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Kinetics and Mechanism of Hydrolysis of Mono-2-chloro-5-nitroaniline Phosphate *via* Conjugate Acid Species

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Kinetic study of mono-2-chloro-5-nitroaniline phosphate has been made in acid region (0.1 to 7.0 mol dm^{-3}) at 60 ºC. The log rate profile has a rate maximum at 4.0 mol dm^{-3}. Ionic strength data upto 3.0 μ requires participation of conjugate acid species and to determine theoretical rates. Theoretical rates, estimated from second empirical term of Debye-Huckel equation, have been found in close agreement with experimental rates. Bimolecular behaviour has been decided by the Arrhenius parameters and by the analysis of molecularity data. The monoesters involves, P-N bond fission which is strengthened by comparative kinetic data.

Key Words: Kinetics, Hydrolysis, Mono-2-chloro-5-nitroaniline phosphate.

INTRODUCTION

The determination of mechanism of hydrolysis of organic phosphates is expected to reveal the possible correlation between the reaction paths of chemical and enzymatic hydrolysis of biologically important phosphate esters[1]. Organic phosphate having C-N-P linkages are of great importance. They are used for antiviral activity[2], insecticidal activity[3], smoke generation[4], for biological investigations and textile commodities[5]. With such a broad spectrum biological activity of azophosphates, the knowledge regarding their bond cleavages and their stabilities are important. Keeping this in view, the hydrolytic bond cleavages of mono-2-chloro-5-nitroaniline phosphate has been investigated. The chosen compound *i.e.*, 2-chloro-5-nitroaniline phosphate for the kinetic study, is reactive *via* different species, depending upon the experimental conditions.

EXPERIMENTAL

Mono-2-chloro-5-nitroaniline phosphate (Ba-salt) was prepared by treating 2-chloro-5-nitroaniline with $POCl_3$[6,7] in pyridine which is used as a solvent. m.f. $C_6H_6N_2O_5PCl$; elemental analysis (%) Calcd. (found): C

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18.58 (19.66); H 1.04 (2.17); N 7.22 (6.44). Kinetic study of the hydrolysis of mono-2-chloro-5-nitroaniline phosphate was carried out at 60 ºC employing 5×10^{-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. 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 monoester 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.

Thus, 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 μ) 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^+} = 1.02, 1.33 and 1.60 × 10^{-2} for 1.0, 2.0 and 3.0 μ, respectively) increases with increase in ionic strength, acid catalyzed 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[9].

$$K_e = K_{H^+} C_{H^+} + K_N \qquad (1)$$

In the above equation, the term K_e, K_{H^+} 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 experimentally observed rates (Table-1) upto 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 as an additional parameters. The rate of hydrolysis of these acidities may be represented as:

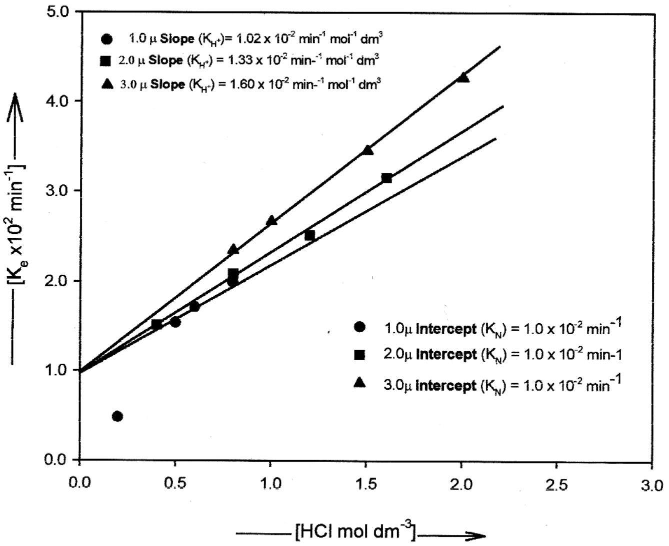


Fig. 1. Acid catalyzed hydrolysis of mono-2-chloro-5-nitroaniline phosphate at constant ionic strength at 60 ºC

TABLE-1
RATES OF HYDROLYSIS OF MONO-2-CHLORO-5-NITROANILINE PHOSPHATE (BARIUM SALT) AT 60 ºC

HCl (mol dm^{-3})	10^3 $K_{H^+}\cdot C_{H^+}$ (min^{-1})	10^3 K_N (min^{-1})	10^3 $K_{calcd.}$ (min^{-1}) from eqn. 1	Water activity $\log(a_{H_2O})^n$	10^3 $K_{obsd.}$ (min^{-1})
0.1	0.835	10.00	10.835	–	6.518
0.2	1.718	10.00	11.718	–	9.717
0.5	4.667	10.00	14.667	–	15.490
1.0	10.720	10.00	20.720	–	24.720
2.0	28.180	10.00	38.180	–	38.002
3.0	55.860	10.00	65.860	–	65.525
4.0	98.190	10.00	108.190	–	108.108
					84.175*
					88.648†
					95.050‡
5.0	79.250	10.00	84.148	$(0.155)^2$	87.710
6.0	59.600	10.00	61.928	$(0.211)^3$	58.930
7.0	30.140	10.00	30.905	$(0.279)^4$	78.720

*10 % dioxane, †20 % dioxane, ‡30 % dioxane.

$$K_e = K_{H^+} C_{H^+} + (a_{H_2O})^n + K_N(a_{H_2O})^n \tag{2}$$

where a_{H_2O} 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

$K_e = 8.128 \times 10^{-3} C_{H^+}$ Exp $(0.12 \times 2.303)\mu + 10.00 \times 10^{-3}$

(ii) In the region > 4.0 mL dm^{-3} HCl

$K_e = 8.128 \times 10^{-3} C_{H^+}$ Exp $(0.12 \times 2.303)\mu\ (a_{H_2O})^n + 10.00 \times 10^{-3}$

It is clear from the above results that 2-chloro-5-nitroaniline phosphate monoester 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[10] are determined for the hydrloysis at 4.0 mol dm^{-3} HCl (Table-2). The magnitudes of Arrhenius parameters fall in the range of a bimolecular reaction[11]. Bimolecular nature of reaction is further supported by Zucker-Hammett[12] (1.508), Hammett (0.621) and Bunnett (W = 8.645, W* = 2.958) plots (figure not shown).

TABLE-2

CALCULATED ARRHENIUS PARAMETERS

HCl (mol dm^{-3})	Temp. (ºC)	$K_e\ 10^3$ (min^{-1})	E (Kcal/mol)	A (s^{-1})	$-\Delta S^{\neq}$ (e-u)
4.0	40	20.45	13.454	1.394×10^6	32.65
4.0	50	50.75			
4.0	60	108.10			
4.0	70	152.81			
4.0	80	327.80			

Bunnett-Olsen parameters[13] (ϕ = 1.353, 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.

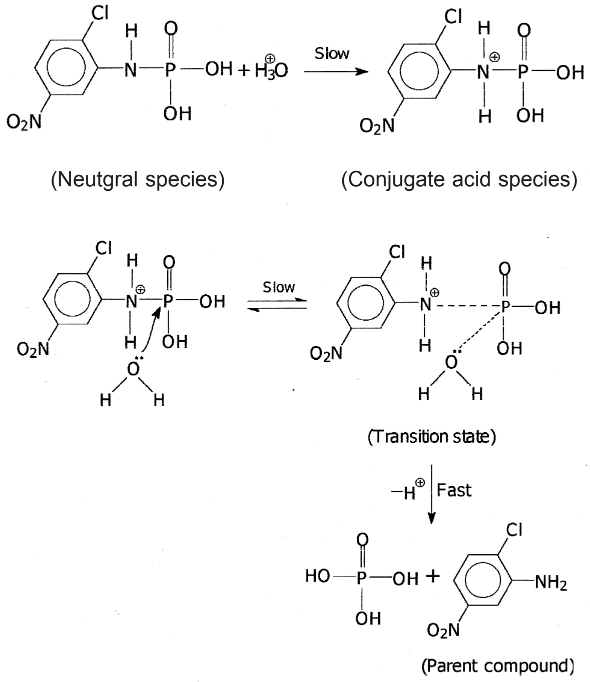
The effect of solvent (Table-1) shows a significant rise in rates, dioxane being a better proton donor than water increase the concentration of conjugate acid species resulting in the increase in rates. Effect of solvent on the rate of hydrolysis may therefore be taken to indicate the formation of transition state in which charge is dispersed.

The effect of concentration of monoester on the rate of hydrolysis also confirms the order of reaction to be one with respect to the monoester by reducing either half ($K_e = 10.80 \times 10^{-2}$ min^{-1}) or double ($K_e = 10.83 \times 10^{-2}$ min^{-1}) the normal concentration ($K_e = 10.81 \times 10^{-2}$ min^{-1}) at 4.0 mol dm^{-3} HCl.

A comparative kinetic data[14] (not shown) also suport the bimolecular nature of the hydrolysis involving P-N bond fission.

Thus, acid hydrolysis of mono-2-chloro-5-nitroaniline phosphate involves bimolecular attack of water on phosphorus of conjugate acid species formed by fast pre-equilibrium proton transfer.

Mechanism



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