate in acidic DMF-Water media

MATERIALS AND METHODS

In this investigation Leucine Analar 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. Solution of HClO4 was prepared by diluting known volume of acid in water. The prepared solution was standardized by titration with previously standardized NaOH using phenolphthalein as an indicator. Doubly distilled analytical grade DMF (SRL) was used. And all other Chemicals used were of analytical grade with 99.9% purity.

Synthesis of Pyridinium Chlorochromate

Pyridinium chlorochromate was synthesized by the method of Corey and Suggs [16] and Agrawal [17]. Purity was checked by iodometrically, melting point, elemental analysis and by the IR and UV-VIS spectral analysis [U. V. - λmax=354 nm; I. R. - λmax (KBr)= 3066, 2033, 1898, 1599, 1533, 1485, 1033, 949, 750 cm-1]



The measurements of rate were carried out at 40 ± 0.1 ℃ in 0.3 mole dm-3 HClO4 under the condition [Leucine] >> [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 1 cm cell placed in the thermostatted compartment of JASCO model 7800 UV/VIS spectrophotometer. The kinetic runs were followed for more then 60-70% completion of the reaction and good first order kinetics were observed. Pseudo-first order rate constant kobs were obtained from the slope of the plots of log (absorbance) versus time.

Stoichiometry and product analysis

Reaction mixture containing known slight excess of PCC over Leucine containing 0.3 mol /dm^3 [HClO4] in 70 vol. % DMF, 30 vol. % water mixture (v/v) were allowed to stand at 40 ºC. When the reaction was completed, the pyridinium chlorochromate concentration was assayed by measuring the absorbance at 354 nm. The result indicated that two moles of PCC reacts with three moles of Leucine, as shown in Equation 1. The qualitative product study was made under kinetic conditions. The main reaction product was identified as 3-Methylbutanal by its 2, 4-D.N.P. 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 visible spectra of the reaction solution after completion of the reaction. The observed Stoichiometry may be represented as

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

Hardness test

Select five tablets randomly. Place one tablet at a time in the hardness tester (Dr Schleuniger Model 5Y) which is already set to O. Apply pressure by pressing the start button of hardness tester apparatus, till the tablet breaks. Note down the reading on the tester i.e. the hardness of the tablet in Newton's. Take the average of five such tablets and calculate the average hardness of the tablets.

RESULTS AND DISCUSSION

Effect of PCC

To see the effect on rate of oxidation of oxidant concentration, the initial concentration of the oxidant is varying between the ranges 1.0×10-3M to 2.5×10-3Mat [HClO4]=3.0×10-1 mol, temperature = 313 K and [Leucine]=2.0×10-2 mol dm. The observed rate constant kob was not affected by a change in initial concentration of PCC in Table 1.

Table 1: Effect of plasticizer film formation with methacrylate polymer

10^3x[PCC] mol dm^{-3}	10^2x[Leucine] mol dm^{-3}	10x[H^+]mol dm^{-3}	Temp. (k)	DMF: H_2O%	$k_{obs}x10^5$ s^{-1}
2.5	2.0	3.0	313	70:30	24.30
2.25	2.0	3.0	313	70:30	23.98
2.0	2.0	3.0	313	70:30	23.66
1.75	2.0	3.0	313	70:30	24.62
1.50	2.0	3.0	313	70:30	24.66
1.0	2.0	3.0	313	70:30	24.30
2.0	1.2	3.0	313	70:30	14.39
2.0	1.43	3.0	313	70:30	18.00
2.0	1.6	3.0	313	70:30	20.46
2.0	2.0	3.0	313	70:30	24.62
2.0	2.4	3.0	313	70:30	30.39
2.0	2.8	3.0	313	70:30	34.54
2.0	3.66	3.0	313	70:30	42.22
2.0	5.0	3.0	313	70:30	53.72
2.0	2.0	1	313	70:30	6.18
2.0	2.0	2.5	313	70:30	19.70
2.0	2.0	3.0	313	70:30	24.56
2.0	2.0	3.5	313	70:30	27.25
2.0	2.0	5.0	313	70:30	39.34
2.0	2.0	7.0	313	70:30	56.42
2.0	2.0	10.0	313	70:30	80.90
2.0	2.0	3.0	298	70:30	7.67
2.0	2.0	3.0	303	70:30	11.51
2.0	2.0	3.0	308	70:30	16.31
2.0	2.0	3.0	313	70:30	24.64
2.0	2.0	3.0	318	70:30	30.00
2.0	2.0	3.0	323	70:30	47.33
2.0	2.0	3.0	313	70:30	24.30
2.0	2.0	3.0	313	60:40	12.79
2.0	2.0	3.0	313	50:50	7.67
2.0	2.0	3.0	313	40:60	2.96
2.0	2.0	3.0	313	30:70	1.60
2.0	2.0	3.0	313	20:80	0.90
2.0	2.0	3.0	313	0.0:100	0.40

CONCLUSION

The reaction is of first order with respect to [PCC], [Leucine], and [H+] ion. The study on the oxidation of Leucine by pyridinium chlorochromate in DMF-water media in the presence of perchloric acid reveals that the neutral amino acid take part in the reaction, protonated amino acid is not involved in the reaction. The Michaelis–Menten type kinetics is observed with respect to Leucine. Although the intercept value [Km=0.007] is very small but the value indicates the formation of complex which may be highly reactive so concentration will be very small at any time. The reaction was carried out at different temperatures. In the temperature range of 298-323 K, Arrhenius equation is valid. The thermodynamic parameters indicate that the reaction is entropy controlled.

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