Oxidation of DL-Alanine by QDC: A Kinetic and Mechanistic Approach in a Partial Non-Aqueous System

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ABSTRACT

The present paper describe the kinetics of oxidation of Dl-alanine by QDC in the presence of perchloric acid in 30% DMF-H_2O(v/v) medium at 40^0C spectrophotometrically at λ_{max} =354nm. The reaction is first order with respect to [QDC], [H^+], and [substrate]. 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. Michaelis- Menten type kinetic was observed with Dl-alanine. The reaction rates were studied at different temperature and the activation parameters has been computed. The main product were identified as Cr (III) and acetaldehyde.

KEYWORDS: Dl-alanine, QDC, DMF, Oxidation.

INTRODUCTION

Oxidation is an essential operation in organic synthesis and several reagent have been developed for a wide variety of transformation [1, 2]. Hexavalent chromium compounds have been widely used as oxidizing agents.QDC has been used for the oxidation of alcohol and aldehyde [3].QDC works as efficiently as Collins reagent [4] and activated manganese dioxide. QDC has emerged as a very useful and versatile oxidant, which is clearly deserving of widespread application.

Some of the organic substrates which have been oxidized by QDC in acid medium, have included benzyl alcohol [5],aryl alkanes[6], toluene and substituted toluene's[7,8], fluorine[9], polynuclear aromatic hydrocarbons[10] and diphenylamines.Sukanya et.al.[11] studied a comparative study of QDC oxidation with hydrophobic dependence amino acid. Hiran.et.al. reported the oxidation of glycine[12] and tyrosine[13] by PBC in aqueous acetic acid in presence of perchloric acid. Dangarh.et.al. reported the kinetic and mechanistic study of oxidative transformation of glycine and alanine[14],l-isoleucine and nor-leucine[15] andphenylalanine[16]by PDC in aquo-acetic acid medium. Hiran et. al. reported the oxidation of alanine [17] by PCC in DMF-Water medium in the presence of perchloric acid. There seems to be no reports on the oxidation of Dl-Alanine by QDC in DMF-Water medium.

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

MATERIALS AND METHODS

Quinolinium dichromate was prepared by the method describe in the literature **[3].** The purity of the compound was checked by spectral analysis.IR (KBr) exhibited band at 930, 875, 765, and 730 cm^{-1}. Dl-alanine (A.R.grade) were used as supplied and purity was checked 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 2M $HClO_4$ under the condition [alanine] >>[QDC], in the solvent system of 30-70 % (v/v) DMF-H_2O. The reaction was initiated by mixing a calculated amount of thermostatted Quinoliniumdichromate in to the reaction mixture. The progress of the reaction was followed by measuring the absorbance of QDC at 354 nm in one cm cell placed in the thermostatted compartment of Systronics VISISCAN -167 spectrophotometer.
The kinetics run were followed for more than 60-70% completion of the reaction and good first order kinetics were observed.

RESULTS AND DISCUSSION

Effect of substrate

The effect of Dl-alanine concentration on the reaction rate was studied at constant [QDC], [$HClO_4$], temperature and DMF% [Table 1]. The reaction rate is increased with increasing of alanine concentrations. A plot of log k against log [substrate] **[Fig-1]** gives a straight line. This revealed that the rate of oxidation is first order with respect to Dl-alanine. The plot of $1/k_{obs}$ versus 1/ [alanine], was found to be linear with small positive intercept, indicates that Michaelis-Menten type kinetics is followed with respect to Dl-alanine.Similar observations have been found in the oxidation of alpha amino acid by Cr (VI) [18].
The variation of the rate of oxidation of Dl-Alanine with QDC can be expressed as

d [QDC]/dt = k[Dl-alanine] [QDC] / K_m + [Dl-alanine]

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 kobs values were plotted against logarithms of the corresponding [H^+], a linear plot was obtained and indicate that first order reaction with respect to the hydrogen ion concentration.

Effect of Solvent composition

Effect of solvent was studied by changing proportion of DMF and water; varied from 10% to 50% DMF v/v. The reaction rate increased with an increase in the percentage of dimethylformamide, suggesting that a low dielectric medium favors the oxidation [**Table-1**]. A plot of log k against 1/D is linear with a positive slope for the Dl-alanine. This indicates an ion- dipole type of interaction in the rate-determining step.

Effect of temperature

The rate of oxidation increases with increase in temperature .The reaction was studied at different temperatures (298-323 K), keeping other experimental conditions constant. **[Table 2].** From the Arrhenius plot of logk_{obs} versus 1/T,**[Fig-2],**activation energy and other thermodynamic parameters were calculated **[Table 3]**. 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[19]. The complex formation is proved by the plot of 1/k_{obs} against 1/ [alanine]. It has been pointed out[20] that if entropy of activation is negative and small the reaction will be slow.

Stoichiometry

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

$3RCH (NH_2) COOH + 2QHCrO_4 + 2H^+ + H_2O \rightarrow 3RCHO + 2 H_3CrO_3 + 3NH_4^+ + 3CO_2 + 2Q$

For Dl-Alanine R= CH_3

CONCLUSION

Oxidative transformation of Dl-alanine is first order with respect to [QDC], [Alanine] and [$HClO_4$].The reaction between alanine and QDC is very slow in the low perchloric acid concentration in DMF-water medium. 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.

TABLE NO. 1

Effect of [Substrate], [H^+] and Solvent

[QDC]=1 x 10^{-3}M T = 313 K

[Subs] x 10^2M	**[$HClO_4$] x M**	**DMF %v/v**	**k_{obs} X 10^5 Sec^{-1}**
1	2	30	20.26
1.5	2	30	23.41
2	2	30	25.48
2.5	2	30	27.63
3	2	30	29.44
1	1	30	6.83
1	1.5	30	15.27
1	2	30	20.26
1	2.5	30	35.15
1	3	30	46.78
1	2	10	15.35

1	2	20	17.77
1	2	30	20.26
1	2	40	27.67
1	2	50	43.10

TABLE NO. 2

[Dl-Alanine] = 1 X 10^{-2} M [*$HClO_4$*] = 2M **[QDC] = 1 X 10^{-3}M** **[DMF]=30% v/v**

Temperature In K	**k_{obs} X 10^5 Sec^{-1}**
298	7.94
303	9.09
308	13.08
313	20.26
318	27.21
323	52.50

TABLE NO. 3
THERMODYNAMIC PARAMETERS

AMINO ACID	**log A**	**Energy of activation $\Delta E^{\neq}$ kJ mol^{-1}**	**Entropy of activation $\Delta S^{\neq}$ J mol^{-1} K^{-1}**	**Enthalpy of activation $\Delta H^{\neq}$ kJ mol^{-1}**	**Free energy of activation $\Delta G^{\neq}$ kJ mol^{-1}**
DL- Alanine	7.95	59.64	-96.51	57.04	87.24

Fig-1Effect of Substrate Concentration

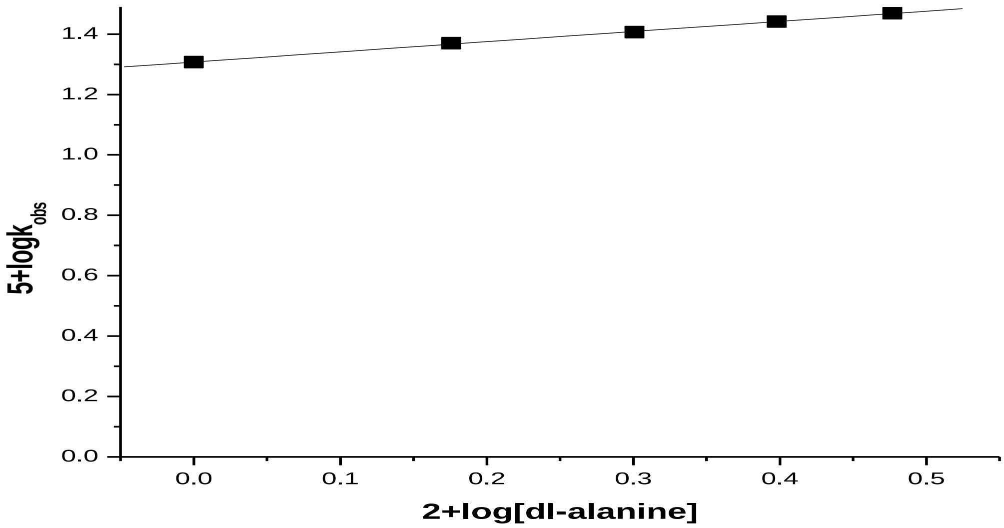
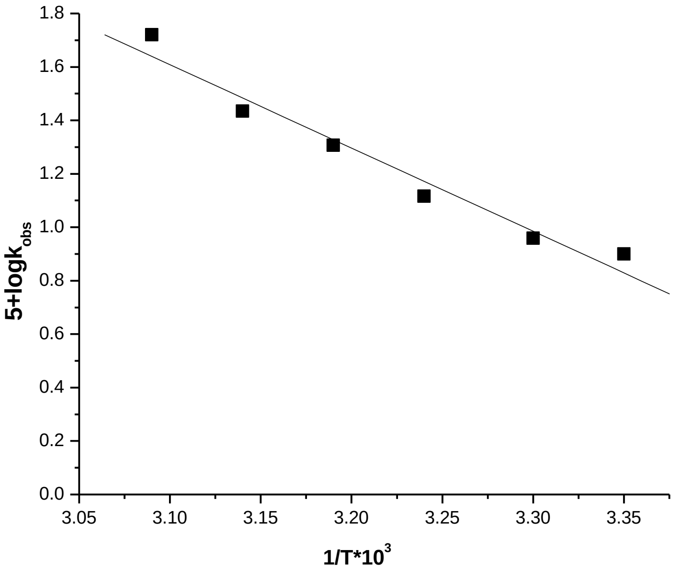


Fig-2 Effect of Temperature



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