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# A Kinetic and Mechanistic Study of Hydrolysis of Mono-6-Chloro-2,4-Dinitroaniline Phosphate in Buffer Medium

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**Abstract:** The kinetics of hydrolysis of Mono-6-chloro-2,4-dinitroaniline phosphate has been performed in buffer medium at 50°C in pH range 0.00 to 7.80. The rate of reaction increases with increase in pH up to 4.00. The maximum value at pH 4.00 has been found due to hydrolysis via mononegative and neutral species. Their dinegative species have been found to be inert. The theoretical rate determined from specific rate and fractions of the neutral species agree closely with the experimental rates. Molecularity, Bond fission have been supported by Arrhenius parameters. Results suggest that the hydrolysis of monoester occurs by the cleavage of P-N bond, which is strengthened by comparative kinetic rate data.

Key words: Kinetics, Hydrolysis; Buffer medium; Mono-6-chloro-2,4-dinitroaniline phosphate.

### 1. Introduction

Phosphate esters are the derivatives of orthophosphoric acid, which can form series of phosphate esters with the combination of alcohols, amines, phenols and their substituted compounds. They comprise a group of monoesters, diesters and triesters depending upon the number of hydroxyl groups which are present at phosphorus moiety respectively<sup>1</sup>. Monoesters and diesters have well-known role in genetic materials, in coenzymes, in energy reservoirs, and as intermediates in biochemical transformations however, triesters do not occur naturally but together with related compounds have found widespread use as herbicides and insecticides<sup>2-3</sup>. The chemistry of phosphate ester compounds is a subject of great attention, on account of their versatile applications in various fields<sup>4-8</sup>. The cleavage of phosphate ester bond is an essential reaction in biological systems<sup>9</sup> and investigation of its reaction mechanism in aqueous solution has been the subject of great experimental and theoretical efforts<sup>10-11</sup>. Hydrolysis is an important chemical process by which any compound reacts with water to form a new bond by cleavage of old bond in original molecule. Phosphate ester hydrolysis is one of the very important chemical and biochemical reaction<sup>12</sup>. Hydrolysis of phosphate ester is a subject of kinetic study due to their uses in engineering, agricultural, medicinal and pharmaceutical chemistry<sup>2-8</sup>. In present investigation the hydrolytic bond cleavage of mono-6-chloro-2,4-dinitroaniline phosphate has been studied in buffer medium.

### 2. Experimental

Mono-6-chloro-2,4-dinitroaniline phosphate (Ba-salt) was synthesized by treating 6-chloro-2, 4-dinitroaniline with  $P_2O_5$  in 1:1 mole ratio by weight in benzene solvent<sup>13</sup>. Kinetic study of the hydrolysis of Mono-6-chloro-2,4-dinitroaniline phosphate was carried out at 50 ±0.05°C by employing 5 x 10<sup>-4</sup> mol dm<sup>-3</sup> concentration of monoester in aqueous medium. The buffer solutions were maintained using appropriate

mixture of KCl, HCl, NaOH and  $H_3BO_3$ . Sverre and Stene<sup>14</sup> have measured pH values of buffer solutions at 20°C and 150°C. The interpolated values of these buffer solutions at 50°C were used. Allen's modified method<sup>15</sup> was used for determination of inorganic phosphate spectrophotometrically. All the chemicals used were of AR grade.

#### 3. Results and Discussion

Hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate has been studied at 50°C in the pH range 0.00 to 7.80 in aqueous medium. Pseudo first order rate coefficients are summarized in Table 1 and pH log rate profile for neutral and mononagative species has been shown by Figure 1. The rate of reaction increases with the increase in pH, it attains maximum value at pH 4.00 and then decreases due to the inertness of dinegative species<sup>16</sup>. The rate maximum at pH 4.00 is due to hydrolysis via mononegative species and dissociation of neutral species into mononegative species is almost complete at this pH. A slight deviation of experimental rate in pH range 0.00 to 1.00 has been found due to the incursion of neutral species. The rate of neutral and mononegative species at different pH are calculated from equation 1 and 2-

$$k_{\rm N} = k_{\rm No} \frac{\rm N}{\rm N+M}$$
(1)  
$$k_{\rm M} = k_{\rm Mo} \frac{\rm M}{\rm M+N}$$
(2)

Where  $k_{No}$  is specific neutral rate,  $k_{Mo}$  is the experimental rate (specific mononegative rate) at pH 4.00 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 following equation,

$$k = k_{\rm Mo} \frac{M}{M+N} + k_{\rm No} \frac{N}{N+M} + k_{\rm H+} C_{\rm H+}$$
 (3)

Where, k is experimental rate. There is good agreement between values of specific neutral rate  $k_{No}$  determined by equation 3 is 4.97 x  $10^{-3}$  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 4.27 x  $10^{-3}$  min<sup>-1</sup>. It is clear from results (Table 1) that in the pH range 0.00 to 1.00, hydrolysis is governed by neutral, conjugated acid and mononegative species. In the pH range 1.00 to 1.20, the reaction moves forward via neutral and mononegative species. In the pH range 1.20 to 7.80, only mononegative species are reactive.

**Table 1:** Estimated and experimental rates of the hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate (Ba-salt) via neutral and mononegative species at 50°C

pН	M/(M+N)	N/(N+M)	$k_{\rm M} { m x10}^3$	$k_{\rm N} {\rm x} 10^3$	$k_{\rm H}^{+} {\rm C_{H}}^{+}$	$k x 10^3$	$k x 10^3$	3+logk	3+logk
			$(\min^{-1})$	$(\min^{-1})$	$x10^{3}$	$(\min^{-1})$	$(\min^{-1})$	Est.	Exp.
					$(\min^{-1})$	Est.	Exp.		
0.00	0.06	0.94	0.71	4.67	20.89	26.27	29.60	1.42	1.47
0.30	0.12	0.88	1.43	4.37	10.00	15.80	17.33	1.20	1.24
0.70	0.25	0.75	2.98	3.73	3.80	10.51	9.88	1.02	0.99
1.00	0.40	0.60	4.76	2.98	1.86	9.60	6.94	0.98	0.84
1.20	0.54	0.45	6.43	2.24	-	8.67	7.88	0.94	0.90
2.20	0.92	0.09	10.95	0.45	-	11.40	8.63	1.06	0.94
3.20	0.99	0.01	11.78	0.05	-	11.83	10.23	1.07	1.01
4.00	1.00	0.00	11.90	-	-	11.90	11.90	1.08	1.08
5.20	0.98	-	11.66	-	-	11.66	10.21	1.07	1.01
6.00	0.85	-	10.12	-	-	10.12	8.79	1.00	0.94
7.80	0.34	-	4.05	-	-	4.05	6.13	0.61	0.79



**Figure 1.** pH log rate profile for the hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate at 50°C

Kinetic rate laws for the hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate monoester may be represented as:

In the region pH 0.00 to 1.00

$$k = k_{\rm H}^+ C_{\rm H}^+ + 11.90 \text{ x } 10^{-3} \frac{\text{M}}{\text{M} + \text{N}} + 4.27 \text{ x } 10^{-3} \frac{\text{N}}{\text{N} + \text{M}}$$

In the region pH 1.00 to 1.20

$$k = 11.90 \times 10^{-3} \frac{M}{M + N} + 4.27 \times 10^{-3} \frac{N}{N + M}$$

In the region pH 1.20 to 7.80

$$k = 11.90 \times 10^{-3} - \frac{M}{M + N}$$

Kinetic runs of different dioxane-water compositions (V/V) have been designed to study the effect of solvent on hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate via neutral and mononegative species at pH 1.20 and 4.00 respectively. It is clear from the results that the rate increases with increase in dioxane content of the medium i.e. with the decrease in polarity of medium. This may be due to better proton donating capacity of dioxane than the water. According to quantitative theory of Ingold<sup>17</sup> this increase is in favour of formation of such a transition state in which charges are dispersed. Rate coefficients have been summarized in Table 2.

Table 2: Effect of solvent on the rate of hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate

pН	% of Dx	$k \ge 10^3$	3+logk	pН	% of Dx	$k \ge 10^3$	$3 + \log k$
	00	7.88	0.90		00	11.90	1.08
1.20	10	8.61	0.94	4.00	10	12.76	1.11
	20	9.51	0.98		20	14.07	1.15
	30	10.63	1.03		30	15.37	1.19
	40	11.72	1.07		40	16.89	1.23

In order to examine the effect of temperature on rate of hydrolysis of neutral and mononegative species of mono-6-chloro-2,4-dinitroaniline phosphate kinetic runs were made at different temperatures from 40 to  $60^{\circ}$ C with the interval of 5°C at pH 1.20 and 4.00. Figure 2 illustrates the plots between log rate coefficients and reciprocal of absolute temperatures. The linearity of plot proves the validity of Arrhenius equation. The slope value of plot was used to determine the Arrhenius parameters, which are shown in Table 3. Small magnitude of energy of activation and high negative value of entropy of Activation clearly show bimolecular nature of reaction.

**Table 3:** Arrhenius parameters for the hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate via neutral and mononegative species

pH	Slope	Ea (Kcal/mol)	$A(Sec^{-1})$	- $\Delta$ S <sup>≠</sup> (e.u.)
1.20	-0.022	10.07	$3.08 \text{ x} 10^6$	39.16
4.00	-0.025	11.44	$3.96 \text{ x} 10^7$	34.08



Figure 2. The plot of  $3+\log k$  versus  $1/T \ge 10^{-5}$  for hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate

Hydrolysis of mono-6-chloro-2,4-dinitroaniline phosphate may undergo either by P-N or C-N bond fission. Comparative kinetic rate data for the hydrolysis of other monoesters studied kinetically shown in Table 4 and 5 and illustrated by Figure 3 and 4. The point of mono-6-chloro-2, 4-dinitroaniline phosphate lies on the linear curve of those monoesters which are known to undergo hydrolysis via P-N bond fission. Thus P-N rather than C-N bond fission appears to be more probable.

Phosphate monoesters	pН	$E_a$	$-\Delta S^{\neq}$ e.u.	Molecularity	Bond Fission
		(Kcal/mol)			
2, 5-dichloro aniline	1.24	5.03	64.77	2	P-N
2, 5-dimethyl aniline	1.24	5.49	63.66	2	P-N
Di isopropylaniline	1.24	6.86	60.33	2	P-N
6-chloro-2,4-diniroaniline	1.24	10.06	39.16	2	Present work
<i>p</i> -toluidine	1.20	10.94	36.19	2	P-N
2-methyl-5-nitroaniline	1.24	10.98	35.85	2	P-N

Table 4: Comparative kinetic data for the hydrolysis of some phosphate monoesters via neutral species

Phosphate monoesters	рН	E <sub>a</sub> (Kcal/mol)	$-\Delta S^{\neq}$ e.u.	Molecularity	Bond Fission
<i>P</i> - methoxyaniline	4.17	9.57	37.96	2	P-N
O-Toluidine	4.17	10.05	40.52	2	P-N
2-chloroaniline	4.17	10.52	38.14	2	P-N
6-chloro-2,4-diniroaniline	4.00	11.44	34.08	2	Present work
<i>p</i> -toluidine	4.17	12.26	31.56	2	P-N
<i>p</i> -chloroaniline	4.17	19.80	6.30	2	P-N

**Table 5:** Comparative kinetic rate data for the hydrolysis of some phosphate monoesters via mononegative species



Figure 3. Isokinetic relationship plot for the hydrolysis of some phosphate monoesters via their neutral species



Figure 4. Isokinetic relationship plot for the hydrolysis of some phosphate monoesters via their mononegative species

The probable reaction mechanism for the hydrolysis of neutral and mononegative species of mono-6-chloro-2,4-dinitroaniline phosphate may be suggested as shown in chart-1 and chart-2.

Chart-1: Mechanism of hydrolysis via neutral species



Chart-2: Mechanism of hydrolysis of esters via mononegative species

(a) Formation of mononegative species



(b) Bimolecular P-N bond fission (Bimolecular attack of water on phosphorous atom of neutral neutral species  $S_N^2$ ).



(c)



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