IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Kinetics Of Oxidation Of A Few α-Amino Acids By Gibbs Reagent

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ABSTRACT

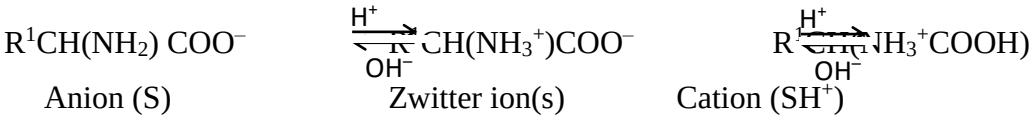
A systematic and comparative study of oxidation of a few α -amino acids like Glycine DL- Leucine ,DL-Isoleucine, DL-alanine, DL-Phenyl Alanine by using 2,6-dichloroquinone-4-chloro-imide has been carried out in aqueous acetic acid-sodium acetate mixtures. The kinetic orders aresimilar that is first order in oxidizing agent for all the substrates. The substrate dependence is first order for all the substrates. If we increase sodium acetate concentration leads to increases the reaction rate. In these analysis we observed that in these oxidations is with alanine as standard, substrates with electron releasing groups like Glycine and alanine and substrates with electron with drawing groups like Phenyl alanine , serine ,Aspartic acid exhibited higher kinetic rates. This shows that there is a dual mechanism operating in these oxidations. log k_1 vs σ plot is not linear as two lines intersect giving two different slopes. The slopes are –2.45 for substrates with electron releasing groups and +1.67 for substrates with electron with drawing groups. Hepler's treatment has been applied to understand the nature of entropy-enthalpy relationship on the kinetics of these reactions. Finally a synchronous oxidative decarboxylation process has been postulated to explain the oxidation of these α -amino acids. The major products are the nitriles.

Key Words :α -amino acids -electron releasing groups –First order kinetics- Electron withdrawing groups- Kinetic order- Entropy- Enthalpy relationship

I. Introduction

A great number of N-halo and metallic reagents have been shown to oxidise α-amino acids with well-documented kinetics (1–8). The current study examines how 2,6 Dichloroquinone -4-Chloro imide oxidises a few α -amino acids under various oxidant, substrate, acidity, and solvent compositions, including acetic acid.

The functional groups that are already present in amino acid molecules undergo changes as part of their chemistry [R1CH(NH2) COOH]. Due to the functional groups' high reactivity in lieu of the hydrocarbon chain's inertness, their undamaged hydrocarbon parts (R) have not been exposed to chemical reactions. The pH of the media affects how quickly amino acids dissociate. This equilibrium exists in highly alkaline or acidic media.



II Experimental

The Estimation of 2,6-dichloro-quinone-4-chloro-imide (DCQCI):

Both the reaction mixture aliquots and the 2,6-dichloro-quinone-4-chloro-imide solution are well estimated iodometrically. An iodine flask holding 5 ml of 5N sulphuric acid and 5 ml of 5% potassium iodide solution is filled with 5.0 ml of 2,6-dichloroquinone-4-chloro-imide solution in a CO2 environment, and it is then left in the dark for three minutes. Subsequently, the mixture is titrated using a burette containing standard sodium thiosulphate until the starch Then the solution is titrated against standard sodium thiosulphate taken in a burette to the disappearance of starch iodine blue endpoint.

III Result and Discussion

1. Effect of varying concentration of oxidant in DL- Alanine and Phenyl Alanine

In the kinetics of oxidation of DL-alanine and Phenyl Alanine by 2,6-dichloroquinone-4-chloro-imide, the reaction is found to be first order in oxidising agent. Plot of log(a-x) vs time is linear. It is also confirmed by constancy of first order rate constants under varying concentrations of oxidant. The rate constants of Alanine and Phenyl alanine are given in Table -1

Table -1

[Substrate] = 0.1 M [NaOAc] = 0.4M

AcOH – H_2O = 10% - 90% (v/v) Temp = 40^0C

Variant	**[Variant] x 10^4 M**	**Rate constants**	
		Dl-Alanine k_1 x 10^4 min^{-1}	**DL-Phenyl Alanine k_1 x 10^4 min^{-1}**
DCQCI	2.5	6.6	10.0
	5.0	6.8	10.5
	10.0	6.4	10.8
	20.0	6.4	9.7

Effect of variation of substrate concentration:

The kinetics of oxidation of DL-alanine by 2,6-dichloroquinone-4-chloro-imide is found to have direct dependence on substrate. The first order rate constants increase with increasing the concentration of substrate. Plot of log $k_1$vs log [S] is linear withunit slope indicating first order dependence on substrate.The rate constants data of Alanine and Phenyl alanine is given in Table-2.

Table -2

[Oxidant] = 5.0 x 10^4 M [NaOAc] = 0.4M

AcOH – H_2O = 10% - 90% (v/v) Temp = 40^0C

Variant	**[Variant] x 10^4 M**	**Rate constants**	
		Dl-Alanine k_1 x 10^4 min^{-1}	**DL-Phenyl Alanine k_1 x 10^4 min^{-1}**
Substrate	0.1	3.5	10.0
	0.2	6.6	18.1
	0.4	17.7	24.2
	0.6	19.7	-

Effect of varying pH on reaction rate:

The change in the kinetic rate of reaction with change in pH by varying the concentration of NaOAc is observed in present investigation. The first order rate constants increase with increase in pH of the medium. The plot of log k_1 vs log [NaOAc] is linear and yields a fractional slope. The kinetic data of Alanine and Phenyl alanine is given in Table-3.

Table -3

[Oxidant] = 5.0 x 10^4 M [Substrate] = 0.1M

AcOH – H_2O = 10% - 90% (v/v) Temp = 40^0C

Variant	**[Variant] x 10^4 M**	**Rate constants**	
		Dl-Alanine k_1 x 10^4 min^{-1}	**DL-Phenyl Alanine k_1 x 10^4 min^{-1}**
NaOAc	0.2	3.75	10.0
	0.4	6.6	16.2
	0.6	9.5	22.2

Kinetic data of Leucine and Isoleucine:

1. Effect of varying concentration of oxidant:

By varying initial concentrations of oxidant, the rate constants are almost constant indicating first order dependence with respect to disappearance of oxidant. The constancy in the first order rate constants can be observed from the results in Table-5. The plots of log(a-x) vs time are linear indicating first order dependence in oxidising agent for both the substrates valine and isoleucine.

Table -5

[Substrate] = 0.1 M [NaOAc] = 0.4M

AcOH – H_2O = 10% - 90% (v/v) Temp = 40^0C

Variant	**[Variant] x 10^4 M**	**Rate constants**	
		Leucine k_1 x 10^4 min^{-1}	**Isoleucine k_1 x 10^4 min^{-1}**
DCQCI	2.5	18.4	10.0
	5.0	18.7	12.5
	10.0	19.0	10.8
	20.0	-	9.7

2. Effect of variation of [substrate] on reaction rate:

The kinetics of oxidation of these substrates isfound to have first order dependence on substrate concentration. Plots of log k_1 vs log [S] are linear withnear unit slopes. The kinetic data is given in Table-6.

Table -6

[DCQCI]= 5.0 x 10^{-4} M [NaOAc] = 0.4M

AcOH – H_2O = 10% - 90% (v/v) Temp= 40^0C

Variant	**[Variant] M**	**Rate Constants**	
		Leucine k_1 x 10^4 min^{-1}	**Isoleucine k_1 x 10^4 min^{-1}**
Substrate	0.025	5.0	4.2
	0.05	12.7	7.5
	0.1	18.7	12.5

Effect of varying sodium acetate concentration:

The kinetic rate increases with increase in the concentration of sodium acetate. The plots of log k_1 vs log [NaOAc] are linear and yield fractional slopes. The kinetic data is given in Table 7.

Table - 7

[DCQCI] = 5.0 x 10^{-4} M [Substrate] = 0.1 M

AcOH – H_2O = 10% - 90%(v/v) Temp = 40^0C

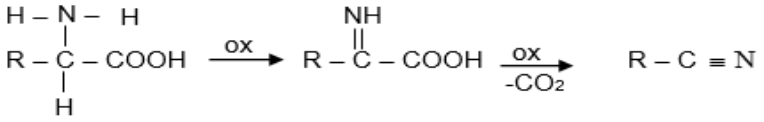
Variant	[Variant] x 10^4 M	Rate Constants	
		Leucine k_1 x 10^4 min^{-1}	Isoleucine k_1 x 10^4 min^{-1}
(NaOAc)	0.1	-	7.0
	0.2	13.0	10.0
	0.4	18.7	12.0
	0.8	40.0	24.0

Ionic Mechanism:

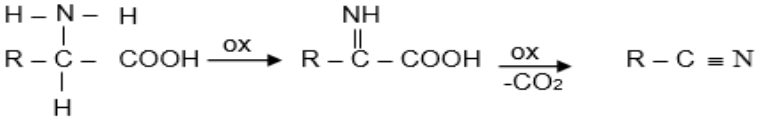
There are two possible paths involving ionic mechanism.

i) Transfer of α-hydrogen and

ii) Synchronous oxidative decarboxylation by the cleavage of $C_1 – C_2$ bond.

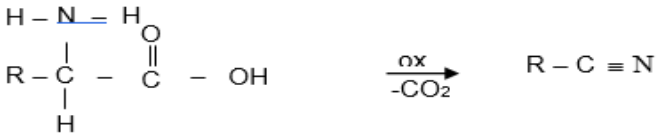


b) Rate determining transfer of H^+ (proton transfer)

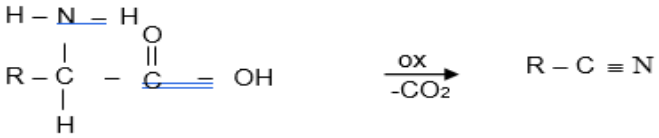


ii)

a) Oxidation being more advanced than decarboxylation in rate determining step.



b) Decarboxylation being more advanced than oxidation in rate determing step.



In general for oxidants with reasonable redox potential the $C_1 – C_2$ bond cleavage is reported to be operative under acid conditions.It appears that the predominant product is nitrile under these conditions. The following rate law and mechanistic pathway are postulated.

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