

## Kinetics and Mechanism of Hydrolysis of Mono-2-chloro Aniline Phosphate in Buffer Medium

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The kinetics of the hydrolysis of 2-chloro aniline phosphate mono-ester has been carried out in buffer solution at 50 °C in the pH range 0.00 to 7.46. The rate of reaction increases with increase in pH up to 4.17. The maximum value at pH 4.17 is due to hydrolysis *via* mono-negative and neutral species. Neutral and mononegative species have been found to be reactive at pH 0.00 to 2.00 and 2.00-7.46, respectively; their dinegative species have been found to be inert. The estimated rate has been confirmed by those determined from specific rate and fractions of the neutral species agree closely with the experimental rates. Bond fission, molecularity have been supported by Arrhenius parameters, solvent effect. The results suggest that the hydrolysis of monoester occurs by the cleavage of P-N bond.

**Key Words:** Kinetics, Buffer medium, Mono-2-chloro aniline phosphate.

### INTRODUCTION

Phosphate esters are known to be an integral part of a number of biologically active molecules ranging from DNA and RNA to pesticides up to nerve agents<sup>1-3</sup>. As a consequence, the reactions that involve phosphate esters play leading roles in the chemical processes of life<sup>1-3</sup>, in energy metabolism and in various cellular signal transduction pathways in biological systems<sup>4</sup>. The treatment of phosphate esters as fungicides not only reduces the occurrence of fungi and damage caused by them, but also promotes better growths<sup>5</sup> of plants by incorporation of phosphate residues in the form of C-O-P<sup>6-8</sup> and C-N-P<sup>9,10</sup> linkages of more complex biologically important molecules of DNA<sup>11</sup> and RNA<sup>12</sup>. Organophosphates are used for smoke generation<sup>13</sup>, floor polishes and as a plasticizer in rubber and plastics<sup>14</sup>, pesticides<sup>15</sup>, additives for petroleum and corrosion inhibitors<sup>16</sup> and also used as an additives in the textile and clothing of uranium and plutonium from other radionuclides in nuclear fuel processing<sup>14</sup>. The ATP era of biochemical development is due to the adenosine triphosphate involved in the numerous biological activities.

### EXPERIMENTAL

Mono-2-chloro aniline phosphate (Ba-salt) was prepared by treating 2-chloro aniline with P<sub>2</sub>O<sub>5</sub> in benzene<sup>17</sup> which is used as a solvent. Kinetic study of the

hydrolysis of mono-2-chloro aniline phosphate is carried out at 50 °C employing  $5 \times 10^{-4}$  mol dm<sup>-3</sup> solution of the monoester in aqueous medium. The buffer solutions were maintained using appropriate mixture of KCl, COOH·C<sub>6</sub>H<sub>4</sub>·COOK, NaOH and H<sub>3</sub>BO<sub>3</sub>. Allen's modified method<sup>18</sup> was used for spectrophotometric determination of inorganic phosphate. All the chemicals used were of AR grade.

## RESULTS AND DISCUSSION

Hydrolysis of mono-2-chloro aniline phosphate has been studied at 50 °C in the pH range 0.00 to 7.46 using suitable buffers. Pseudo first order rate coefficients are shown in Table-1. The rate of reaction increases with the increase in pH up to 4.17. The maximum value at pH 4.17 is due to hydrolysis *via* mononegative species and dissociation of neutral species. After pH 4.17 the fall in rates is due to the inertness of the dinegative species<sup>19</sup>. The neutral and mononegative species at different pH rates are calculated from the eqns. 1 and 2:

$$K_N = K_{NO} \cdot N/(N+M) \quad (1)$$

$$K_M = K_{MO} \cdot M/(M+N) \quad (2)$$

where  $K_{NO}$  is specific neutral rate,  $K_{MO}$  is the specific mononegative rate at pH 4.17 and  $N/(N+M)$ ,  $M/(M+N)$  are the fraction of neutral and mononegative species, respectively. The results summarized in Table-1 show that there is close agreement between calculated and experimental rates. The value of specific neutral rates ( $K_{NO}$ ) was determined from the relation:

$$K_e = K_{MO} \cdot M/(M+N) + K_{NO} \cdot N/(N+M) + K_H^+ \cdot C_H^+ \quad (3)$$

where,  $K_e$  is experimental rate. There is good agreement of  $K_{NO}$  values obtained by eqn. 3 and ionic strength data. The value of  $K_{NO}$  determined by eqn. 3 is  $4.58 \times 10^{-3}$  min<sup>-1</sup> at different pH from 0.00 to 1.00 and the value of  $K_{NO}$  obtained from ionic strength data is  $5.0 \times 10^{-3}$  min<sup>-1</sup>. It is clear from Table-1 that in the region pH 0.00 to 1.00, hydrolysis governed by neutral, conjugate acid and mononegative species. In the region pH 1.00 to 1.24, the reactions proceed *via* neutral and mononegative species. In the region pH 1.24-7.46, only mononegative species are reactive. Kinetic rate laws for the hydrolysis of mono-2-chloro aniline phosphate monoester may be represented as:

In the region pH 0.00 to 1.00

$$K_e = K_H^+ C_H^+ + 6.65 \times 10^{-3} \cdot M/(M+N) + 4.58 \times 10^{-3} \cdot N/(N+M)$$

In the region pH 1.00 to 1.24

$$K_e = 6.65 \times 10^{-3} \cdot M/(M+N) + 4.58 \times 10^{-3} \cdot N/(N+M)$$

In the region pH 1.24 to 4.17

$$K_e = 6.65 \times 10^{-3} \cdot M/(M+N)$$

Table-2 shows a significant rise in rates with increase in dioxane percentage. This may be due to better proton donating capacity of dioxane than the water. Effect of solvent on the rate of hydrolysis may, therefore, be taken to imply a bimolecular nucleophilic reaction with the formation of a transition state in which the charge is dispersed. This is in accordance with Chanley's observations<sup>20</sup>.

TABLE-1  
ESTIMATED AND EXPERIMENTAL RATES OF THE HYDROLYSIS OF MONO-2-  
CHLORO ANILINE PHOSPHATE (Ba-salt) *via* NEUTRAL AND MONONEGATIVE  
SPECIES AT DIFFERENT pH VALUES AT 50 °C

pH	M/(M+N)	N/(N+M)	$K_M \times 10^3$	$K_N \times 10^3$	$K_H^+ C_H^+ 10^3$	$K_e \times 10^3$ Est.	$K_e \times 10^3$ Ext.	$3 + \log K_e$ Est.	$3 + \log K_e$ Ext.
0.00	0.063	0.937	0.42	4.290	12.74	17.45	19.27	1.24	1.28
0.30	0.119	0.881	0.79	4.030	5.71	10.53	10.91	1.02	1.04
0.70	0.253	0.747	1.68	3.420	2.14	7.24	7.20	0.86	0.86
1.00	0.403	0.597	2.68	2.730	1.05	6.46	5.10	0.81	0.71
1.24	0.540	0.450	3.59	2.060	–	3.59	3.91	0.55	0.59
2.20	0.915	0.085	6.08	0.390	–	6.08	4.36	0.78	0.64
3.33	0.993	0.007	6.60	0.030	–	6.60	5.54	0.82	0.74
4.17	0.999	0.001	6.64	0.004	–	6.64	6.65	0.82	0.82
5.60	0.980	–	6.52	–	–	6.52	5.58	0.81	0.75
6.43	0.850	–	5.65	–	–	5.65	4.35	0.75	0.64
7.46	0.340	–	2.26	–	–	2.26	2.37	0.35	0.37

TABLE-2  
RATE OF HYDROLYSIS OF MONO-2-CHLORO ANILINE  
PHOSPHATE IN BUFFER MEDIA AT 50 °C

pH	Dioxane (%)	$K_e \times 10^3 \text{ min}^{-1}$	pH	Dioxane (%)	$K_e \times 10^3 \text{ min}^{-1}$
1.24	0.0	3.91	4.17	0.0	6.65
	5.0	4.09		5.0	6.99
	10.0	4.35		10.0	7.40
	15.0	4.73		15.0	7.77
	20.0	5.82		20.0	8.28

Arrhenius parameter for hydrolysis *via* neutral and mononegative species are summarized in Table-3 which are in favour of a bimolecular reaction.

TABLE-3  
ARRHENIUS PARAMETER FOR THE HYDROLYSIS OF MONO-2-CHLOROANILINE  
PHOSPHATE (Ba-salt) *via* NEUTRAL & MONONEGATIVE SPECIES AT 50 °C

pH	E (kcal/mol)	A ( $\text{s}^{-1}$ )	$-\Delta S^\ddagger$ (e.u.)
1.24	8.24	$8.67 \times 10^4$	46.29
4.17	10.52	$5.22 \times 10^6$	38.14

Tables 4 and 5 summarizes comparative kinetic rate data of other monoesters that undergo hydrolysis *via* neutral and mononegative species also supports the bimolecular nature of hydrolysis involving P-N bond fission.

TABLE-4  
COMPARATIVE KINETIC DATA FOR THE HYDROLYSIS OF SOME  
PHOSPHATE MONOESTER *via* THEIR NEUTRAL SPECIES

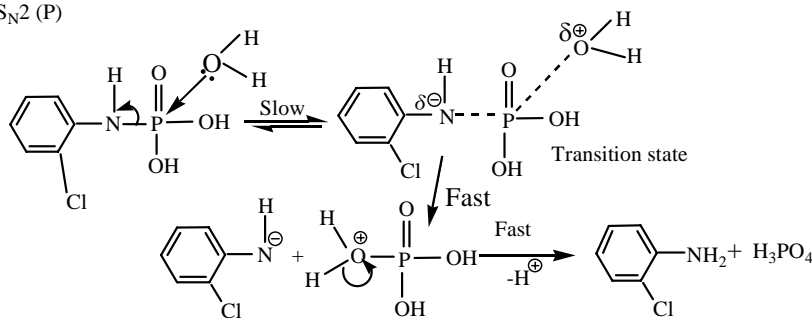
Phosphate monoesters	pH	E (kcal/mol)	$-\Delta S^\ddagger$ e. $\mu$ .	Molecularity	Bond fission
<i>p</i> -Toluidine	1.24	10.94	36.19	2	P-N
2-Chloroaniline	1.24	8.24	46.29	2*	Present work
2,5-Dimethylaniline	1.24	5.49	63.66	2	P-N
2,5-Dichloroaniline	1.24	5.03	64.77	2	P-N
2-Chloro-5-nitroaniline	1.24	3.38	69.57	2	P-N

TABLE-5  
COMPARATIVE KINETIC DATA FOR THE HYDROLYSIS OF SOME PHOSPHATE  
MONOESTER *via* THEIR MONONEGATIVE SPECIES

Phosphate monoesters	pH	E (kcal/mol)	$-\Delta S^\ddagger$ e. $\mu$ .	Molecularity	Bond fission
<i>p</i> -Toluidine	4.17	12.26	31.56	2	P-N
<i>o</i> -Toluidine	5.20	10.05	40.52	2	P-N
2-Chloro,5-nitroaniline	4.17	9.56	49.90	2	P-N
2-Chloroaniline	4.17	10.52	38.14	2*	Present work
Diisopropyl aniline	4.17	8.69	54.74	2	P-N

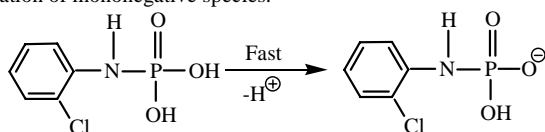
The probable reaction mechanism for the hydrolysis of mononegative and neutral species of mono-2-chloroaniline phosphate may be suggested as shown below:

(a) Bimolecular P-N bond fission (Bimolecular attack of water on phosphorous atom of the neutral species  $S_N2$  (P))

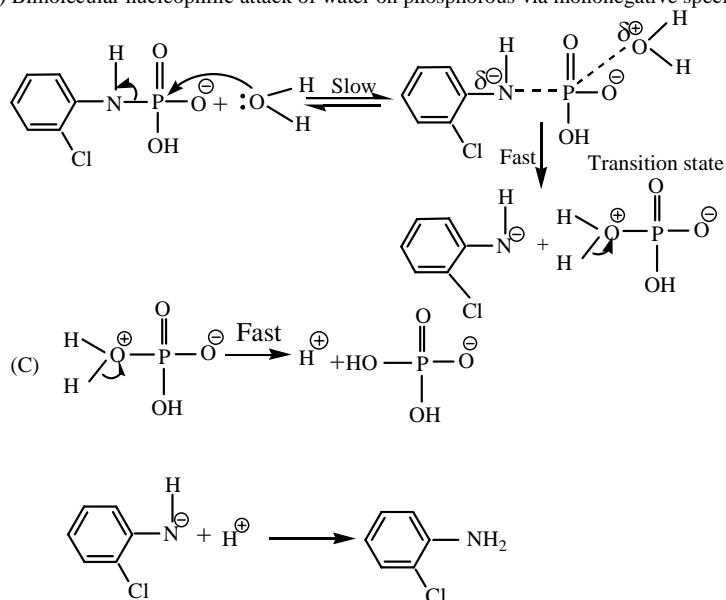


The mechanism of hydrolysis of these monoesters via mononegative species.

(a) formation of mononegative species.



(b) Bimolecular nucleophilic attack of water on phosphorous via mononegative species  $S_N2(P)$ .



Parent compound  
**Mechanism of hydrolysis**

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