OXIDATION OF GLYCINE BY Cr (Chromium) (VI) OXIDANTS IN DMF- H2O MEDIUM: A COMPARATIVE STUDY

Chemistry

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ABSTRACT

A comparative study of oxidation of glycine by different Cr (VI) oxidants [PCC, PDC, and QDC] has been studied in DMF-H2O medium in the presence of perchloric acid spectrophotometrically. The reactions are found first order with respect to all three oxidants, [H+], and [glycine]. Michaelis-Menten type kinetics was observed. The reaction rate increased with increasing volume percentage of DMF in reaction mixture. The reaction was studied at different temperature [298-323K] & the activation parameters were computed. The oxidation product was identified as Cr (III) and formaldehyde. The oxidation rate order was found with respect to different oxidants are: PDC > PCC > QDC.

KEYWORDS:

Kinetics, Oxidation, glycine, PCC, PDC, QDC.

1. INTRODUCTION

Oxidation of α-amino acids is of great importance both from chemical point of view and its bearing on the mechanism of amino acids metabolism. The study of amino acids is one of the most exciting fields of organic chemistry. They play a significant role in a number of metabolic reactions like biosynthesis of polypeptide, protein and nucleotides. Different Cr (VI) oxidants are used for the oxidation of amino acids.

Hiran et al. reported the oxidation of glycine [1] and tyrosine[2] by PBC in aqueous acetic acid in presence of perchloric acid. Kinetics of oxidation of Alanine[3], L-Cysteine[4], Methonine[5], by PCC. Karim and Mohant [6-10] studied the oxidation of several amino acids by QDC in DMF in presence aqueous sulfuric acid. Dangarh & Thakur reported the kinetic and mechanistic study of oxidative transformation of some alpha-amino acid [11-13] by PDC in aquo-acetic acid medium. There seems to be no reports on the comparative study of oxidation of glycine by different Cr (VI) oxidants.

2. MATERIALS AND METHODS

Oxidants Pyridiniumchlorochromate [14], Pyridiniumdichromate [15] Quinoliniumdichromate[16] were prepared by the method describe in the literature. The purity of the oxidants was checked by spectral analysis. glycine (A.R.grade) was 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 313K in 2M HClO4 under the condition [glycine] >> [oxidants], in the solvent system of 30-70 % (v/v) DMF-H2O. The progress of the reaction was followed by measuring the absorbance of oxidants at 354 nm in one cm cell placed in the thermostatted compartment of Systronics VISISCAN -167 spectrophotometer.
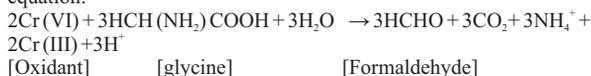
The kinetics run were followed for more than 60-70% completion of the reaction and good first order kinetics were observed.

3. RESULTS AND DISCUSSION

3.1 Stoichiometry and product analysis

To determine the stoichiometry of a reaction a known slight excess of oxidant was added to a known amount of Glycine by keeping all other condition of reaction is constant and after some hours the residual of oxidant was determined spectrophotometrically at 354nm. The product of oxidation was corresponding aldehyde i.e. formaldehyde and was identified by its 2, 4-dinitro phenyl hydrazine derivative. The stoichiometry of the reaction was found to correspond to the equation:

$2Cr(VI) + 3HCH(NH_2)COOH + 3H_2O \rightarrow 3HCHO + 3CO_2 + 3NH_4^+ + 2Cr(III) + 3H^+$

[Oxidant]   [glycine]   [Formaldehyde]

3.2 Effect of Oxidants

When substrate was in excess, the rate of which oxidants disappears

followed the first –order kinetics. The first order rate constants are independent of the initial concentration of the oxidants when varied in the range (0.5 – 4.0) X 10^{-3} mol/dm-3 at 313K. Among three Cr (VI) oxidants Glycine oxidized faster with PDC.

3.3 Effect of Substrate

The effect of glycine concentration on the reaction rate studied at constant [Oxidants], [HClO4], temperature and DMF% [table 1]. The reaction rate increases with increasing of glycine concentration. A plot of log k_{obs} against log [subs] gives a straight line [fig-1] with respect to all the three oxidants. This revealed that the rate of oxidation is first order with respect to substrate. It has been found that the plot of (1/k) versus (1/ [subs]) is straight line with small intercept, indicates that Michaelis- Menten type kinetics is observed. The reaction proceeds through the formation of a complex between the oxidant and glycine. The variation of the rate of oxidation of Glycine with oxidants can be expresses as

d [oxidants] / dt = k [glycine] [oxidants] / K_M + [glycine]

3.4 Effect of H+ ion

In order to study the effect of [H+] on the rate of reaction, kinetic runs were carried out keeping the concentrations of all other reactants are constant and varying the [H+] with HClO4. From [table 1], it is clear 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+], linear plots with a positive slope was obtained and indicate that first order reaction with respect to the hydrogen ion concentration. Under the present experimental conditions (1-3 mol dm-3 [H+]), the protonated chromium (VI) is presumed to be the reactive species since the rate increases with increase in [H+].

3.5 Effect of solvent composition

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 1], suggesting that a low dielectric medium favors the oxidation. A plot of log k against 1/D is linear with a positive slope for glycine under study. This indicates an ion-dipole type of interaction in the rate –determining step.

3.6 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 increases with increasing temperature [table 2]. From the Arrhenius plot of $\log k_{obs}$ versus 1/T[fig-2]**,** activation energy and other thermodynamic parameters was 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. The complex formation is proved by the plot of $1/k_{obs}$ against 1/ [glycine]. It has been pointed out that if entropy of activation is negative and small the reaction will be slow.

4   CONCLUSION

At room temperature the reaction between glycine and oxidants are very slow in the low perchloric acid concentration in DMF-water medium. The oxidation of glycine by oxidants are first order with respect to [oxidants], [glycine] and [$HClO_4$].The Zwitter ionic form of glycine is oxidized to give aldehyde. 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. Among three Cr (VI) oxidants glycine oxidized faster with PDC. The reactivity of oxidation of glycine towards three oxidants was found to be PDC > PCC > QDC.

TABLE NO. 1 Effect of [Substrate], [H$^+$] and Solvent [Oxidants]=1 x 10^{-3}M   T = 313 K

[Subs] x10^{-2} M	[HClO$_4$] x M	DMF % v/v	k$_{obs}$ X 10^5 Sec^{-1}		
			PCC	PDC	QDC
1	2	30	21.72	26.29	21.18
1.5	2	30	24.83	29.05	27.78
2	2	30	25.75	32.16	36.46
2.5	2	30	28.21	34.62	41.22
3	2	30	33.35	35.81	44.14
1	1	30	5.14	7.25	5.94
1	1.5	30	14.50	19.99	14.24
1	2	30	21.72	26.29	21.18
1	2.5	30	42.87	46.13	33.70
1	3	30	55.46	56.11	37.80
1	2	10	11.47	11.51	14.39
1	2	20	16.88	17.08	18.00
1	2	30	21.72	26.29	21.18
1	2	40	32.51	47.40	52.43
1	2	50	50.32	69.16	69.12

TABLE NO. 2 [Glycine] = 1 X 10^{-2} M   [HClO$_4$] = 2M [Oxidants] = 1 X 10^{-3}M   [DMF]=30% v/v

| Temperature In K	k$_{obs}$ X 10^5 Sec^{-1}		
	PCC	PDC	QDC
298	4.22	10.09	6.56
303	7.98	16.54	10.40
308	17.96	20.22	18.61
313	21.72	26.29	21.18
318	35.00	41.53	41.79
323	46.21	69.74	64.67

TABLE NO. 3 THERMODYNAMIC PARAMETERS [Substrate] = 1 X 10^{-2} M [HClO$_4$] = 2M [Oxidant] = 1 X 10^{-3}M [DMF]=30% v/v T=313K

Glycine with	log A	ΔE$_a^{\#}$ kJ mol^{-1}	ΔS$^{\#}$ J mol^{-1}K^{-1}	ΔH$^{\#}$ kJ mol^{-1}	ΔG$^{\#}$ kJ mol^{-1}
PCC	10.66	75.66	-44.75	73.06	87.07
PDC	7.69	57.39	-101.51	54.79	86.56
QDC	9.95	71.46	-58.37	68.86	87.13

Fig-1 Variation of rate with Glycine concentration by different oxidants
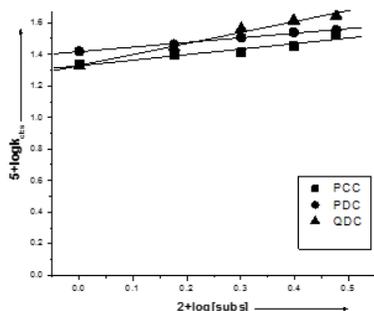
Fig-2 Variation of rate with Temperature by different oxidants
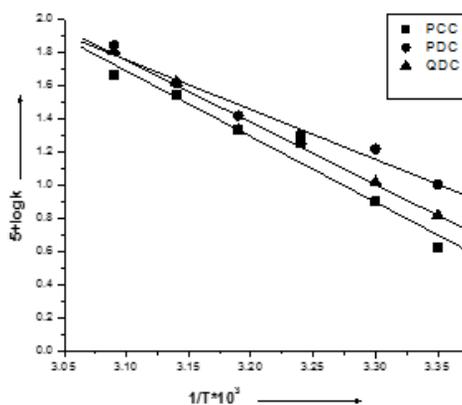
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