Kinetics and Mechanism of Hydrolysis of Synthesied 4-Bromo Aniline Phosphoro Mono-Amidate via Conjugate Acid Species (Barium Salt)

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The study of kinetics of hydrolysis of 4-bromo aniline phsophoro mono-amidate, which is a substituted ester of orthophosphoric acid has been carried out in acid concentration ranging from 1.0–6.0 M of HCl at 70°C. The solvent used is 10% aqueous (v/v) dioxanes water mixture. The maximum rate of hydrolysis was observed at 4.0 M HCl; later at higher acid region the rates decreased due to water activity. The various concepts such as Hammett acidity.function, Zucker-Hammett hypothesis, Bunnett parameter, are an evidence to predict biomolecularity of the reaction. The Arrhenius parameters, *i.e.*, energy of activation, frequency factor and entropy of activation are falling in the range of bimolecularity of the reaction. The effects of ionic strength were used to determine probable reaction path.

INTRODUCTION

The present study on the kinetics of hydrolysis of C—N—P linkage compounds[1] have been carried out on derivatives of orhophosphoric acid. It comprises a group of mono, di and tri esters. The kinetic runs were set up for obtaining the first order rate coefficient, with the concentration of mono amidate maintained at 5.0×10^{-4} M unless otherwise specified. The rate of hydrolysis increased up to 4.0 M and then decreased, indicating the participation of conjugate acid species.[2] The pH log rate profile of mono benzyl phosphate[3, 4] at 75.6°C has been reported and found to hydrolyse relatively 40 times as fast as the mono anion of dibenzyl phosphate. Molecularity of solvent does not undergo much change in its concentration.[5] The study of order of reaction, the effect of substrate concentration is also significant; keeping this aim in view a series of kinetic runs were set up using varying concentrations of substrate, in which hydrolysis is mainly governed by first order rate constant and independent of initial concentration. It is in accordance with the nature of acid catalysis.

The effect of solvent on the rate of reaction depends upon the changes of free energy of the transitional state relative to the initial state. Various equations and theories in such studies have been proposed[6, 7]. According to the qualitative theory[8] changes in the reaction rate due to the changes in the nature of transitional

state formed out of the reactant. Bimolecular hydrolysis more commonly involves P—N bond fission in allyl esters. Abnormal catalysis has been observed due to electron repelling part of allyl esters.

EXPERIMENTAL

Synthesis of phosphoro mono-amidate is carried out by phosphorylation[9] method using $POCl_3$ in the present study. The characterization of the synthesised compound was accomplished with the aid of elemental analysis and IR analysis. The study of reaction rates was determined by using Allen's modified method[10]. All the chemicals used were either AR quality or Merck extra pure quality.

The kinetic study[11] of the hydrolysis of 4-bromo aniline phosphoro mono-amidate has been set up for varying ionic strengths 1.0–6.0 M HCl at 70°C. Rate coefficient measured by direct determination of inorganic phosphate formed during the course of hydrolysis is shown in Table-1.

TABLE-1
RATE OF HYDROLYSIS OF 4-BROMO ANILINE PHOSPHORO MONO-AMIDATE
AT CONSTANT IONIC STRENGTH AT 70°C

Ionic strength (μ)	HCl (M)	KCl (M)	$K_e \times 10^{-3}$ (min^{-1})
0.0	0.40	0.60	17.76
	0.60	0.40	20.14
	0.90	0.20	20.74
	1.00	0.00	21.31
2.0	1.20	0.80	22.95
	1.40	0.60	23.47
	1.60	0.40	24.15
	2.00	0.00	24.90
3.0	1.50	1.50	25.29
	2.20	0.80	29.55
	2.80	0.20	32.24
	3.00	0.00	35.00

Fig. 1 states the relation between rate constant and acid molarity. Three linear curves for different ionic strength are obtained (which make positive slope $4 + \log K_e = 1.57, 1.61, 171$) with the rate axis and do not pass through the origin indicating participation of neutral species. Each line represents acid catalysed hydrolysis at the ionic strength which can be represented by

$$K_e = K_{H^+} C_{H^+}$$

where K_e and K_{H^+} are total acid catalysis rate and specific acid catalysis rate depends on ionic strength. The values of intercept and slope plotted between log of rate constant and ionic strength slope (b'_{H^+} and b'_N) relationship may be represented as acid rate.

$$K_{H^+} = K_{H_0^+} \exp b'_{H^+} \cdot \mu$$

or
$$\log K_{H^+} = \log K_{H_0^+} b'_{H^+} \cdot \mu$$

The neutral rates in hydrolysis have been represented as,

$$K_N = K_{N_0} \exp b_N \cdot \mu$$

or
$$\log K_n = \log K_{N_0} + b'_N \cdot \mu$$

The above equations were used to estimate both acid and neutral rates in acid region up to 4.0 M. The lowering of estimated rates for 5.0–6.0 M is explained by considering water activity[12] as an additional parameter.

$$K_{H^+} C_{H^+} (aH_2O)_n = K_{H_0^+} C_{H^+} \exp b'_{H^+} \cdot \mu(aH_2O)_n$$

where $(aH_2O)_n$ is water activity and n is an integer.
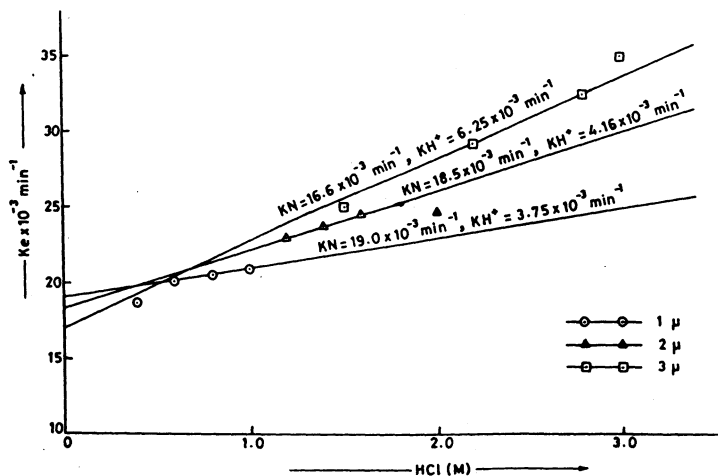

Fig. 1. Constant ionic strength hydrolysis of 4-bromoaniline phosphoro-mono-amidate (barium salt) at 70°C

or $\log (K_{H^+} \cdot C_{H^+}) + n \log (aH_2O) = \log(K_{H_0^+} \cdot C_{H^+}) + (b'_{H^+} \cdot \mu) + n \log H_2O$

$$K_N(aH_2O)_n = K_{N_0} \exp b'_N \cdot \mu(aH_2O)_n$$

Finally we get

$$K_e = K_{H^+} \cdot C_{H^+} \cdot (aH_2O)_n + K_N(aH_2O)_n$$

The effect of solvent on the rate of reaction was observed by varied concentrations of dioxane-water mixture (10%, 20%, 30%). The data reveal that with the increase in the dioxane content, the rate also significantly increases. The concentration effect was observed in varying concentrations of substrate (0.001, 0.0005, 0.00025) performed at 4.0 M HCl where hydrolysis is governed by first order rate constant and independent of initial concentration.

In order to determine molecularity, whether it is uni or bimolecular, the concept of Zucker-Hammett hypothesis[13] ($4 + \log K_e$ vs. $\log C_{H^+}$, 1.20) Bunnett[14] ($w = 10$, $w^* = 4.0$) and Bunnett-Olsen parameter[15] ($\phi = 1.66$), Arrhenius parameter[16], i.e., energy of activation $E = 3.64$ kcal/mol, frequency factor $A = 11.04$, entropy of activation $\Delta S^{\#} = -60.54$ e.u, support the bimolecular reaction path.

RESULTS AND DISCUSSION

The study of kinetics of hydrolysis of 4-bromo aniline phosphoro mono-amidate has been carried out using acid and buffer solution in aqueous medium 10% dioxane-water mixture (v/v) at 70°C, the concentration is 5×10^{-4} M otherwise specified. The good pseduo first order rate coefficients have been obtained for all the kinetic runs. Rate of the reaction is dependent on the concentration of substrate, water taking part as a nucleophile without change in the concentration.

The substrate concentration effect reveals that the rate is independent of the initial concentration of phosphoroamidate; therefore the kinetics involved is that of first order reaction. The solvent effect reveals that with the increase in the dioxane content the rate constant also increases which is significant. It is evident that this increase is not in accordance with qualitative theory. Hence this deviation may be attributed to the better proton donating property of acid dioxane medium.

The ionic strength depicts that the acid catalysed hydrolysis is subjected to the positive effect of ionic strength and the neutral species is also subjected to the negative effect of ionic strength. The value obtained by using the concept of molecularity favours the bimolecular nature of hydrolysis and dependence of acid catalysis rate on water activity (H_2O, involved as proton transfer agent in rate determined step). Further Arrhenius plot is drawn between log rate constant and reciprocal of absolute temperature; linearity of the curve shows uniformity of the reaction. The value evaluated for E. kcal/mol, A, sec^{-1}, comparative higher negative value of $\Delta S^{\#}$ e.u indicates that the reaction is bimolecular.

ACKNOWLEDGEMENTS

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