Asian Journal of Chemistry Vol. 18, No. 2 (2006), 997–1001

Kinetics and Mechanism of Hydrolysis of 2,5-Dichloro Aniline Monophosphate in Hydrochloric Acid Medium

C.P. SHINDE*, R.K. SINGH and M.K. SINGH
School of Studies in Chemistry, Jiwaji University, Gwalior-474 011, India

Kinetics of the hydrolysis of 2,5-dichloro aniline monophosphate has been investigated in acid medium (0.1 to 7.0 mol dm^{-3} HCl) at 80°C and the spectrophotometric method is employed for the estimation of inorganic phosphate, the ultimate product of hydrolysis. pH log rate profile has a rate maxima at 4.0 mol dm^{-3} HCl. Hydrolysis of the monoester in the acid region has been shown to be mainly *via* their conjugated acid species and the contribution of the neutral species is negligibly small. Rate data at constant ionic strength was used to identify reactive species and to determine theoretical rates. Theoretical rates, estimated from second empirical terms of Debye-Hückel equation, have been found to be in close agreement with experimental rates. Arrhenius parameters concept of molecularity and other kinetic rate data support a bimolecular nucleophilic attack of water on the phosphorus atom of the conjugate acid species of 2,5-dichloro aniline monophosphate. The suitable mechanistic steps involving the formation of transition state in which the charges are dispersed is proposed. Kinetic rate data and isokinetic relationship have been used to propose the probable P-N bond fission.

Key Words: Kinetics, Mechanism, Hydrolysis, 2,5-Dichloro aniline monophosphate.

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. 2,5-Dichloro aniline monophosphate was chosen for the kinetic study as this compound is reactive *via* different species depending upon the experimental conditions.

EXPERIMENTAL

2,5-Dichloro aniline monophosphate (Ba-salt) was prepared by the H_3PO_4 method by phosphorylation of 2,5-dichloro aniline in the mixture of dry benzene and pyridine; m.f. $C_6aH_6O_3Cl_2NP$; Found (%): C = 27.50, H = 2.98, N = 5.42, P = 13.45, Cl = 30.85; Calcd. (%): C = 29.75, H = 2.47, N = 5.78, P = 12.80, Cl = 29.33.

Kinetic study of the hydrolysis of 2,5-dichloro aniline monophosphate (Ba-salt) was carried out at 80°C employing (5×10^{-4} mol dm^{-3}) solution of the compound, which was followed by spectrophotometric estimation by Allen's modified method[5] in aqueous medium, while constant ionic strengths were maintained using appropriate mixture of NaCl and HCl.

RESULTS AND DISCUSSION

The rate of hydrolysis of 2,5-dichloro aniline monophosphate was studied in acid medium (0.1–7.0 mol dm^{-3} HCl) at 80°C. In Table-1, the pseudo-first order rate constants are summarised, from which it is quite clear that the 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) molecules into their respective conjugate acid species with the lowering of concentration of a nucleophile (water), which plays its role in the rate determining step of bimolecular hydrolytic reaction.

TABLE-1
ESTIMATED AND EXPERIMENTAL DATA FOR THE HYDROLYSIS OF 2,5-DICHLORO ANILINE MONOPHOSPHATE AT 80°C

HCl (mol dm^{-3})	$KH^{\oplus}CH^{\oplus} \times 10^2$ (min^{-1})	$K_N \times 10^2$ (min^{-1})	$K_e \times 10^2$ (min^{-1}) (Estm.)	Water activity (n)	$K_e \times 10^2$ (min^{-1}) (Expt.)
0.1	0.073	1.380	1.453	—	1.303
0.2	0.152	1.348	1.500	—	1.422
0.5	0.420	1.258	1.678	—	1.681
1.0	1.000	1.122	2.122	—	2.234
2.0	2.824	0.891	3.715	—	3.475
3.0	5.984	0.707	6.691	—	6.621
4.0	11.271	0.562	11.833	—	11.872
				(3)	14.12a
					15.76b
5.0	19.860	0.446	20.306	6.960	6.413
				(4)	
6.0	33.728	0.354	34.082	4.880	4.571
				(5)	
7.0	55.590	0.281	55.871	2.249	2.134

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

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 strength is represented by a linear curve that makes a positive slope with acid axis, indicating the presence of acid catalysis. Since the $K_H^{\oplus}$ (slope) is increasing with increase in ionic strength, acid catalysis is subjected to positive effect of ionic strength, *i.e.*, positive salt effect (Fig. 1).

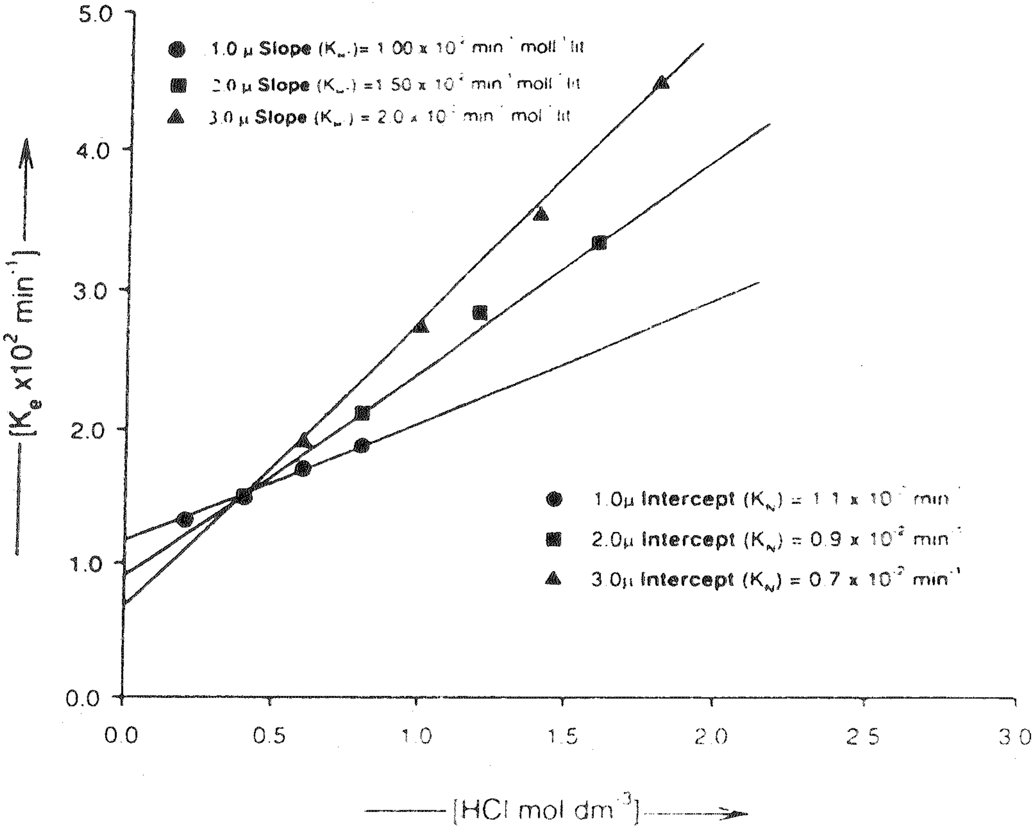


Fig. 1. Acid hydrolysis of 2,5-dichloro aniline monophosphate at constant ionic strength at 80°C

Intercepts on the rate axis are the indications for the participation of neutral species. Hydrolysis of 2,5-dichloro aniline monophosphate indicates that rates decrease with increasing ionic strength, so there is negative influence of the ionic strength of neutral rates.

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 terms of Debye-Hückel equation[6].

$$K_e = K_H^{\oplus} C_H^{\oplus} + K_N \quad (1)$$

In the above equation (1), the terms K_e, $K_H^{\oplus}$ and K_N are the observed rate constants, the specific acid catalyzed and specific neutral rate at that ionic strength respectively.

The sum of neutral and acid rates agrees well with the experimentallly 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. The hydrolysis of these acidities may be represented as

$$K_e = K_H^{\oplus} C_H^{\oplus} (a_{H_2O})^n + K_N (a_{H_2O})^n \quad (2)$$

where a_{H_2O} is water activity and n is integer. The revised estimated rates now agree well with the experimentally observed rates (Table-1).

It is clear from the above results that 2,5-dichloro monoaniline phosphate in acid solutions occurs *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 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 the charge is dispersed.

Arrhenius parameters[9] are determined for the hydrolysis at 3.0 and 5.0 mol dm^{-3} HCl (Table-2). The magnitude of Arrhenius parameters falls in the range of bimolecular reaction. Bimolecular nature of reaction is further supported by Zücker-Hammett[10] (1.0), Hammett[11] (0.55) and Bunnett[12] ($W = 8.00$, $W^* = 3.57$) plots (figure not shown). Bunnett-Olson parameters[13, 14] $\phi = 1.42$ (> 0.58) suggest that water is included as a proton transfer agent in the rate determining step (figure not shown).

The effect of concentration of monoester on the rate of hydrolysis also confirms the order of reaction[15] to be one with respect ot the monoester by reducing either half ($K_e = 11.85 \times 10^{-2}$ min^{-1}) or double ($K_e = 11.92 \times 10^{-2}$ min^{-1}) the normal concentration ($K_e = 11.87 \times 10^{-2}$ min^{-1}) at 4.0 mol dm^{-3} HCl.

TABLE-2
CALCULATED ARRHENIUS PARAMETERS

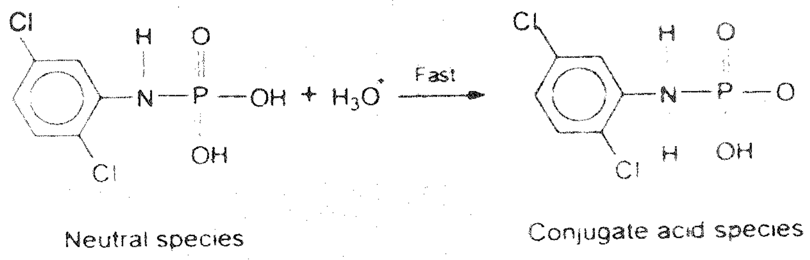
HCl (mol dm^{-3})	Temp. (°C)	$K_e \times 10^{-2}$ (min^{-1}) (exp.)	E (kcal/mol)	A (s^{-1})	$-\Delta s^{\#}$ (e.u.)
3.0	90	8.912			
3.0	80	6.621	7.321	3.757×10^{3}	53.67
3.0	60	3.483			
5.0	90	8.413			
5.0	80	6.413	6.864	1.897×10^{3}	55.03
5.0	60	3.311			

Comparative kinetic[16, 17] data (figure not shown) also support the bimolecular nature of hydrolysis involving attack of water on phosphorus of the monoester.

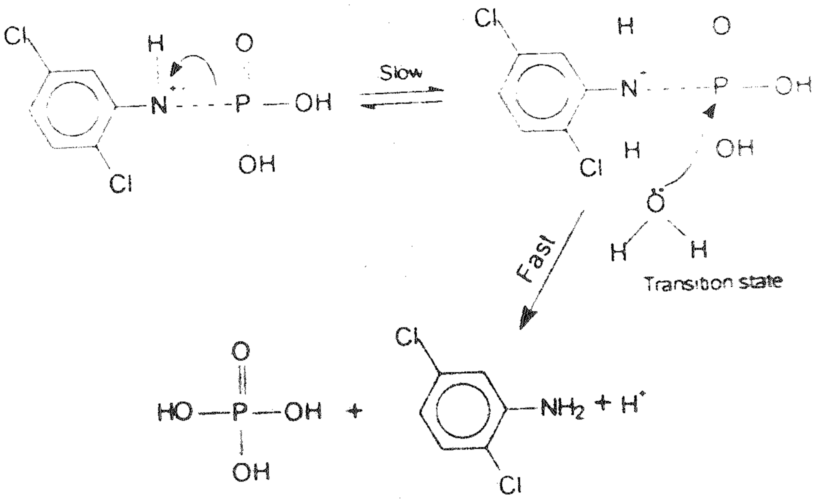
Probable mechanism of hydrolysis

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

(a) Formation of 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**, 5517 (1955).
2. C.A. Vernon and V.A. Walch, *J. Am. Chem. Soc.*, **64**, 1553 (1942).
3. L.F. Audrieth and A.D.F. Toy, *J. Am. Chem. Soc.*, **64**, 1553 (1942).
4. E.F. Norman Hitchcock, A.C. Robert, R. Crswell and E. Derbysire, *Bull. Soc. Chem. (France)*, **42**, 391 (1965).
5. R.J.L. Allen, *J. Bio. Chem.*, **34**, 858 (1940).
6. J.E. Lefler and E. Gurunwald, The Rates and Equilibria of Organic Reactions, John Wiley & Sons, New York, pp. 177, 286 (1963).
7. E.D. Hughes and C.K. Ingold, *J. Chem. Soc.*, 224 (1935).
8. P.W.C. Barnard, C.A. Bunton, D. Kellerman, M.M. Mhala, B. Silver, C.A. Vernon and V.A. Welch, *J. Chem. Soc.*, 227, 229 (1966).
9. S.Z. Arrhenius, *Phys. Chem.*, **4**, 226 (1889).
10. L. Zücker and P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1932).
11. L.P. Hammett, Physical Organic Chemistry, McGraw-Hill, London, p. 335 (1940).
12. J.F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961).
13. J.F. Bunnett and F.P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).
14. C.P. Shinde and R. Patil, *Asian J. Chem.*, **7**, 134 (1995).
15. E.S. Swinbourne, Analysis of Kinetic Data, Nelson, London, p. 53 (1971).
16. R.D. Gilliom, Introduction to Physical Organic Chemistry, Addison-Wesley, pp. 167–169 (1970).
17. C.P. Shinde, R. Patil and V. Shirdhonkar, *Asian J. Chem.*, **10**, 245 (1998).

(*Received*: 23 March 2005; *Accepted*: 12 December 2005) AJC-4521