



Hydrolytic Study of Mono-2, 3-dichloroaniline Phosphate in Buffer Medium

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ABSTRACT

The hydrolytic study of mono-2, 3-dichloroaniline phosphate has been carried out in buffer solution at 60°C in the pH range 0.00 to 7.45. The rate of reaction increases with increase in pH up to pH 4.10. The maximum value at pH 4.10 is due to hydrolysis via mononegative and neutral species. After pH 4.10 the rate of reaction decreases due to dissociation of mononegative species into dinegative species. The nature of dinegative species has been found to be inert. The experimental and theoretical rate values are in good agreement. Molecularity, bond fission have been supported by Arrhenius parameters. The monoester involves P-N bond fission, which is strengthened by comparative kinetic rate data.

Keywords: Hydrolysis; Buffer medium; Mono-2, 3-dichloroaniline phosphate; Mononegative species.

INTRODUCTION

Phosphate esters are compounds with interesting biological and pharmacological properties and are widely used as pesticides, drugs and nerve gases. Their accumulation and their effect in the environment are of great importance [1-2]. Phosphate esters are most naturally occurring phosphorous compounds. Many of the essential chemicals in life processes are phosphate esters. These include the genetic substances DNA and RNA as well as cyclic AMP (adenosine monophosphate) [3]. Phosphate esters are important surfactants, which are widely used in many fields, as chemical fibers, daily chemical products, plastic and paper-making [4-5]. The hydrolytic cleavage of phosphoric esters is an important reaction in both environmental and biological chemistry [6-7]. The chemistry of substituent exchange, such as hydrolysis, at phosphorus (V) centres has received considerable attention because such processes occur in many crucial enzymatic reactions and are relevant to the detoxification of some pesticides and chemical weapons [8-9]. In present investigation the hydrolytic bond cleavage of mono-2, 3-dichloroaniline phosphate has been studied in buffer medium.

MATERIALS AND METHODS

2,3-dichloroaniline (parent compound) used for the synthesis was obtained from Sigma Aldrich. The solutions of ammonium molybdate (98% Sigma Aldrich) and 2, 4-diaminophenol dihydrochloride (98% Sigma Aldrich) were prepared in triply distilled water and used for the kinetic measurements. All other chemicals used during the experiment were of analytical grade.

Mono-2, 3-dichloroaniline phosphate was synthesized in the laboratory by Cavalier [10] method. The method involves the reaction of parent compound (2, 3-dichloroaniline) with phosphorylating agent phosphorus pentoxide (P_2O_5) in 1:1 mole ratio. The confirmation of synthesized compound was done by elemental and IR spectrum analysis. Kinetic study of the hydrolysis of mono-2, 3-dichloroaniline phosphate was carried out at $60^\circ C$ employing 5×10^{-4} mol dm^{-3} solution of the monoester in aqueous medium. The buffer solutions were maintained using appropriate mixture of KCl, $COOH.C_6H_4.COOK$, NaOH and H_3BO_3 . The inorganic phosphate produced during ester hydrolysis was determined spectrophotometrically using Allen's modified method [11].

RESULTS AND DISCUSSION

Hydrolysis in Buffer medium: The Hydrolysis of mono-2,3-dichloroaniline phosphate has been studied at $60^\circ C$ in the pH range 0.00 to 7.45 in aqueous medium. Pseudo first order rate coefficients are summarized in table 1 and pH log rate profile for neutral and mononegative species has been shown by figure 1. The rate of reaction increases with the increase in pH, it attains maximum value at pH 4.10 and then decreases due to the inertness of dinegative species [12]. The rate maximum at pH 4.10 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.

$$k_N = k_{N_0} \frac{N}{N+M} \quad (1)$$

$$k_M = k_{M_0} \frac{M}{M+N} \quad (2)$$

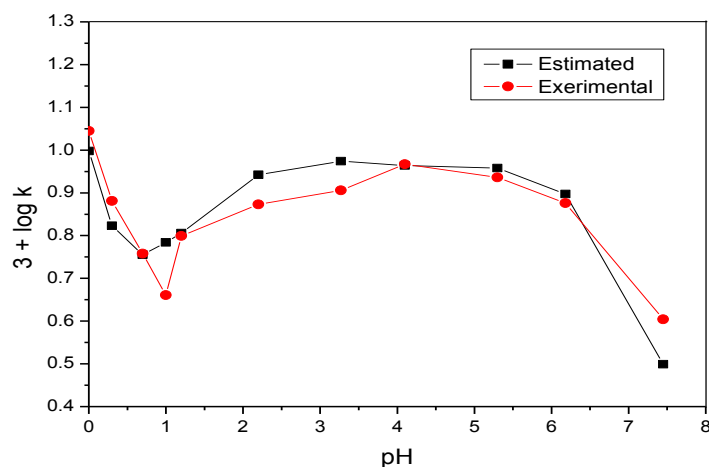
Where k_{N_0} is specific neutral rate, k_{M_0} is the experimental rate (specific mononegative rate) at pH 4.10 and $N/(N+M)$, $M/(M+N)$ are the fraction of neutral and mononegative species, respectively. The results summarized in table-1 show that there is close agreement between calculated and experimental rates. The value of specific neutral rates (k_{N_0}) was determined from the following equation:

$$k = k_{M_0} \frac{M}{M+N} + k_{N_0} \frac{N}{N+M} + k_{H^+} C_{H^+} \quad (3)$$

Where, k is experimental rate. There is good agreement between values of specific neutral rate k_{N_0} determined by equation 3, $3.03 \times 10^{-3} \text{ min}^{-1}$ at different pH from 0.00 to 1.00 and the value of k_{N_0} obtained from ionic strength data is $3.07 \times 10^{-3} \text{ min}^{-1}$. 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 7.45, only mononegative species are reactive.

Table 1. Estimated and experimental rates of the hydrolysis of mono-2,3-dichloroaniline phosphate via neutral and mononegative species at 60°C.

pH	N/N+M	M/M+N	$k_M \times 10^3$ (min ⁻¹)	$k_N \times 10^3$ (min ⁻¹)	$k_{H^+} \cdot C_{H^+}$ $\times 10^3$ (min ⁻¹)	$k_e \times 10^3$ (min ⁻¹) (Estd.)	$k_e \times 10^3$ (min ⁻¹) (Expt.)	3+log k_e (Estd.)	3+log k_e (Expt.)
0.00	0.937	0.063	0.584	2.876	6.501	9.961	11.10	0.998	1.045
0.30	0.881	0.119	1.104	2.705	2.847	6.656	7.604	0.823	0.881
0.70	0.747	0.253	2.347	2.293	1.052	5.692	5.732	0.755	0.758
1.00	0.597	0.403	3.739	1.833	0.512	6.084	4.586	0.784	0.661
1.20	0.450	0.540	5.011	1.381	-	6.392	6.308	0.806	0.799
2.20	0.085	0.915	8.491	0.261	-	8.752	7.461	0.942	0.873
3.27	0.007	0.993	9.215	0.215	-	9.430	8.056	0.974	0.906
4.10	0.001	0.999	9.270	0.003	-	9.273	9.280	0.964	0.967
5.30	-	0.980	9.094	-	-	9.094	8.635	0.958	0.936
6.18	-	0.850	7.888	-	-	7.888	7.513	0.897	0.876
7.45	-	0.340	3.155	-	-	3.155	4.021	0.499	0.604

**Figure 1.** pH log rate profile for the hydrolysis of mono-2,3-dichloroaniline phosphate at 60°C.

Kinetic rate laws for the hydrolysis of mono-2,3-dichloroaniline phosphate may be represented as:
In the region pH 0.00 to 1.00

$$k = k_{H^+} \cdot C_{H^+} + 9.28 \times 10^{-3} \frac{M}{M+N} + 3.07 \times 10^{-3} \frac{N}{N+M}$$

In the region pH 1.00 to 1.20

$$k = 9.28 \times 10^{-3} \frac{M}{M+N} + 3.07 \times 10^{-3} \frac{N}{N+M}$$

In the region pH 1.20 to 7.45

$$k = 9.28 \times 10^{-3} \frac{M}{M+N}$$

Solvent Effect: Kinetic runs of different dioxane-water compositions (v/v) have been designed to study the effect of solvent on hydrolysis of mono-2,3-dichloroaniline phosphate via neutral and mononegative species at pH 1.20 and 4.10 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 [13] 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-2,3-dichloroaniline phosphate.

pH	% of Dioxane (v/v)	$k \times 10^3$ (min^{-1})	pH	% of Dioxane (v/v)	$k \times 10^3$ (min^{-1})
1.20	0	6.31	4.10	0	9.28
	5	7.22		5	10.18
	10	8.16		10	11.26
	15	8.83		15	11.85
	20	9.50		20	12.48

Temperature Effect: In order to study the effect of temperature on rate of hydrolysis of neutral and mononegative species of mono-2,3-dichloroaniline phosphate, kinetic runs were made at different temperatures from 40 to 60°C with the interval of 5°C at pH 1.20 and 4.10. 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-2,3-dichloroaniline phosphate via neutral and mononegative species.

pH	Slope	E_a (kJ mol^{-1})	A (Sec^{-1})	$-\Delta S^\ddagger$ ($\text{J K}^{-1} \text{mol}^{-1}$)
1.20	-0.0288	55.14	2.80×10^6	130.79
4.10	-0.0314	60.12	2.49×10^7	112.63

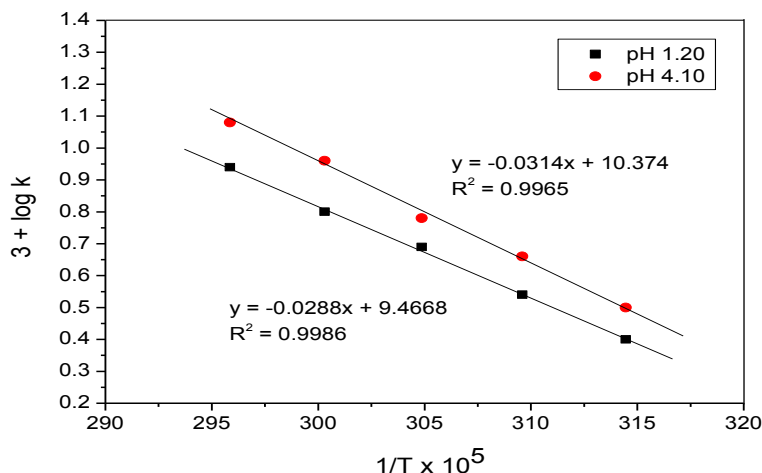


Figure 2. The plot of $3 + \log k$ versus $1/T \times 10^5$ for hydrolysis of mono-2,3-dichloroaniline phosphate.

Bond Fission: Hydrolysis of mono-2,3-dichloroaniline 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-2,3-dichloroaniline 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.

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

Phosphate monoesters	pH	E_a (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	Molecularity	Bond fission
6-chloro-2,4-dinitroaniline	1.24	42.09	163.84	2	P-N
<i>p</i> -toluidine	1.20	45.77	151.42	2	P-N
2-methyl-5-nitroaniline	1.24	45.94	149.99	2	P-N
2-chloroaniline	1.24	34.48	193.72	2	P-N
N-ethyl- <i>o</i> -toluidine	1.20	38.28	180.33	2	P-N
2,3-dichloroaniline	1.20	55.14	130.79	2*	Present work

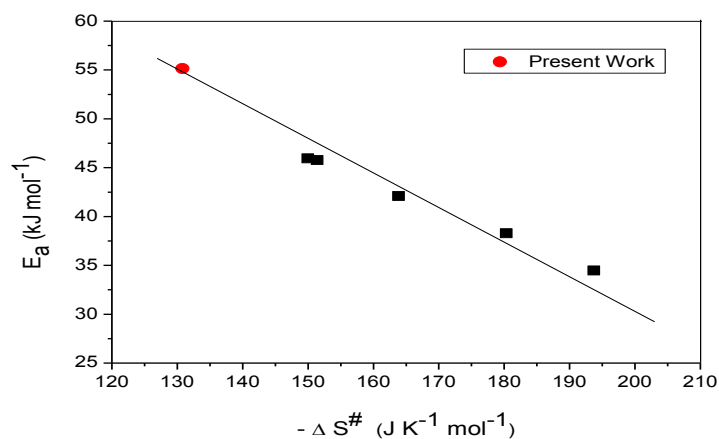


Figure 3. Isokinetic relationship plot for the hydrolysis of some phosphate monoesters via their neutral species

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

Phosphate monoesters	pH	E_a (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	Molecularity	Bond fission
6-chloro-2,4-dinitroaniline	4.00	47.86	142.59	2	P-N
<i>p</i> -toluidine	4.17	51.29	132.05	2	P-N
<i>p</i> -methoxyaniline	4.17	40.04	158.82	2	P-N
N-ethyl- <i>o</i> -toluidine	4.00	57.45	116.39	2	P-N
2,3-dichloroaniline	4.10	60.12	112.63	2*	Present work

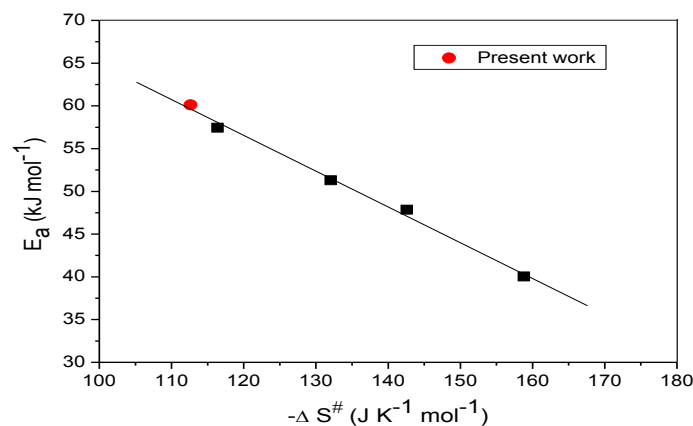
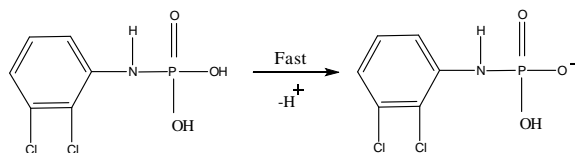


Figure 4. Isokinetic relationship plot for the hydrolysis of some phosphate monoesters via their mononegative species.

Mechanism: The probable reaction mechanism for the hydrolysis of mononegative species and neutral species of mono-2,3-dichloroaniline phosphate may be suggested as given below.

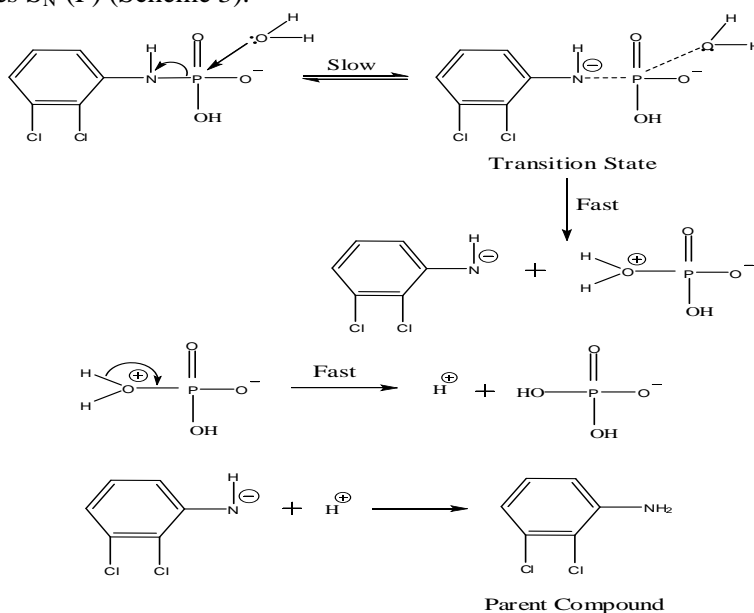
Mechanism of hydrolysis of monoester via mononegative species: Formation of mononegative species (Scheme 1):



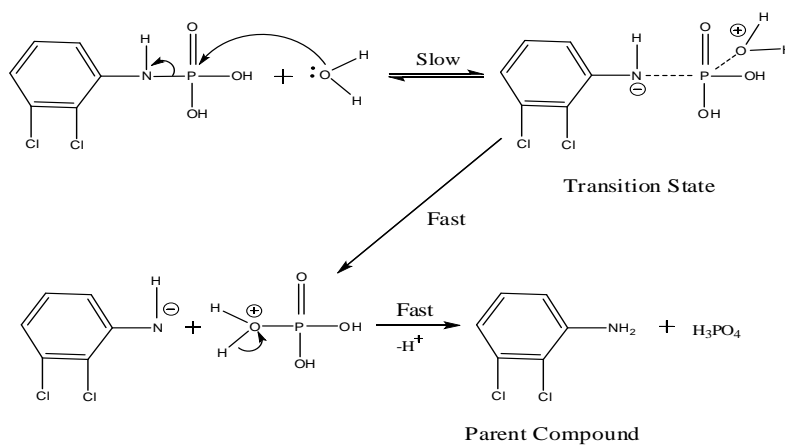
Scheme 1

Bimolecular nucleophilic attack of water on phosphorus atom of the mononegative species $S_N^2(P)$ (Scheme 2).

Mechanism of hydrolysis of monoester via neutral species: Bimolecular attack of water on phosphorus atom of the neutral species $S_N^2(P)$ (Scheme 3).



Scheme 2



Scheme 3

APPLICATIONS

The probable reaction mechanism and rates of reactions obtained from the study of hydrolytic reactions have fundamental importance. The study may provide substantial basis for understanding the reactions of phosphate ester and the ways in which the ester can be used in industrial and agricultural branches of chemistry due to its various applications.

CONCLUSIONS

Kinetics of the hydrolysis of mono-2, 3-dichloroaniline phosphate in the range of pH 1.00 to 7.45 was found to be reactive via neutral and mononegative species. The maximum value at pH 4.10 is due to hydrolysis via mononegative species and dissociation of neutral species. After pH 4.10 the fall in rates is due to the inertness of the dinegative species. The estimated rate has been confirmed by those determined from specific rate and fractions of the neutral species agree closely with experimental rates. Bond fission, molecularity have been supported by Arrhenius parameters and solvent effect. Mono-2,3-dichloroaniline phosphate involves P-N bond fission, which is strengthened by comparative kinetic rate data.

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