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

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Investigation of mono-*p*-sulphonic acid 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 second empirical term of Debye-Hückel equation have been found in close agreement with experimental rates. The effects of ionic strength, temperature, solvent and concentration are provided to identify the reactive species and molecularity. Bimolecular behaviour has been decided by the Arrhenius parameters and by the analysis of molecularity data. The monoester involves P—N bond fission which is strengthened by comparative kinetic data.

INTRODUCTION

Phosphates having C—N—P linkages are of great importance. They are used as pesticides, insecticides[1], plasticizers[2], synthetic lubricants[3] etc. Keeping this in view the hydrolytic bond cleavages of mono-*p*-sulphonic acid phosphate have been investigated.

EXPERIMENTAL

Mono-*p*-sulphonic acid aniline phosphate was prepared by treating sulphanalic acid with $POCl_3$[4,5] in pyridine which is used as a solvent.

The reactions were carried out at 98°C employing 5.0×10^{-4} mol dm^{-3} solution of monoester which was subsequently followed by the Allen's[5] modified method of colorimetric estimation of inorganic phosphate in aqueous media maintaining constant ionic strength by means of HCl and NaCl. All the chemicals were used of BDH quality.

RESULT AND DISCUSSION

The rate of hydrolysis of mono-*p*-sulphonic acid aniline phosphate was studied in HCl (0.1 to 7.0 mol dm^{-3}) at 98°C. In Table-1 the pseudo-first order rate constants are summarised, from which it is quite clear that rate of hydrolysis increases up to 4.0 mol dm^{-3} but further increase in acid molarity decreases the rate as it can be attributed to the complete conversion of the ester 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 μ, 2.0 μ, 3.0 μ) which were maintained by adequate mixture of NaCl and HCl. Hydrolysis of each ionic strength is denoted by a linear curve that makes a positive slope with the acid axis, indicating the presence of acid catalysis. Since the slopes ($K_{H^\oplus}$ 6.0×10^{-3}, 6.07×10^{-3} and 6.60 mol^{-1} min^{-1} 1) for 1.0, 2.0 and 3.0 μ respectively increase with increase in ionic strength, three curves make intercepts on the rate axis indicating the presence of side reaction of the neutral species.

From the study of ionic strength effect, the total rates contributed by conjugate acid and neutral forms can be calculated by the following second empirical term of Debye-Hückel[6] equation.

$$K_e = K_{H^\oplus} \cdot C_{H^\oplus} + K_N \qquad \text{(i)}$$

In the above equation the terms K_e, $K_{H^\oplus}$, K_n are observed rate constants, the specific neutral rates of that ionic strength respectively.

The sum of the 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[6-8] as an additional parameter represented as

$$K_e = K_{H^\oplus} \cdot C_{H^\oplus}(a_{H_2O})^n + K_N(a_{H_2O})^n \qquad \text{(ii)}$$

where a_{H_2O} is water activity and n is an integer. It is clear from the above result that mono-*p*-sulphonic acid aniline phosphate in acid solution occurs via both conjugate acid and neutral species and their rates are subjected to water activity.

Effect of solvent (Table-1) on the rate of hydrolysis may, therefore, be taken to indicate the formation of transition state in which charge is dispersed.

Arrhenius parameters[9] determined for the hydrolysis at 3.0 and 5.0 mol dm^{-3} HCl (Table-2). The magnitudes of Arrhenius parameters fall in the range of bimolecular reaction. Bimolecular nature of reaction is further supported by Zücker-Hammett[11] (1.0), Hammett (0.44) and Bünnett (W = 6.18, W* = 2.1) plot (Fig. not shown).

Bünnett-Olsen[10] parameter ($\phi = 1.2$ 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 monoester on the rate of hydrolysis also confirms the order of reaction to be on with respect to the monoester by reducing either half ($K_e = 35.061 \times 10^{-3}$ min^{-1}) or double ($K_e = 35.110 \times 10^{-3}$ min^{-1}) and the normal concentration ($K_e = 35.038 \times 10^{-3}$ min^{-1}) at 4.0 mol dm^{-3} HCl.

Comparative kinetic data also support the bimolecular nature of hydrolysis involving attack of water on phosphorus of the monoester.

TABLE-1
ESTIMATED AND EXPERIMENTAL DATA FOR THE HYDROLYSIS OF MONO-*p*-SULPHONIC ACID ANILINE PHOSPHATE AT 98°C

HCl (mol dm^{-3})	$K_N \times 10^3$ (min^{1})	$K_{H^+} \cdot C_{H^+} \times 10^3$ (min^{-1})	$K_e \times 10^3$ (min^{-1}) (Calc.)	$-\log a_{H_2O}$	$K_e \times 10^3$ (min^{-1}) (Calc.)	$K_e \times 10^3$ (min^{-1}) (Obs.)
0.1	3.817	0.564	4.381		4.381	3.352
0.2	3.876	1.133	5.010		5.010	4.117
0.5	4.061	1.668	5.729		5.724	5.215
1.0	4.388	8.842	10.230		10.230	8.912
2.0	5.123	12.919	17.262		17.262	17.748
3.0	5.982	26.205	24.901		24.901	26.300, 24.112^{a} 22.010^{b}
4.0	6.985	34.032	33.190		33.190	35.038, 34.110^{a} 33.812^{b}
5.0	8.156	34.032	42.188	(0.155)^{1}	31.870	31.280
6.0	9.523	42.432	51.955	(0.211)^{2}	25.574	21.760
7.0	11.119	51.428	62.547	(0.279)^{4}	15.054	16.590

a = 10% dioxane for 3.0 and 4.0 mol dm^{-3}
b = 20% dioxane for 3.0 and 4.0 mol dm^{-3}

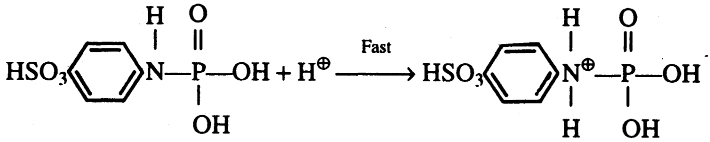
TABLE-2
CALCULATED ARRHENIUS PARAMETERS

HCl (mol dm^{-3})	Temp. (t°C)	$K_e \times 10^3$ (min^{-1})	E (K.Cal/mol)	A (Sec^{-1})	$-\Delta S^{\neq}$ e.u.
3.0	98	26.300	12.311	4.45	57.74
3.0	90	17.579			
3.0	80	11.220			
5.0	98	31.280	12.767	5.80	57.40
5.0	90	20.417			
5.0	80	13.182			

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

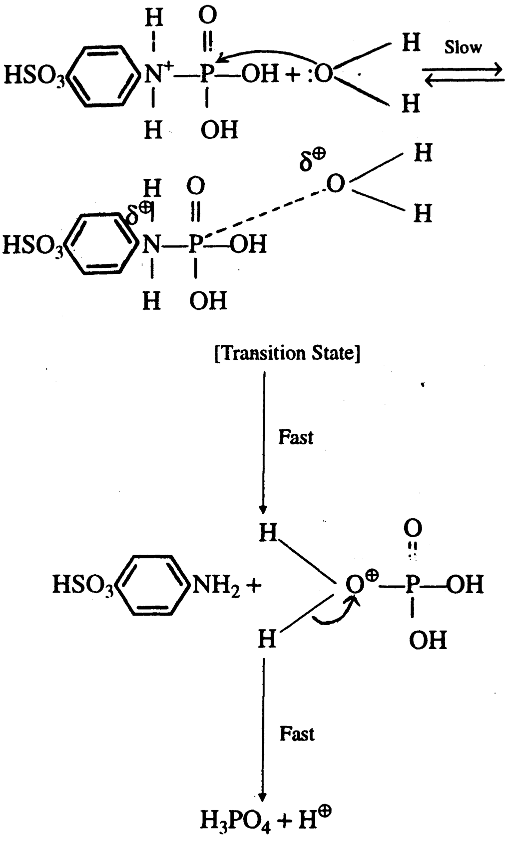
(a) Formation of conjugate acid species

(a)



(I) Neutral species (II) Conjugate acid species

(b) Bimolecular nucleophilic attack of water on.phosphorus via conjugate acid species S_{N^2} (P)



REFERENCES

1. A.H. Schlesinger, *Chem. Abstr.*, **49**, 5517e (1955).
2. L.F. Audrieth and A.D.F. Toy, *J. Am. Chem. Soc.*, **64**, 1553 (1942).
3. E.F. Normal Hitchocock, A.C. Robert, Rohar Corswell and Derbysire, 1, 042, 391 (1965).
4. P. Rudert, *Ber.*, **26**, 565 (1893).
5. R.J.L. Allen, *J. Biochem.*, **34**, 858 (1940).
6. J.E. Leffler and E. Gurnwald, The Rates and Equilibria of Organic Reactions, John Wiley and Sons Inc., New York, pp. 177, 286 (1963).
7. E.D. Hughes and C.K. Ingold, *J. Chem. Soc.*, 224 (1933).
8. P.W.C. Barnard, C.A. Vernon and V.A. Welch, *J. Chem. Soc.*, **227**, 229 (1966).
9. S.Z. Arrhenius, *Phy. Chem.*, **4**, 226 (1889).
10. J.E. Bünnett and F.P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).
11. R.D. Gillion, Introduction to Physical Organic Chemistry, Addison-Wesley Pub., pp. 167, 169 (1970).

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