

Kinetics and Mechanism of Hydrolysis of Di-*p*-sulphonic Acid Aniline Phosphate in Acidic Medium

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Investigation of di-*p*-sulphonic acid aniline phosphate was carried out by using "Allen's" modified method of colorimetry in acid medium from 0.1 to 7.0 mol dm⁻³ at 98°C in 20% dioxane-water mixture (V/V). 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 of kinetic studies are provided to identify the reactive species. Molecularity and bond fission are also discussed in terms of Zücker-Hammett hypothesis, Hammett acidity functions, Bünnett and Bünnett-Olsen parameters and isokinetic relationship.

INTRODUCTION

Phosphates having C-N-P linkages are of great importance. They are used as pesticides, insecticides¹, fire retardants², plasticizers³ and synthetic lubricants⁴ etc. The undertaken compound, *i.e.*, di-*p*-sulphonic acid aniline phosphate, was chosen for the kinetic study as this compound is reactive *via* different species depending upon the experimental conditions.

EXPERIMENTAL

Di-*p*-sulphonic acid aniline phosphate was prepared by the method of POCl₃^{5, 6} by phosphorylation of *p*-amino-sulphonic acid in the mixture of pyridine and benzene. The acid hydrolysis of the present ester (5 × 10⁻⁴ mol dm⁻³) in the acid range (0.1 to 7.0 mol dm⁻³ HCl at 98° ± 0.5°C) was carried in 20% aqueous dioxane (v/v) medium. The inorganic phosphate obtained during hydrolysis was estimated colorimetrically by Allen's modified method⁶, while constant ionic strengths were maintained using appropriate mixture of NaCl and HCl.

RESULTS AND DISCUSSION

The rate of hydrolysis of di-*p*-sulphonic acid aniline phosphate was studied in HCl from 0.1 to 7.0 mol dm⁻³ HCl at 98°C in 20% dioxane-water medium. In Table-1 the pseudo-first order rate constants are summarised, from which it is clear that rate of reaction increases up to 4.0 mol dm⁻³ HCl^{7, 8} but further increases in acid molarity really decrease the rates as it can be attributed to the complete conversion of the ester (basic) molecules 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 strengths⁹ (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 that makes a positive slope. Since the K_H^\ominus is slope increasing with increase in ionic strength, acid catalysis is subjected to positive effect of ionic strength. Intercept on rate axis shows the participation of a species other than conjugate acid species.

TABLE-1
ESTIMATED AND EXPERIMENTAL PSEUDO-FIRST ORDER RATE COEFFICIENTS FOR THE HYDROLYSIS OF DI-*p*-SULPHONIC ACID ANILINE PHOSPHATE AT 98°C

HCl mol dm ⁻³	10 ⁴ K _H ⁺ ·C _H ⁺ min ⁻¹	10 ⁴ K _N min ⁻¹	10 ⁴ K _e estimated from eq. (ii)	- log (a _{H₂O}) ⁿ	10 ⁴ K _e estimated from eq. (iv)	10 ⁴ K _e experimental min ⁻¹
0.1	0.616	3.307	4.124		4.124	3.310
0.2	1.233	3.715	4.948		4.948	3.521
0.5	3.083	3.935	4.244		4.244	4.375
1.0	6.615	5.888	12.054		12.054	11.430
2.0	12.331	10.471	22.802		22.802	23.890
3.0	18.495	18.620	37.117		37.117	36.897, 27.797 ^a 37.819 ^c , 19.010 ^b 39.010 ^d
4.0	24.660	33.113	57.773		57.773	56.991
5.0	30.829	58.880	89.709	(0.155) ³	50.966	54.673, 40.738 ^a 60.421 ^c , 27.797 ^b 63.110 ^d
6.0	36.995	104.71	141.705	(0.211) ⁵	46.218	46.067
7.0	43.161	186.20	229.36	(0.279) ⁷	45.189	40.839

Note: a = 90°, b = 80°, c = 30% dioxane, d = 40% dioxane

By the 2nd empirical term of the Debye-Hückel¹⁰ equation the total rates contributed by conjugate acid and neutral forms can be estimated as:

$$K_e = K_{H_0}^\ominus \cdot C_{H_0}^\ominus + K_N \quad (i)$$

From the above equation (i) the acid and the neutral rates contributing to the experimental rate constants can be written as follows:

$$K_e = K_{H_0}^\ominus \cdot C_{H_0}^\ominus \exp b'_H (a_{H_2O})^n + K_{N_0} \exp b'_N (a_{H_2O})^n \quad (ii)$$

where $K_{H_0}^\ominus$ and K_{N_0} are specific conjugate acid and specific neutral rate coefficients at zero ionic strength respectively and b'_H and b'_N are constants.

The rates estimated from (ii) are in close agreement with the experimentally observed rates up to 4.0 mol dm⁻³ HCl (Table-1).

In the region of 0.1 mol dm⁻³ to 4.0 mol dm⁻³ the rate law is represented by eq. (iii).

$$K_e = 6.16 \times 10^{-4} \exp (0.00 \times 2.303) \mu + 3.311 \times 10^{-4} \exp (0.25 \times 2.303) \mu \quad (iii)$$

The rates above 4.0 mol dm⁻³ HCl, however, deviate probably due to decrease in the reactivity of the neutral forms as a result of decreases in water activity.

Therefore, the rates beyond 4.0 mol dm^{-3} HCl were calculated employing Bronsted-Bjerrum¹¹ (Eq. (iv)).

$$K_e = K_{H_0} \cdot C_{H^+} \exp b_{H^+} \cdot \mu (a_{H_2O})^n + K_{N_0} \cdot \exp b_N \cdot \mu \quad (\text{iv})$$

Hence the rate law beyond 4.0 mol dm^{-3} HCl may be represented by Eq. (v).

$$K_e = 6.16 \times 10^{-4} \cdot C_{H^+} \exp (0.0 \times 2.303)\mu + (a_{H_2O})^n + 3.311 \times 10^{-4} \exp (0.25 \times 2.303)\mu \quad (\text{v})$$

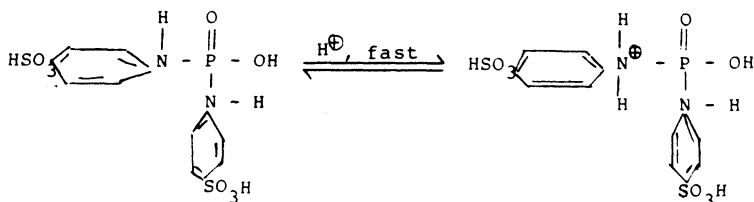
where $(a_{H_2O})^n$ is water activity term¹² and n is an integer, which increases with increase in acidity. The revised estimated rates now agree well with the experimentally observed rates (Table-1). It is clear from the above results that di-*p*-sulphonic acid aniline phosphate in acid solution occur via both conjugate acid and neutral species and their rates are subjected to both ionic strength and water activity.

Solvent effect (Table-1) shows a significant rise in rate; dioxane being a better proton donor than H_2O 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. This is in accordance with Chanley's observation.¹³ Thermodynamic parameters¹⁴ for the reaction in 3.0 mol dm^{-3} HCl were found to be $E = 0.152 \text{ kcal/mol}$, $A = 6.225 \times 10^5 \text{ sec}^{-1}$, $\Delta S^* = -57.084 \text{ e.u.}$ The corresponding values at 5.0 mol dm^{-3} HCl were $E = 9.609 \text{ kcal/mol}$, $A = 9.231 \times 10^{+5} \text{ sec}^{-1}$, $\Delta S^* = -56.304 \text{ e.u.}$ These values are indicative of bimolecular nature of hydrolytic reaction. Bimolecular nature of reaction is further supported by slopes of plots of Zücker and Hammett¹⁵ (1.076), Hammett¹⁶ (0.625), Bünnett¹⁷ ($W = 6.22$, $W^* = 1.58$). Bünnett and Olsen¹⁸ ($\phi = 1.0$) suggested that water is involved as a proton transfer agent in the rate determining step.

Since the rate coefficients are fairly similar and are independent of initial concentration of diester the reaction may be taken to be kinetically of first order.¹⁹ The hydrolysis of the diester occurs via the cleavage of P—N bond; fission follows the isokinetic relationship^{20, 21}.

By observing the above evidences and discussions the most tentative mechanistic routes for the conjugate acid species may be formulated as:

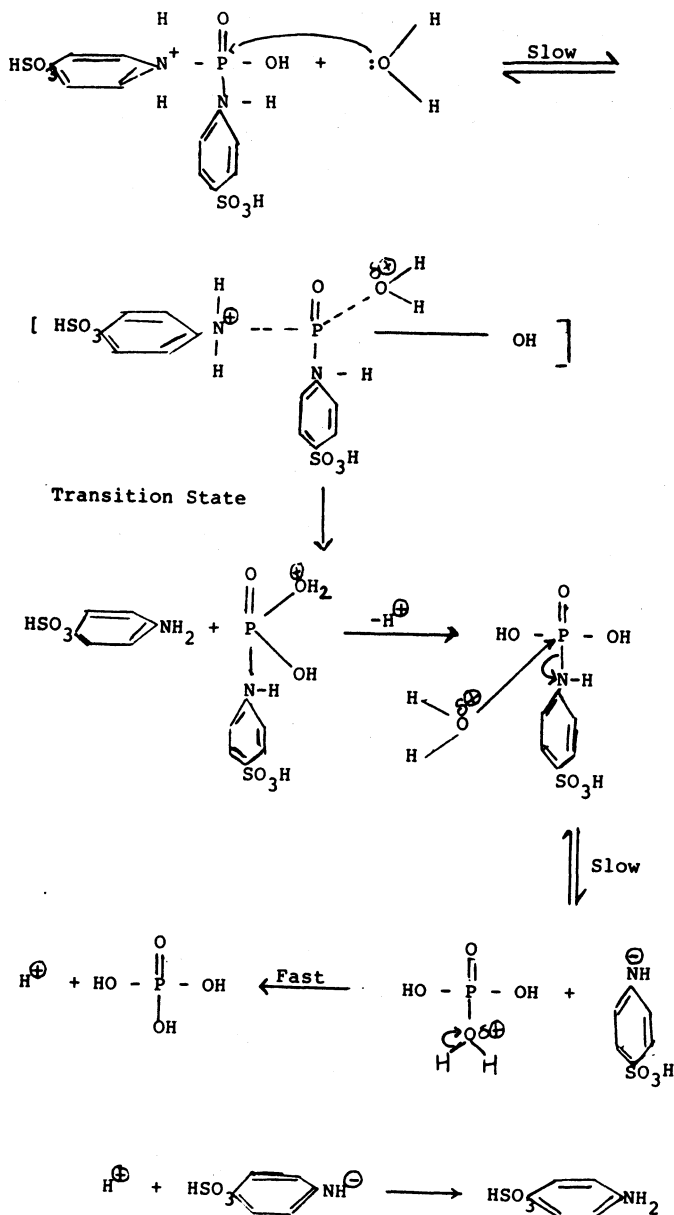
(a) Formation of conjugate acid species by fast pre-equilibrium proton transfer:



Neutral species

Conjugate acid species

(b) Bimolecular nucleophilic attack of water on phosphorus of the conjugate acid species $S_N^2(P)$:



REFERENCES

1. A.H. Schlesinger, *Chem. Abstr.*, **49**, 5517e (1955).
2. C.A. Vernon and V.A. Walch, *J. Chem. Soc., Sec. B: Physical Organic Chemistry* (1966).
3. L.F. Audrieth and A.D.F. Toy, *J. Am. Chem. Soc.*, **64**, 1553 (1942).
4. E.F. Norman, Hitchcock, A.C. Robert, Rohar Corswell and Derbysire, 1,042,391 (1965).
5. P. Rudert, *Ber*, **26**, 565 (1893).
6. R.J.L. Allen, *J. Biochem.*, **34**, 858 (1940).
7. M.M. Mhala an Shashi Prabha, *Indian J. Chem.*, **8**, 972 (1976).
8. M.M. Mhala, M.D. Patwardhan and G. Kasturi, *Indian J. Chem.*, **7**, 145 (1969).
9. K.J. Laidler, *Chemical Kinetics*, Tata McGraw-Hill, New Delhi, p. 229 (1965).
10. M.C. Bailly, *Bull. Soc. Chem. (Fr.)*, **2**, 340, 405 (1942).
11. P.W.C. Barnard, C.A. Bunton, D. Kellerman, M.M. Mhala, B. Silver, C.A. Vernon and V.A. Welch, *J. Chem. Soc. (B)*, 227 (1966).
12. J.F. Bünnett, *J. Am. Chem. Soc.*, **83**, 4956, 4982 (1961).
13. J.D. Chanley and E.J. Feageson, *J. Am. Chem. Soc.*, **80**, 2686 (1958).
14. S.Z. Arrhenius, *Phys. Chem.*, **4**, 226 (1889).
15. L. Zücker and P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1932).
16. L.P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, London, p. 335 (1940).
17. J.F. Bünnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961).
18. J.F. Bünnett and F.P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).
19. E.S. Swinbourne, *Analysis of Kinetic Data*, Nelson, London, p. 53 (1971).
20. E.M. Kosower, *An Introduction to Physical Organic Chemistry*, Wiley, New York, pp. 51–59 (1968).
21. R. Patil, C.P. Shinde and N. Kulshrestha, *Asian J. Chem.*, **7**, 342 (1995).

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