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Kinetics and Mechanism of Hydrolysis of Mono-*p*-Butyl Aniline Phosphate in Acid Media

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Investigation of *p*-butyl aniline phosphate was carried out by using "Allen's" modified method of colorimetry, in aqueous medium from 0.1 to 7.0 mol dm^{-3} HCl at 98°C. Ionic strength data exhibit different contribution of neutral species and presence of acid catalysis. Theoretical rates estimated from 2nd empirical term of Debye-Hückel equation have been found in close agreement with experimental rates. Ionic strength, temperature, solvent and concentration of kinetic studies are provided to identify the reactive species and molecularity. Molecularity and bond fission are also discussed in terms of Zücker-Hammett hypothesis, Hammett acidity functions, Bunnett and Bunnett-Olsen parameters and isokinetic relationship.

INTRODUCTION

Phosphates having C—N—P linkages are of great importance. They are used as pesticides, insecticides,[1] fire retardants,[2] plasticizers[3], synthetic lubricants[4] etc. The undertaken compound, *i.e.*, mono-*p*-butyl aniline phosphate, was chosen for the kinetic study as this compound is reactive via different species depending upon the experimental conditions.

EXPERIMENTAL

Mono-*p*-butyl aniline phosphate was prepared by the method of $POCl_3$[5, 6] by phosphorylation of *p*-butyl aniline in the mixture of pyridine and benzene. The reactions were carried out at 98°C employing 5.0×10^{-4} mol dm^{-3} solution of mono ester which was subsequently followed by the Allens[6] modified method of colorimetric estimation of organic phosphate in aqueous media maintaining constant ionic strength by means of HCl and NaCl. All the chemicals used were of BDH quality.

RESULTS AND DISCUSSION

The rate of hydrolysis of mono-*p*-butyl aniline phosphate was studied in HCl (0.1–7.0 mol dm^{-3} HCl) at 98°C. In Table-1 the pseudo-first order rate constants are summarised, from which it is quite clear that rate of reaction increases up to 4.0 mol dm^{-3} but further increase in acid molarity really decreases the rate as it can be attributed to the complete conversion of the ester (basic) molecule into their respective conjugate acid species with the lowering of concentration of a nucleophile (water), which plays its role in rate determining step of bimolecular hydrolytic reaction.

In order to determine whether or not there is effect of ionic strength or presence of acid catalysis, kinetic runs were made at three different ionic strengths (1.0, 2.0 and 3.0 μ) which were maintained by adequate mixture of NaCl and HCl. Hydrolysis at each ionic strength is represented by a linear curve (figure not shown) that makes a positive slope. Since the $K_{H^{\oplus}}$ is slope increasing with increase in ionic strength, acid catalysis is subjected to positive effect of ionic strength.

TABLE-1

ESTIMATED AND EXPERIMENTAL DATA FOR THE HYDROLYSIS OF MONO-*p*-BUTYL ANILINE PHOSPHATE AT 98°C

HCl (mol dm^{-3})	$K_N \times 10^3$ (min^{-1})	$K_{H^{\oplus}}C_{H^{\oplus}} \times 10^3$ (min^{-1})	$Ke \times 10^3$ min^{-1} Estm	$-\log {}^{a}H_2O$ water activity	$Ke \times 10^3$ (min^{-1}) Estm	$Ke \times 10^3$ (min^{-1}) Expt.	
0.1	2.54	0.69	3.15		3.15	3.45	
0.2	2.62	1.41	4.05		4.05	4.25	
0.5	2.95	3.64	6.59		6.59	6.24	
1.0	3.55	7.67	11.22		11.22	12.34	
2.0	5.13	17.02	22.15		22.15	22.34	
3.0	7.41	28.32	35.73		35.73	35.45	53.24[a] 54.65[b]
4.0	10.78	41.88	52.59		52.59	52.98	
5.0	15.49	58.07	73.56	$(0.155)^2$	44.24	41.45	
6.0	22.38	77.29	19.68	$(0.211)^4$	33.58	30.95	
7.0	32.35	100.20	132..38	$(0.279)^4$	23.44	20.13	

Note: a = 10% dioxane, b = 15% dioxane

From the study of ionic strength effect, the total rates contributed by conjugate acid and neutral forms can be calculated by the following 2nd empirical term of Debye-Hückel[7] equation

$$Ke = K_{H^{\oplus}}C_{H^{\oplus}} + K_N \qquad (1)$$

In the above equation the terms Ke, $K_{H^{\oplus}}$ K_N are observed rate constants, the specific acid catalysed and specific neutral rates at that ionic strength respectively.

The sum of neutral and acid rates agrees well with the experimentally observed rates (Table-1) up to 4.0 mol dm^{-3} HCl. The lowering in rates in 5.0, 6.0 and 7.0 mol dm^{-3} HCl can be explained by considering water activity[7–9] as an additional parameter represented as

$$Ke = K_{H^{\oplus}}C_{H^{\oplus}}(^{a}H_2O)^n + K_N(^{a}H_2O)^n \qquad (2)$$

where $^{a}H_2O$ is water activity and n is an integer. The revised estimated rates now agree well with the experimentally observed rates (Table-1). It is clear from the above result that mono-*p*-butyl aniline phosphate in acid solution occurs via both conjugate acid and neutral species and their rates are subjected to water activity.

Solvent effect (Table-1) shows a significant rise in rates, dioxane being a better proton donor than water, increases the concentration of conjugate acid species resulting in the increase in rates. Effect of solvent on the rate of hydrolysis may therefore be taken to indicate the formation of transition state in which charge is dispersed.

Arrhenius parameters[10] are determined for the hydrolysis at 3.0 and 5.0 mol dm^{-3} HCl (Table-2). The magnitude of Arrhenius parameter falls in the range of bimolecular reaction. Bimolecular nature of reaction is further supported by Hammett[11] (0.51), Zücker Hammett[12] (1.25) and Bunnett[13], $w = 7.60$, $w^* = 2.28$ plot (not shown).

TABLE-2

CALCULATED ARRHENIUS PARAMETERS

HCl mol dm^{-3}	Temp. t°C	$Ke \times 10^{-3}$ (min^{-1}) exp.	'E' (kcal/$mole^{-1}$)	A (sec^{-1})	$-\Delta s \neq$ e.u.
3.0	98	35.75	11.12	2.11×10^{-3}	45.77
3.0	80	22.90			
3.0	50	5.49			
5.0	98	41.45	10.25	7.53×10^{-2}	47.81
5.0	80	18.62			
5.0	50	4.16			

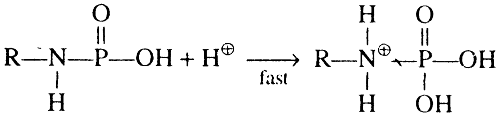
Bunnett Olsen parameter[14] ($\phi = 1.08$ which is greater than 0.58) suggests that water is involved as a proton transfer agent in the rate determining step.

The effect of concentration of mono ester on the rate of hydrolysis also confirms the order of reaction to be on with respect to the monoester by reducing either half ($Ke = 52.28 \times 10^{-3}\ min^{-1}$) or double ($Ke = 52.98 \times 10^{-3}\ min^{-1}$) the normal concentration ($Ke = 52.98 \times 10^{-3}\ min^{-1}$) at 4.0 mol dm^{-3} HCl.

Comparative kinetic[15] data (not shown) also support the bimolecular nature of hydrolysis involving attack of water on phosphorus of the monoester.

On the basis of above evidences and discussions, the most tentative mechanistic routes may be formulated as:

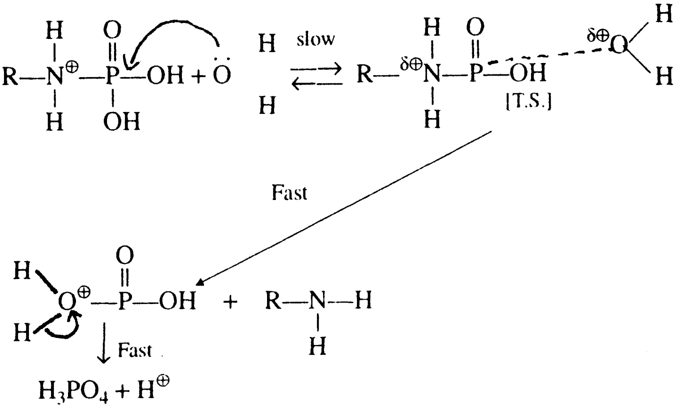
(a) Formation of conjugate acid species



$$R-\underset{H}{\underset{|}{\ddot{N}}}-\overset{O}{\overset{\|}{P}}-OH + H^{\oplus} \xrightarrow[\text{fast}]{} R-\underset{H}{\underset{|}{\overset{H}{\overset{|}{N^{\oplus}}}}}-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-OH$$

Neutral species Conjugate acid species

(b) Bimolecular nucleophilic attack of water on phosphorus via conjugate acid species S_N2 (P)



$[R = C_4H_9—C_6H_5]$

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