Oxidative Cleavage of Glycine with N-Chlorobenzimidazole in Aqueous Acetic Acid Medium

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Abstract: *The oxidative cleavage of glycine with N-chlorobenzimidazole (CBI) has been studied in aqueous acetic acid medium. The rate shows first order dependence each on [CBI] and [glycine] and inverse first order on [H⁺]. The rate of the oxidation increases with decrease in dielectric constant of solvent medium indicating ion-dipole interaction. Polymerization was not observed when acrylonitrile is added to the reaction mixture. The kinetic runs were carried out at four different temperatures and thermodynamic parameters have been evaluated. Addition of benzimidazole retards the rate. The rate of reaction is not influenced by the addition of electrolyte like sodium perchlorate. A mechanism in consistent with the kinetic data has been proposed.*
Keywords*: Kinetics, Cleavage, Iodometry, N-chlorobenzimidazole, glycine.*

I.   Introduction

The chemistry of N- halo compounds has evoked considerable interest, as they are sources of halonium cations which act as oxidizing agents. Kinetics of oxidation of organic compounds by N-halo compounds have received considerable attention [1-8]. N-chloro(1-chloro) benzimidazole (CBI) is gaining importance as a mild oxidant and utilized for the oxidation of various organic substrates [9-12].

Oxidation of glycine by various N-halo oxidants such as N-bromoanisamide [13], N-bromophthalimide [14], N-bromosuccinimide [15], N-chloropyrazinamide [16] and   N-chlorosaccharin [17] has been reported. An extensive literature reveals that no systematic kinetic work hitherto has been done on the oxidation of glycine using CBI. In the present investigation, the reaction kinetics of glycine with CBI has been studied in aqueous acetic acid medium.

II.   Materials and methods

CBI was prepared and purified by literature method [18]. Acetic acid was refluxed over chromic oxide for 6 hours and the fraction distilling at 118°C was collected and used. Glycine, perchloric acid and all other reagents used were of AR grade.

Kinetic measurements

All kinetic measurements were made under pseudo first order conditions by keeping large excess of [glycine] over oxidant [CBI]. Mixtures containing requisite amounts of solutions of glycine, perchloric acid and solvents were equilibrated at 308K. A measured amount of pre-equilibrated (308K) standard solution of CBI was added to this mixture and the kinetics of the reaction was followed iodometrically by withdrawing aliquots of the reaction mixture at regular time intervals. To maintain the desired temperature (within $\pm$ 0.1°C) the reaction mixture was kept in a thermostated water bath. Duplicate kinetic runs showed that the rate constants were reproducible within $\pm$ 3%.

The plot of log [CBI] Vs time was found to be linear (r>0.99) indicating the first order dependence of the reaction rate and from the slopes of such plots pseudo first order rate constants were evaluated. Preliminary experiments showed that the reaction were not sensitive to change in ionic strength, hence no attempt was made to keep it constant.

Stoichiometry and product anlaysis

The stoichiometry of the reaction was determined by equilibrating mixing various ratios of [CBI] *versus* [glycine] at 308K for 48 hours under kinetic conditions. Estimation of unconsumed CBI revealed that 1 mole of CBI was required to oxidize 1 mole of the glycine.

Product analysis shows that formaldehyde was formed as the major product which was confirmed by spectral studies and TLC. The liberated CO_2 was detected by lime water test [19] and ammonia was confirmed by Nessler's reagent [20].

III. Results and discussion

The oxidations of glycine were carried out in 70% acetic acid - 30% water medium (v/v) in presence of a large excess of substrate and perchloric acid.

The oxidation kinetics of glycine with CBI has the following salient features.

Effect of oxidant variation:

The kinetics of oxidation of glycine has been studied at various initial concentration of the CBI and at fixed concentration of other reactants (Table-1). The plot of log [CBI] *versus* time plots yields a straight line indicating a first order dependence of rate on oxidant.

Table-1 Effect of [CBI], [glycine], [H^+] and % CH_3COOH on the reaction rate at 308K

[CBI] x 10^{-3} mol.dm^{-3}	[glycine]x 10^{-2} mol.dm^{-3}	[HClO$_4$]x 10^{-2} mol.dm^{-3}	CH_3COOH %	k_{obs} x 10^{-3} s^{-1}
3.0	5.0	5.0	70	1.48
4.0	5.0	5.0	70	1.59
5.0	5.0	5.0	70	1.67
6.0	5.0	5.0	70	1.81
7.0	5.0	5.0	70	1.90
5.0	3.0	5.0	70	1.03
5.0	4.0	5.0	70	1.40
5.0	5.0	5.0	70	1.67
5.0	6.0	5.0	70	2.02
5.0	7.0	5.0	70	2.43
5.0	5.0	2.0	70	5.02
5.0	5.0	3.0	70	3.83
5.0	5.0	4.0	70	2.70
5.0	5.0	5.0	70	1.67
5.0	5.0	6.0	70	1.03
5.0	5.0	5.0	50	1.13
5.0	5.0	5.0	60	1.43
5.0	5.0	5.0	70	1.67
5.0	5.0	5.0	80	2.11
5.0	5.0	5.0	90	2.66

Effect of substrate variation:

The rate of reaction increases linearly with an increase in the concentration of glycine (Table-1). The plot of log k_{obs} *versus* log [substrate] gave a straight line passing through origin indicating a first order dependence on substrate.

Effect of [H^+] variation:

The dependence of the reaction rate on the concentration of H^+ was studied at constant concentration of oxidant, substrate and other reagents and varying the initial concentration of HClO$_4$. The k_{obs} values decrease with increase in the HClO$_4$ concentration (Table-1) and the order was found be inverse first.

Effect of acetic acid variation:

The effect of dielectric constant of reaction medium was studied by adding acetic acid in the reaction medium at constant concentration of other reactants. The rate of reaction increases with increasing acetic acid content in the solvent medium (Table-1).

Effect of temperature variation:

The reaction has been studied in the temperature range 308-323 K and the results are recorded (Table-2). Using Arrhenius equation, the energy of activation for the substrate has been calculated and this value was subsequently utilized in computing various other thermodynamic parameters. The results are presented in Table-3.

Table-2 Effect of temperature on the reaction rate

[CBI] = 5.0 x 10^{-3} mol.dm^{-3} [glycine]   = 5.0 x 10^{-2} mol.dm^{-3}
Solvent = 70% CH_3COOH [$HClO_4$]   = 5.0 x 10^{-2} mol.dm^{-3}

Temperature (K)	k_{obs} x 10^{-3} s^{-1}
308	1.67
313	2.14
318	3.09
323	4.65

Table-3 Activation parameters for the oxidation of glycine

Thermodynamic parameters	
E_a kJ mol^{-1}	56.70
ΔH^* kJ mol^{-1}	54.13
ΔG^* kJ mol^{-1}	151.15
ΔS^* JK^{-1} mol^{-1}	-49.40
ln A	1.6846

The effect of one of the products of the oxidation has been investigated by adding various [benzimidazole] keeping all other reactant concentration as constant. There is a slight decrease in reactivity with the increase in the initially added benzimidazole (BI). The retardation of rate on the addition of benzimidazole suggests a pre-equilibrium step that involves a process in which benzimidazole is one of the products.

Mechanism and rate law

The decrease in the reaction rate with increasing [$HClO_4$] and retardation of reaction rate with added benzimidazole suggest HOCl being the most probable oxidizing species.
The following mechanism has been proposed

Rate law is given by

(S- glycine, BI - benzimidazole)

IV. Conclusion

The kinetic study clearly demonstrates the formation of followed by its yield the products in the oxidative cleavage of glycine with N-chlorobenzimidazole in aqueous acetic acid medium. The rate law shows first order dependence each on [CBI] and [glycine] and inverse first order on [H$^+$]. The mechanism proposed for this oxidation kinetics is in accordance with the observed kinetic facts.

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