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Kinetic Study of Hydrolysis of Mono-3,5-dimethylaniline Phosphate in Buffer Medium

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In present investigation, hydrolysis of mono-3,5-dimethylaniline phosphate was studied in buffer medium at 50 °C in pH range 0.00 to 7.68. The rate of hydrolysis was measured by determining the rate of inorganic phosphate by spectrophotometer. Pseudo first order rate coefficients were obtained. The rate of reaction increased with increase in pH up to 4.04. The maximum value at pH 4.04 is 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 fraction of the neutral species agree closely with the experimental rates. Bond fission and bimolecular nature of hydrolysis have been supported by Arrhenius parameters and study of solvent effect. The hydrolysis of monoester involves P-N bond fission, which is strengthened by comparative kinetic rate data.

Keywords: Hydrolysis, Buffer medium, Mononegative species, Mono-3,5-dimethylaniline phosphate.

INTRODUCTION

Phosphate esters are the derivatives of orthophosphoric acid, which can form a series of phosphate esters with alcohols, amines, phenols and their substituted compounds. Phosphate esters are important due to their versatile applications in various fields [1-6]. Many multi-ring phosphate ester heterocycles are used as pesticides [7], bactericides [8,9], antibiotics [10] and act as HIV protease inhibitors [11]. Phosphate esters have also achieved importance in industry as solvent and fuel additives for explosion control. These esters are also used as additives in the textile and clothing dyeing industry. Hydrolysis of phosphate ester is a subject of kinetic study due to their various uses in engineering, agricultural, medicinal and pharmaceutical chemistry. Therefore, phosphate esters have been the subject of extensive experimental [12] and theoretical [13] studies.

EXPERIMENTAL

Mono-3,5-dimethylaniline phosphate has been synthesized by Cavilier method [14]. Kinetic study of hydrolysis of mono-3,5-dimethylaniline phosphate has been studied at 50 ± 0.5 °C employing 5×10^{-4} mol dm^{-3} solution of the monoester in aqueous medium. The buffer solutions were prepared using appropriate mixture of KCl, COOH, C_6H_4, COOK, NaOH and H_3BO_3. The inorganic phosphate produced during hydrolysis has been determined spectophotometrically using Allen's modified method [15]. All the solutions have been prepared in triply distilled water. All the chemicals used were of AR grade.

RESULTS AND DISCUSSION

The kinetics of hydrolysis of mono-3,5-dimethylaniline phosphate has been studied in the range of pH 0.00 to 7.68 at 50 ± 0.5 °C. Pseudo-first-order rate constants obtained are shown in Table-1. From the result, it may be seen that the rate of reaction increases with the increase in pH up to 4.04. The maximum value at pH 4.04 is due to hydrolysis *via* mononegative species and dissociation of neutral species into mononegative species is almost complete at this pH. After pH 4.04 the fall in rates is due to the inertness of the dinegative species [16].

The rate of neutral and mononegative species at different pH are calculated from the eqns. 1 and 2:

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

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

where k_{N_o} is specific neutral rate, k_{M_o} (specific mononegative rate) is experimental rate at pH 4.04 and N/N + M and M/M + N are the fraction of neutral and mononegative species respectively. The value of specific neutral rate *i.e.* k_{N_o} was determined from the reaction:

$$k = k_{M_o} \frac{M}{M+N} + k_{N_o} \frac{N}{N+M} + k_{H^+} \cdot C_{H^+} \quad (3)$$

TABLE-1
ESTIMATED AND EXPERIMENTAL RATES OF THE HYDROLYSIS OF MONO-3,5-DIMETHYLANILINE PHOSPHATE *via* NEUTRAL AND MONONEGATIVE SPECIES AT DIFFERENT pH VALUES AT 50 °C

pH	M/(M + N)	N/(N + M)	$k_M \times 10^3$ (min^{-1})	$k_N \times 10^3$ (min^{-1})	$k_H^+C_H^+ \times 10^3$ (min^{-1})	$k \times 10^3$ (min^{-1}) Estd.	$k \times 10^3$ (min^{-1}) Expt.	3 + log k Estd.	3 + log k Expt.
0.00	0.06	0.94	0.50	2.75	13.93	17.18	16.45	1.24	1.22
0.30	0.12	0.88	0.99	2.58	6.61	10.18	10.24	1.01	1.01
0.70	0.25	0.75	2.07	2.20	2.56	6.83	6.52	0.83	0.81
1.00	0.40	0.60	3.30	1.76	1.27	6.33	5.10	0.80	0.71
1.22	0.54	0.45	4.46	1.32	–	5.78	5.66	0.76	0.75
2.20	0.92	0.09	7.60	0.26	–	7.86	6.34	0.90	0.80
3.35	0.99	0.01	8.18	0.03	–	8.21	7.57	0.91	0.88
4.04	1.00	0.00	8.26	–	–	8.26	8.26	0.92	0.92
5.36	0.98	–	8.09	–	–	8.09	6.78	0.91	0.83
6.16	0.85	–	7.02	–	–	7.02	5.82	0.85	0.76
7.68	0.34	–	2.81	–	–	2.81	4.41	0.45	0.64

where, k is experimental rate. There is good agreement between values of k_{N_o} determined by eqn. 3 and ionic strength data. The value of k_{N_o} determined by eqn. 3 is 2.93×10^{-3} min^{-1} at different pH 0.00 to 1.00 and the value of k_{N_o} obtained from ionic strength data is 2.10×10^{-3} min^{-1}. It is clear from Table-1 that in the region pH 0 to 1; the hydrolysis is governed by neutral, conjugate and mononegative species. In the region pH 1 to 1.2, the reactions proceed *via* neutral and mono negative species. In the region pH 1.20 to 7.68, only mono-negative species are reactive.

Kinetic rate law for the hydrolysis of mono-3,5-dimethylaniline phosphate may be represented as:

In the region pH 0 to 1:

$$k = k_{H^+} \cdot C_{H^+} + 8.26\times10^{-3}\frac{M}{M+N} + 2.93\times10^{-3}\frac{M}{N+M} \quad (4)$$

In the region pH 1 to 1.2:

$$k = 8.26\times10^{-3}\frac{M}{M+N} + 2.93\times10^{-3}\frac{N}{N+M} \quad (5)$$

In the region pH 1.20 to 7.68:

$$k = 8.26\times10^{-3}\frac{M}{M+N} \quad (6)$$

Effect of solvent: Table-2 shows a significant rise in rate constant with increase in dioxane percentage. This may be due to better proton donating capacity of dioxane than water. According to Chanley's observation [17], 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.

TABLE-2
RATE OF THE HYDROLYSIS OF MONO-3,5-DIMETHYLANILINE PHOSPHATE IN BUFFER MEDIA AT 50 °C

pH	Dioxane (%) v/v	$k \times 10^3$ (min^{-1})	pH	Dioxane (%) v/v	$k \times 10^3$ (min^{-1})
1.22	00	5.66	4.04	00	8.26
	05	7.51		05	10.28
	10	9.34		10	11.75
	15	11.86		15	13.16
	20	13.22		20	14.92

Temperature effect: In order to determine the Arrhenius parameters, kinetic runs were carried out at different temperatures at pH 1.22 and pH 4.04. Fig. 1 shows the plots between log rate constant and reciprocal of absolute temperature at pH 1.22 and pH 4.04. Linearity of the plot shows the validity of Arrhenius equation. Arrhenius parameters summarized in Table-3 are in favour of a bimolecular reaction.

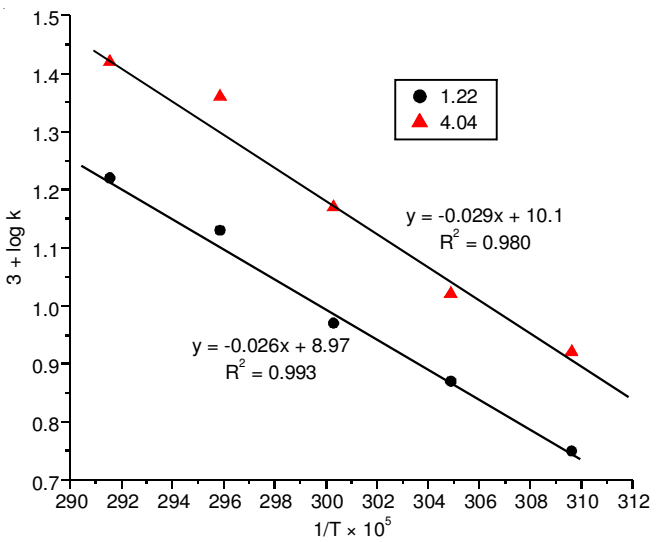


Fig. 1. Arrhenius plot for the hydrolysis of mono-3, 5-dimethylaniline phosphate

TABLE-3
ARRHENIUS PARAMETERS FOR THE HYDROLYSIS OF MONO-3,5-DIMETHYLANILINE PHOSPHATE *via* NEUTRAL AND MONONEGATIVE SPECIES AT 50 °C

pH	Slope	Parameters		
		E (kcal mol^{-1})	A (s^{-1})	$-\Delta S^{\neq}$ (e.u.)
1.22	-0.026	11.90	6.34×10^5	34.16
4.04	-0.029	13.27	7.80×10^7	29.16

A comparative kinetic rate data for the hydrolysis of some phosphate monoesters *via* neutral and mononegative species as described by Figs. 2 and 3 also supports the bimolecular nature of hydrolysis involving P-N bond fission.

The probable reaction mechanism for the hydrolysis of mononegative and neutral species of mono-3,5-dimethylaniline phosphate may be suggested as given below.

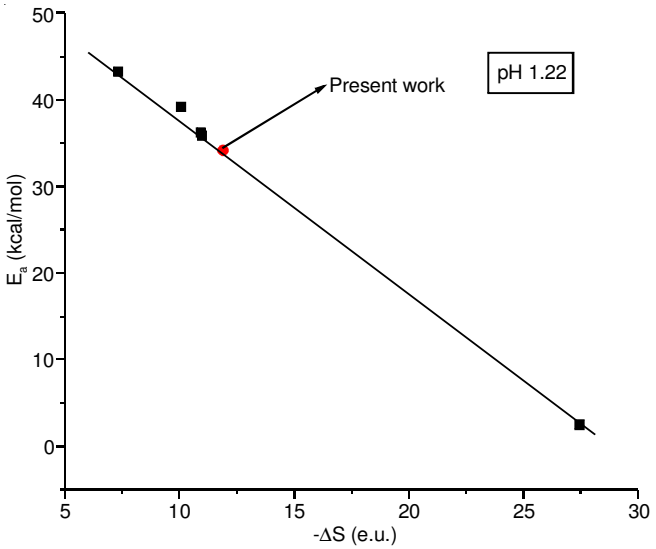


Fig. 2. Isokinetic relationship plot for the hydrolysis of some phosphate monoesters *via* their neutral species

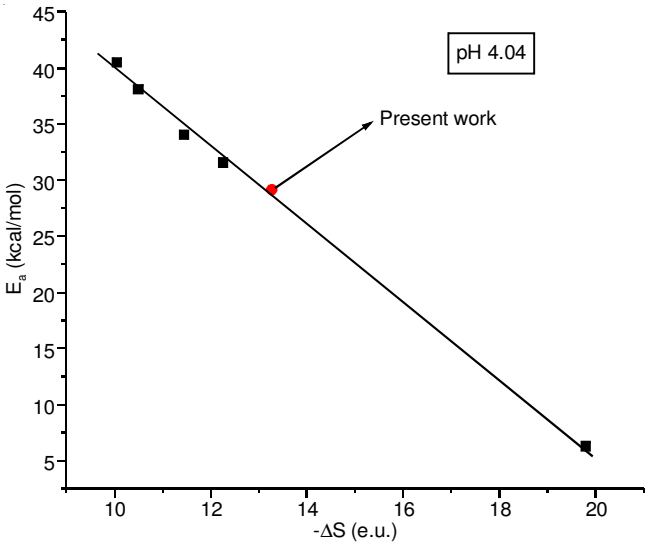
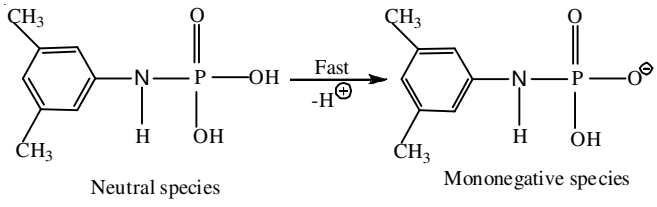


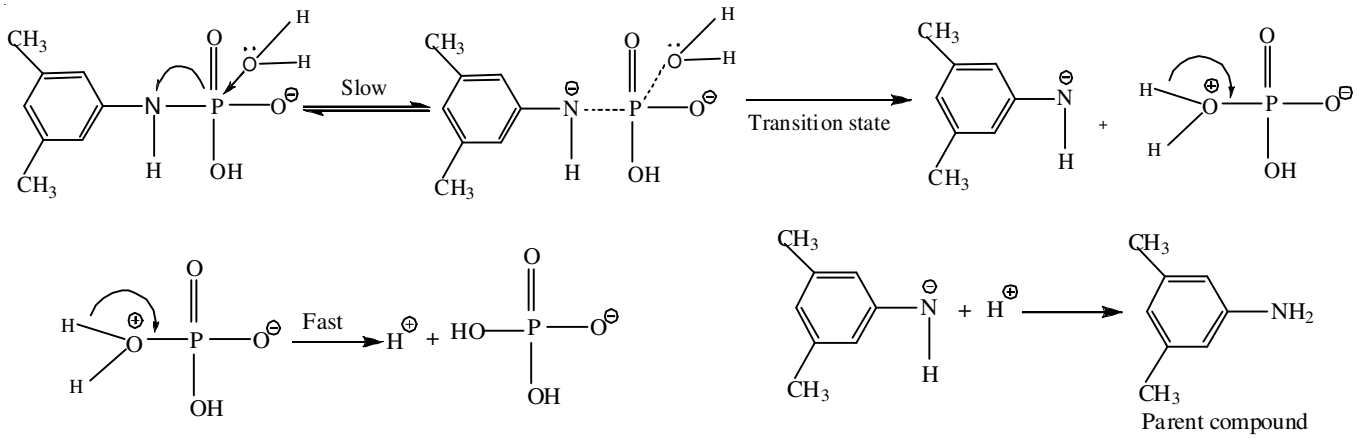
Fig. 3. Isokinetic relationship plot for the hydrolysis of some phosphate monoesters *via* their mononegative species



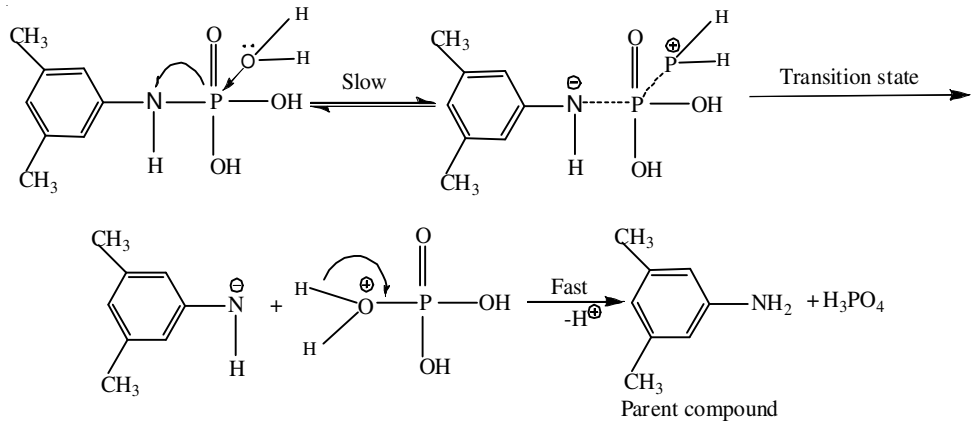
Formation of mononegative species

Conclusion

The neutral and mononegative species are found to be reactive in mono-3,5-dimethylaniline phosphate. The rate maximum value at pH 4.04 is due to conversion of neutral species into mononegative species. The estimated rates have been found to be in good agreement with experimental rates. A comparative kinetic rate data supports the bimolecular nature



Bimolecular nucleophilic attack of water on phosphorus *via* mononegative species S_N^2 (P)



Bimolecular attack of water on phosphorus atom of the neutral species S_N^2 (P)

of hydrolysis involving P-N bond fission. The probable reaction mechanism for the hydrolysis of mono-3,5-dimethylaniline phosphate *via* mononegative and neutral species has been suggested.

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