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KINETICS AND MECHANISM OF HYDROLYSIS OF DI-2-CHLORO-5-NITRO ANILINE PHOSPHATE VIA CONJUGATE ACID SPECIES

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Abstract: Acid hydrolysis of Di-2-chloro-5-nitro aniline phosphate has been carried out in the acid region 0.1 to 7.0 mol dm^{-3} HCl at $80^{o}C$ in 10% aqueous dioxane (v/v) medium. Ionic strength data exhibits different contribution of conjugate acid species and presence of acid catalysis. Theoretical rates, estimated from second empirical term of Debye-Huckel, closely agree with those experimentally observed. Bimolecular behaviour of the hydrolytic reaction has been decided by the use of different concepts and hypothesis e.g., Hammett acidity function, Zucker-Hammett equation, Bunnett parameters, Bunnett-Olsen parameter, Arrhenius parameters and Solvent effect . The most probable mechanism for the hydrolytic reaction has been given by using Isokinetic relationship. The Diester involves P-N bond fission which is strengthened by comparative kinetic data.

Key words: Di-2-Chloro-5-Nitro Aniline Phosphate, Conjugate acid species

Introduction

Organic compounds of phosphorus are essential constituents of protoplasm and DNA and play an important role for maintenance of life.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 Di-2-chloro-5-nitro aniline phosphate has been investigated. Diesters are reasonably stable towards alkali and attack occurs only under drastic conditions. Acid hydrolysis of the diesters proceeds more readily.

Experimental

Di-2-chloro-5-nitro aniline phosphate was prepared by treating 2-chloro-5-nitro aniline with $POCl_3$[7] in pyridine which is used as a solvent. Molecular formula $C_{18}H_{12}ON_3PCl_6$; Theoretical (%) : C=35.40, H=2.23, N=13.76; Observed(%) : C=36.55, H=2.40, N=14.53. Melting point of diester was observed $116^{0}c$ while that of parent compound 2-chloro-5-nitro aniline was observed $108^{0}c$. Kinetic study of the hydrolysis of Di-2-chloro-5-nitro aniline phosphate was carried out at $80^{o}C$ 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 diester in the range of 0.1 to 7.0 mol dm^{-3} HCl are found to increase with the increase in acid molarity upto 2.0 mol dm^{-3} HCI (Table-1). Further increase in acidity decreases the rate uniformly upto 7.0 mol dm^{-3} HCl. A maximum rate at 2.0 mol dm^{-3} HCl is attributed to complete conversion of the substrate into its conjugate acid species. The decrease after 2.0 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[9,10].

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 □) 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^+}=4.69, 3.14 and 2.04x10^{-3} for 1.0, 2.0 and 3.0 □ respectively) decreases with increase in ionic strength, acid catalysed hydrolysis is subjected to negative salt effect. Lines of the different ionic strengths pass through the origin indicates that only acid catalysed rates are susceptible to salt effect and there is almost no contribution of neutral rate to the overall reaction rate.

Figure - 1

Acid catalysed hydrolysis of Di-2-chloro-5-nitro aniline phosphate at constant Ionic strength at 80°C

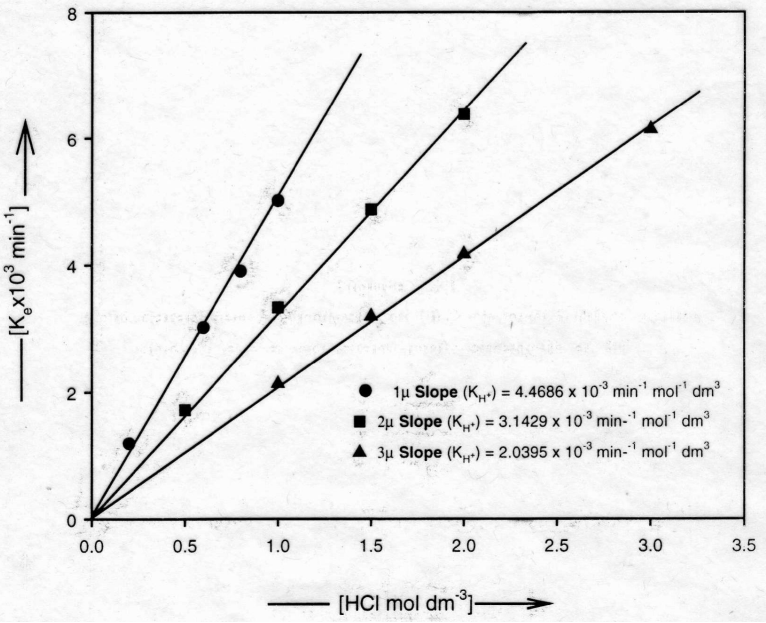


Table-1: Estimated and Experimental rates for the hydrolysis of Di-2-chloro-5-nitro aniline phosphate at 80^{0}C

HCl (mol dm^{-3})	$K_H^{\oplus}C_H^{\oplus}10^3$ (min^{-1})	K_ex10^3 (min^{-1}) (Est.)	K_ex10^3 (min^{-1}) (Expt.)	4+log K_e (Est.)	4+log K_e (Expt.)
0.1	0.6339	0.6339	0.8668	0.8020	0.9379
0.2	1.216	1.216	1.4653	1.0849	1.1659
0.5	2.685	2.685	2.7591	1.4289	1.4407
1.0	4.365	4.365	5.0132	1.6400	1.7001
2.0	5.768	5.768	6.3755	1.7610	1.8045
			6.2846^a		1.7983
			6.3755^b		1.8044
			7.5126^c		1.8758
			8.0432^d		1.9055
3.0	5.716	5.716	5.9137	1.7571	1.7718
4.0	5.035	5.035	5.2680	1.7020	1.7216
5.0	4.159	4.159	4.2624	1.6189	1.6296
6.0	3.298	3.298	3.4251	1.5183	1.5346
7.0	2.542	2.542	2.9124	1.4051	1.4642

a=10% dioxane, b=20% dioxane, c=40% dioxane,d=60%

This suggests that reaction obeys the following equation :

$$K_{H^+} = K_{H^+}.C_{H^+} = K_{Ho^+}.\exp.b_{H^+}.\mu \text{----------} (1)$$

Where, K_{H^+}, K_{Ho^+}, b_{H^+} and μ are specific rate constant at that ionic strength, specific rate constant at zero ionic strength, a constant and ionic strength respectively. This proves the validity of second empirical terms of Debye-Huckel equation[10]. Equation (1) may be written as :

$$\log K_{H^+} = \log K_{Ho^+} + b'_{H^+}.\mu \quad \text{-----------} (2)$$

Where, b'_{H^+}. = Slope and $\log K_{H^+}$ = Intercept, are –0.18 and 0.82 for experimental rates respectively.

Equation (2) has been used for calculating the specific acid catalysed rates (K_{H^+}) at different acidities. Thus, rate constant in acid medium can be written as :

$$K_e = K_{H^+} C_{H^+}$$

$$K_e = K_{H0^+} C_{H^+} \text{ x.exp } b'_{H^+}.\mu \quad \text{------------} (3)$$

The rate constant calculated from equation (3) have been found to agree well with the experimental rates for the region 0.1 to 7.0 mol dm^{-3} acid. This is shown in table –1.

From the effect of ionic strength on the rate of hydrolysis of diester, it may be concluded that the bend in the pH log rate profile at 2.0 mol dm^{-3} acid is caused by negative effect of ionic strength on the rate of acid catalysed hydrolysis and the overall reaction is made up of the rates via conjugate acid species only. Finally, the rate law is given as follows :

$$K_e = 6.607 \times 10^{-3} \text{ min}^{-1} C_{H^+}.\exp(-0.18 \times 2.303)\mu$$

Arrhenius parameters[11] are determined for the hydrolysis at 2.0 mol dm^{-3} HCl (Table-2). The magnitudes of Arrhenius Parameters fall in the range of a bimolecular reaction[12]. Bimolecular nature of reaction is further supported by Zucker-Hammett[13] (0.612), Hammett (0.184) and Bunnett (ω=9.41, ω^*-6.45) plots (figure not shown).

Bunnett-Olsen Parameter[14] (ϕ=1.39, 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 ω and ϕ 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 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 diester on the rate of hydrolysis also confirms the order of reaction to be one with respect to the diester by reducing either Half (K_e=6.19x10^{-3} min^{-1}) or double (K_e=6.37x10^{-3} min^{-1}) the normal concentration (K_e=6.39x10^{-4} min^{-1}) at 2.0 mol dm^{-3} HCl.

A comparative kinetic data[15,16] (not shown) also support the bimolecular nature of the hydrolysis involving P-N bond fission.

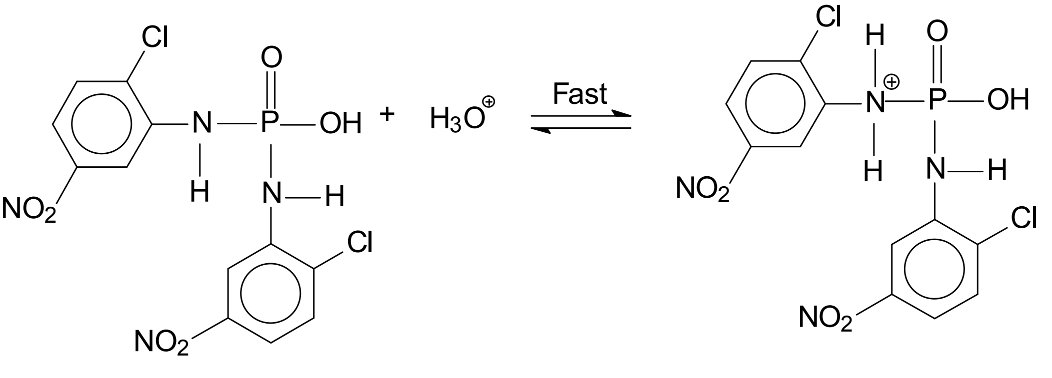
Thus, acid hydrolysis of Di-2-chloro-5-nitro aniline phosphate involves bimolecular attack of water on phosphorous of conjugate acid species formed by fast pre-equilibrium proton transfer.

Table-2: Calculated Arrhenius Parameters

HCl (mol dm^{-3})	Temp. t^{o}C	K_e10^3 (min^{-1})	E (Kcal/mol)	A (Sec^{-1})	$\Delta S^{\neq}$ (e.u)
2.0	80	6.3755	17.84	1.175x10^{4}	-28.53
2.0	90	12.6510			
2.0	98	21.9823			

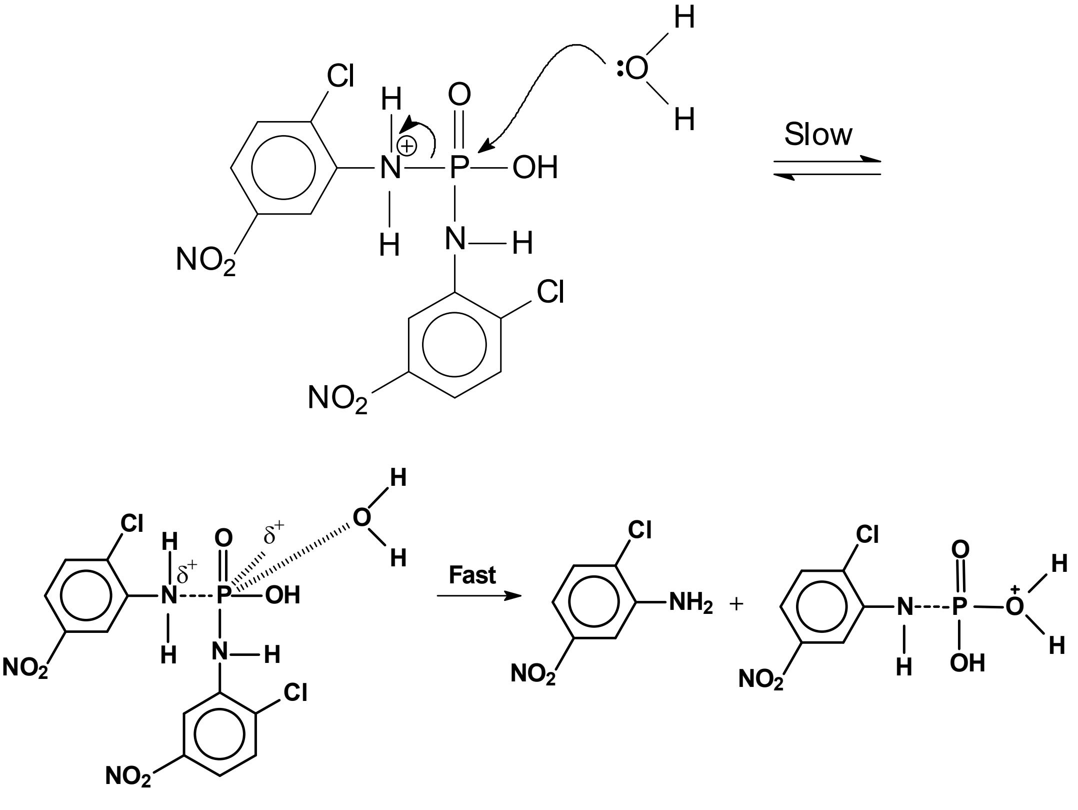
Mechanism: On the basis of experimental results, hydrolysis of Di-2-chloro-5-nitro aniline phosphate via conjugate acid species may be formulated as :

(A) Formations of conjugate acid species by a fast pre-equilibrium proton transfer.

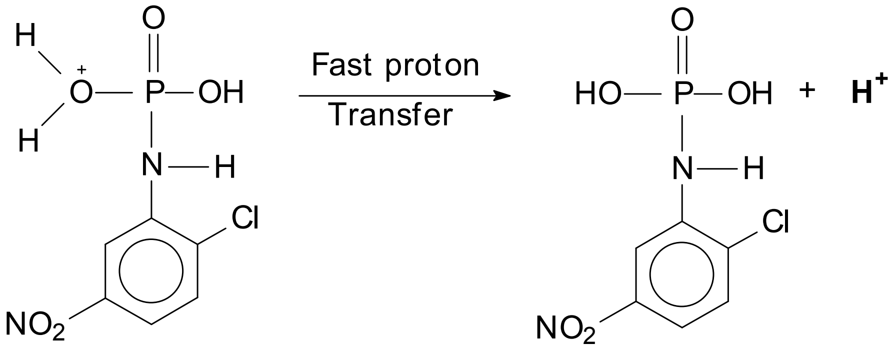


(Neutral species) (Conjugate acid species)

(B) Bimolecular heterolysis of the conjugate acid species :



(Transition State)



(Monoester)

Note : This is followed by the hydrolysis of monoester into inorganic phosphate .

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