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Mechanistic and kinetic approach to the hydrolysis of tri-2,5-dichloro aniline phosphate in acidic media

M.K. SINGH

Department of Chemistry,Government P.G. College, Dholpur - 328 001 (India).

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ABSTRACT

Kinetic study of Tri-2,5-dichloro aniline phosphate has been made in acid region (0.1 to 7.0 mol dm^{-3} HCl) at 80°C. Acid log rate profile has a rate maximum at 4.0 mol dm^{-3}. Ionic strength data upto 3.0 m requires participation of conjugate acid species and to determine theoretical rates. Computed ionic strength data support this,since the estimated rates in the acid medium closely agree with those experimentally observed.PH,Salt, temperature.solvent, solvent-isotope,substrate concentration effects etc. have been studied.Bimolecular behaviour has been decided by the Arrhenius parameters and analysis of molecularity data. The triesters involves P-N bond fission which is strengthened by comparative kinetic data.

Key words: Tri-2,5-dichloro aniline phosphate, kinetic approach.

INTRODUCTION

The chemistry of phosphate esters continues to attract the attention of chemists due to their versatile application in the analytical[1,2], biological[3,4] and industrial fields[5,6]. Organic phosphates, having C-N-P linkages, are of great importance. Keeping this in view, the hydrolytic bond cleavages of Tri-2,5-dichloro aniline phosphate has been investigated. The chosen compound i.e. 2,5-dichloro aniline phosphate, for the kinetic study, is reactive via neutral species and conjugate acid species, depending upon the experimental conditions.

EXPERIMENTAL

Tri-2,5-dichloro aniline phosphate was prepared by treating 2,5-dichloro aniline with H_3PO_4[7] in pyridine which is used as a solvent. Molecular formula $C_{18}H_{12}ON_3PCl_6$; Found (%) : C=43.97, H=4.13, N=8.70; calculated (%) : C=43.79, H=2.28, N=7.92. Kinetic study of the hydrolysis of Tri-2,5-dichloro aniline phosphate was carried out at 80°C employing $5x10^{-4}$ mol dm^{-3} solution of the compound which was followed by colorimetric estimation by Allen's modified method[8]. The constant ionic strengths were maintained using mixtures of HCl and NaCl. All the chemicals used belonged to BDH (A.R.) and Riedel qualities. Values of pseudo first order rate constants were calculated for each run from the standard equation.

RESULTS AND DISCUSSION

The pseudo first order rate coefficients for the hydrolysis of the present triester in the range of 0.1 to 7.0 mol dm^{-3} HCl are found to increase with the increase in acid molarity upto 4.0 mol dm^{-3} (Table-1). Further rise in acidity decreases the rate constants. The rate constants are found to be hundred times less than that of mono-2,5-dichloro aniline phosphate ester[9].A maximum rate at 4.0 mol dm^{-3} HCl is attributed to complete conversion of the substrate into its conjugate acid species. The decrease after 4.0 mol dm^{-3} HCl is attributed to the lowering of concentration of attacking nucleophile taking part in the reaction i.e. due to variation in water activity.

In order to determine whether or not there is effect of ionic strength or the presence of acid catalysis, kinetic runs were made at three different ionic strengths (1.0, 2.0 and 3.0 m) which were

maintained by adequate mixture of NaCl and HCl. Hydrolysis at 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+=1.50, 1.75 and 2.14x10^{-4} for 1.0, 2.0 and 3.0 m respectively) increases with increase in ionic strength, acid catalysed is subjected to positive effect of ionic strength. These linear curves meet at one point on rate axis indicating the participation of neutral species. The constant value of intercepts shows the constant contribution of 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 2nd empirical term of Debye-Huckle equation[10].

$$K_e = K_H + C_H + + K_N \quad ...(1)$$

In the above equation, the term K_e, K_H+ and K_N are the observed rate constants, the specific acid catalysed and specific neutral rate at that ionic strength respectively. It is due to the effect of water activity.

The sum of neutral and acid rates agrees well with the experimentally observed rates (Table 1) upto 4.0 mol dm^{-3} HCl. However this tendency discontinued after 4.0 mol dm^{-3} HCl which is due to the effect of water activity[10,11]. Concentration of water and hence water activity would be affected by a change over from 4.0 mol dm^{-3} to higher mol dm^{-3} acid . The rates of hydrolysis, if bimolecular, would then be lowered partly by more concentrated nature of acid and partly by conversion of neutral water into its protonated form, which would not act as a nucleophilic reagent to bring about bimolecular hydrolysis. The lowering in rates

Table 1: Rates of hydrolysis of Tri-2,5-dichloro aniline phosphate at 80°C

HCl (mol dm^{-3})	10^4K_H+.C_H+ (min^{-1})	10^4K_N (min^{-1})	$10^4K_{Calc.}$ (min^{-1}) from equ^n (1)	Water activity-log $(a_{H2O})^n$	10^4 $K_{obs.}$ (min^{-1})
0.1	0.1281	5.00	5.1281	-	5.1654
0.5	0.6872	5.00	5.6872	-	5.6691
1.0	1.5004	5.00	6.5004	-	6.5004
2.0	3.5763	5.00	8.5763	-	8.4802
3.0	6.3932	5.00	11.3932	-	11.2269
4.0	10.1592	5.00	15.1592	-	15.0297
					15.0297[a]
					16.1293[b]
					16.9156[c]
5.0	15.1346	5.00	12.4125	$(0.155)^2$	10.2885
6.0	20.4245	5.00	10.0391	$(0.211)^3$	8.6709
7.0	30.0953	5.00	7.1474	$(0.279)^4$	7.0278

a=5% dioxane, b=10% dioxane, c=15% dioxane

Table 2: Calculated arrhenius parameters

HCl (mol dm^{-3})	Temp. t°C	K_e10^4 (min^{-1})	E (Kcal/mol)	A (Sec^{-1})	-DS[1] (e.u)
4.0	90	23.052	13.454	5.34×10^3	-43.8068
4.0	80	15.029			
4.0	70			8.740	

in 5.0, 6.0 and 7.0 mol dm^{-3} HCl can be explained by considering water activity as an additional parameters. The rate of hydrolysis of these acidities may be represented as –

$$K_e = K_H + C_H + + (a_{H2O})^n + K_N(a_{H2O})^n \quad ...(2)$$

Where a_{H2O} is water activity and n is an integer. The revised estimated rates now agree well with experimentally observed rates (Table -1).

The rate law may, therefore, be formulated as :

i) In the region 0.1 to 4.0 mol dm^{-3} HCl
$K_e = 1.26x10^{-4}C_H$+Exp (0.076x2.303)μ + $5.00x10^{-4}$ min^{-1}

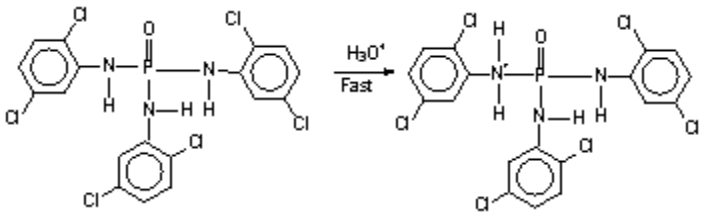
ii) In the region > 4.0 ml dm^{-3} HCl
$K_e = 1.26x10^{-4}$ C_H+ Exp (0.076x2.303)μ $(a_{H2O})^n$ +5.00 x 10^{-4} min^{-1}

It is clear from the above results that 2,5-dichloro aniline phosphate triester in acid solutions occurs via both conjugate acid and neutral species and their rates are subjected to both ionic strength and water activity.

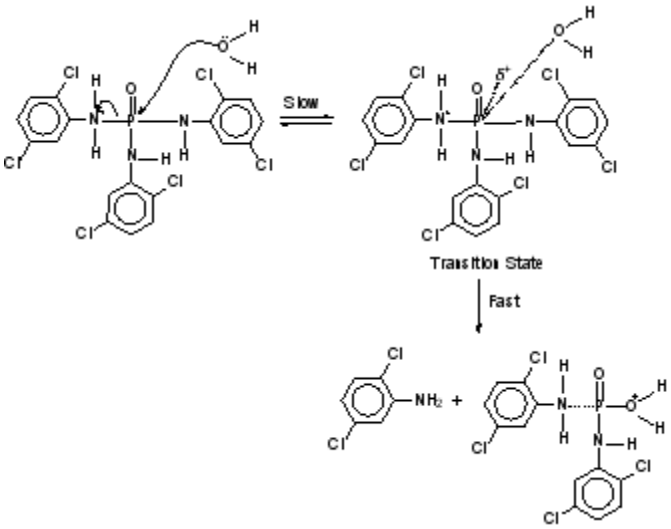
Arrhenius parameters[12] are determined for the hydrolysis at 4.0 mol dm^{-3} HCl (Table-2). The magnitudes of Arrhenius Parameters fall in the range of a bimolecular reaction[13]. Bimolecular nature of reaction is further supported by Zucker-Hammett[14] (0.875), Hammett (0.30) and Bunnett (w=8.0, w*-2.678) plots (figure not shown).

Bunnett-Olsen Parameter[15] (f=1.571, which is greater than 0.58) suggests that water is involved as a proton-transfer agent in the rate determining step. It is interesting to note that the values of both w and f are consistently high and consistent with water playing an additional role beyond that of a nucleophile.

The effect of solvent (Table-1) shows a significant rise in rates, dioxane being a better proton donor than water increase the concentration



(a) Formation of conjugate acid species



(b) Hydrolytic attack of water on the phosphorus of conjugate acid species (SN^2)

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.

The effect of concentration of triester on the rate of hydrolysis also confirms the order of reaction to be one with respect to the triester by reducing either Half (K_e=15.21x10^{-4} min^{-1}) or double (K_e=15.45x10^{-4} min^{-1}) the normal concentration (K_e=15.02x10^{-4} min^{-1}) at 4.0 mol dm^{-3} HCl.

A comparative kinetic data[9,16] (not shown) also support the bimolecular nature of the hydrolysis involving P-N bond fission. Thus, acid hydrolysis of Tri-2,5-dichloro aniline phosphate involves bimolecular attack of water on phosphorous of conjugate acid species formed by fast pre-equilibrium proton transfer.

Mechanism

The mechanism of hydrolysis of Tri-2,5-dichloro aniline phosphate via conjugate acid species based on above results and discussion may be formulated as follows :

This is followed by the hydrolysis of diester into monoester and then into inorganic phosphate.

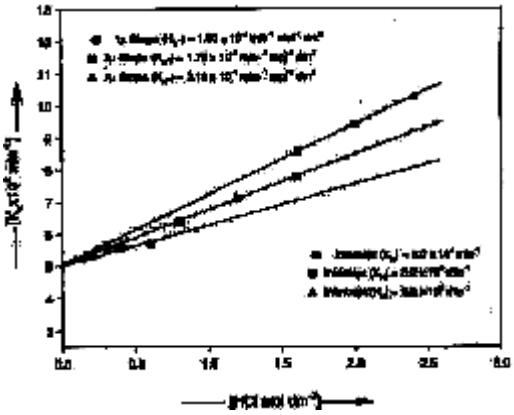


Fig. 1: Acid catalysed hydrolysis of Tri-2, 5-dichloro aniline phosphate at constant ionic strength at 80°C

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