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Hydrolytic reactivity study of O,O-Diethyl-O-p-NO_2-phenyl phosphate ester in buffer media

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ABSTRACT

The organophosphorus compound under study, O, O-diethyl O-p-NO_2-phenyl phosphate was synthesized and characterized using suitable spectroscopic techniques. The hydrolysis is performed in the pH range 1.24 to 7.46in the presence of 1% dioxane-water mixture at $98(\pm0.5)^0$C. The hydrolytic reactivity study shows pseudo first-order rate coefficients and the maximum rate value was observed at pH 1.24 which is largely contributed by the neutral species only. The bimolecular nature of the present compound is further assisted by temperature, solvent, reagent and concentration effects studies. It is also understood that the hydrolysis is remarkably promoted by the action of nucleophilic fluoride ions [$S_E2(P)$].

Key words: Kinetics, Buffer media, Neutral species, Allen's modified method and Organophosphate esters

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INTRODUCTION

Organophosphorus compounds are commonly used as insecticides[1] and pesticides[2] even though they show extreme toxicity to human beings[3]. These specific organophosphate esters may contain C-O-P or C-N-P linkages or both. They are found to have useful applications as flame-retardants[4], plasticizers[5] and even as prodrugs[6]. Various reviews regarding the kinetics[7] and mechanisms of hydrolysis[8,9] of phosphate esters in neutral[10,11,12], alkaline[13,14] and acidic[15,16] media have been found from time to time. Several patterns are followed during hydrolysis depending upon the solvent[17], the pH range[18] or upon catalytically active additives. In most of the hydrolytic studies of aromatic phosphate ester, the P-O bond fission[19] occurs and the molecularity[20] may be either unimolecular or bimolecular reaction within the substrate ester and water. In most of the cases, neutral, protonated mono-negative and di-negative forms were found to be the reactive species.

MATERIALS AND METHODS

In the present study, the synthesis of O,O-diethyl O-p-NO_2-phenyl phosphate (paraoxon) was carried out by adopting the procedure performed by Batra and his co-workers[21] where a one-step method for the phosphorylation of 4-NO_2-phenol in a two-phase system using tetra-n-butyl ammonium bromide at room temperature. Characterization of the synthesized compound was performed by suitable spectroscopic techniques and found to be similar with the reported data.

The kinetic study during the hydrolysis of the above phosphate triester was carried out using Allen's modified method[22] for the quantitative estimation of phosphorus liberated as inorganic phosphoric acid. Spectronic-20^+ spectrophotometer was used for recording optical density measurements.

RESULTS AND DISCUSSION

Hydrolysis of O,O-diethyl O-p-NO_2-phenyl phosphate has been examined in the pH range 1.24 to 7.46 using suitable buffers in 1% dioxane-water mixture at $98(\pm0.5)^0$C. Fig-1 shows the pH log rate profile in which the rate of the reaction decreases gradually except at pH 2.50 and 5.60 where there are steep downfalls in reaction rate. This is the case of abnormal condition for triesters[23] where they usually show a rate maximum at pH 4.17. The graph clearly indicates that the rate of the reaction follows first-order.

Arrhenius parameters[24] have been determined for hydrolysis of O,O-diethyl O-p-NO_2-phenyl phosphate from rates at pH 1.24 at three varied temperatures. The calculated parameters(Table-1) include low E value; high frequency factor (A); high negative value of activation ($\Delta S^{\neq}$); high enthalpy of activation ($\Delta H^{\neq}$); and a high +ve free energy ($\Delta G^{\neq}$). These parameters for the hydrolysis via neutral species are in favour of a bimolecular reaction.

Solvent effect study during hydrolysis was made at pH 1.24 in 10% (0.768×10^{-4} min^{-1}), 50% (1.322×10^{-4} min^{-1}) and 65% (0.845×10^{-4} min^{-1}) dioxane-water where no co-relation study about the different concentration of solvent could be achieved.

Effect of concentration change to half (4.00×10^{-4} M) of the phosphate ester leads to almost a slight difference in magnitude of the rate (0.78×10^{-4} min^{-1}) at normal concentration(8.00×10^{-4} M) and thus support the pseudo-first order rate data. Making the concentration double(16.00×10^{-4}M) brings about a much higher change up to double (1.47×10^{-4} min^{-1}) in the rate value. This study (Table-2) clearly shows the pseudo-first order reaction rate for the hydrolysis of O, O-diethyl O-p-NO_2-phenyl phosphate triester.

Parent concentration effect was also performed at pH 1.24 by keeping the parent concentration constant at 8.0×10^{-4} M and varying the substrate (4-NO_2-phenol) concentrations at 4.0×10^{-4} M, 8.0×10^{-4} M and 16.0×10^{-4} M respectively. The result shows little variation which indicates that there is no interaction between the cleaved molecule of 4-NO_2-phenol with the present molecule.

The following order of reactivity is observed when different nucleophilic reagents were used during hydrolysis at pH 1.24:

Nucleophilic reagents:	F′	>>>	H_2O	>	Cl′	>	Br′
10^4 min^{-1}:	22.92		1.24		0.80		0.75

The rate of hydrolysis is much higher in the presence of fluoride ions which may be accounted for by the elimination [S_E2(P)] rather than substitution [S_N2(P)] mechanism of the hydrolysis of phosphate ester by the attack of slowly nucleophilic fluoride ions.

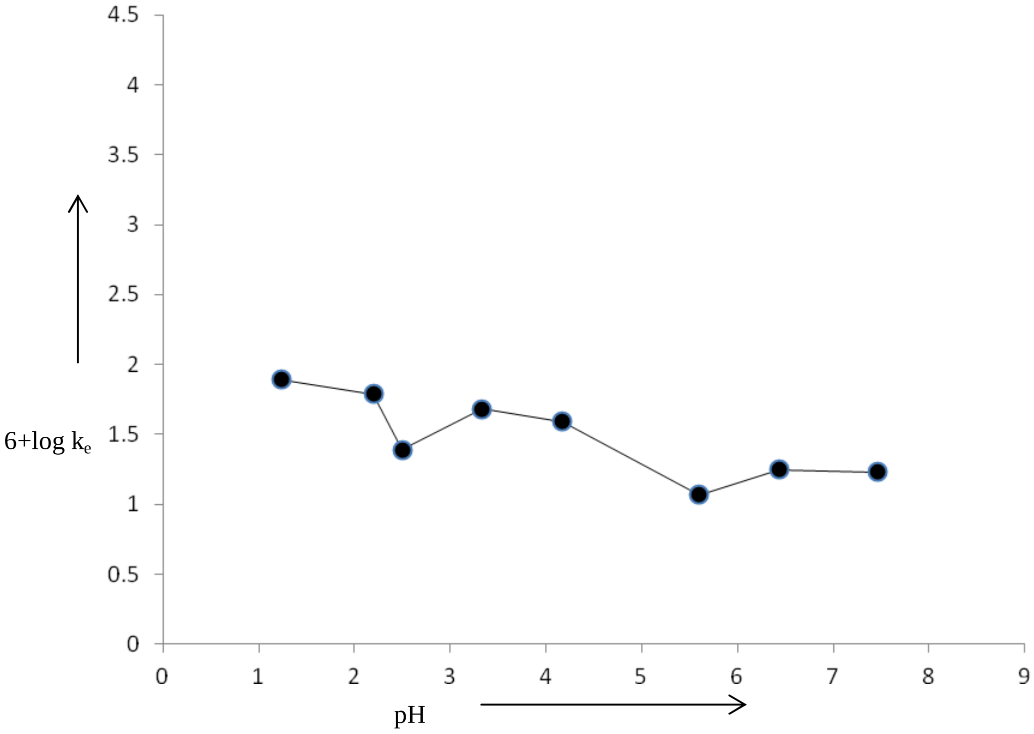
Table-1: Calculated Arrhenius Parameters for the Hydrolysis of O, O-diethylO-p-NO_2-phenyl phosphate at pH 1.24

Energy of Activation 'E'	Frequency factor 'A'	Entropy of Activation $\Delta S^{\neq}$	Enthalpy of Activation $\Delta H^{\neq}$	Free energy $\Delta G^{\neq}$
42.93 KJ / mol	21.90×10^6 sec^{-1}	-33.07 e.u.	39.86 KJ/ mol	94.09 KJ/ mol

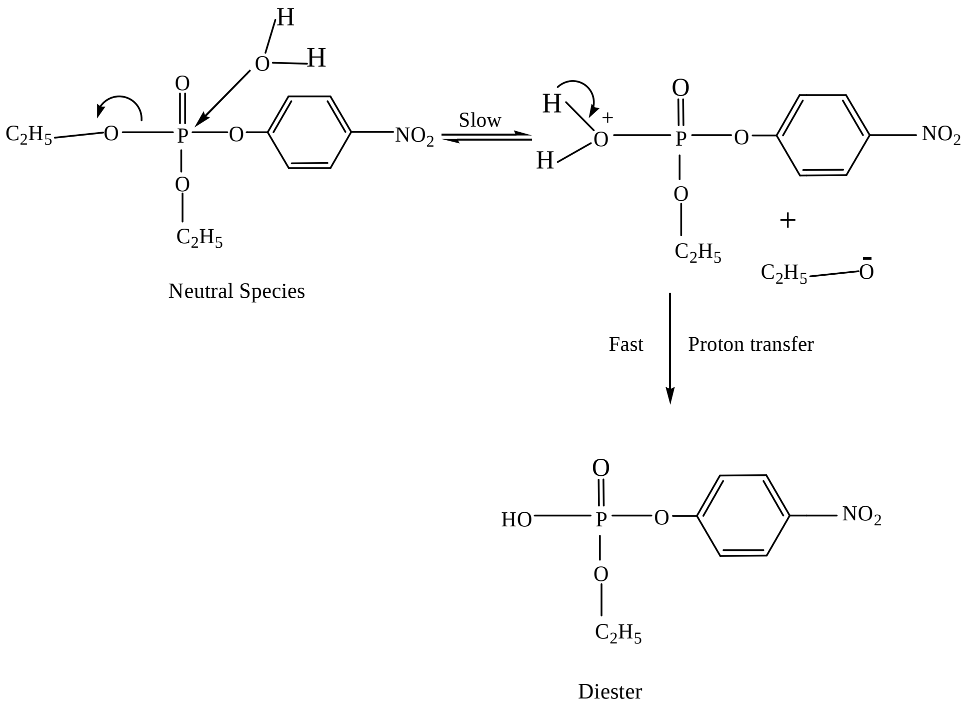
Table-2: Observed Rate Data for the Hydrolysis of O, O-diethyl O-p-NO_2-phenyl phosphate with Various Concentrations in the pH 1.24 at $98(\pm0.5)^0$C

S.No.	pH	Compound Concentration	$10^4 k_e$ (Obsd.) min^{-1}
1	1.24	4.0×10^{-4} M	0.61
2	1.24	8.0×10^{-4} M	0.78
3	1.24	16.0×10^{-4} M	1.47

Fig-1: Experimentally Observed Rates for the Hydrolysis of O, O-diethyl O-p-NO_2-phenyl phosphate in pH region at 98(+0.5)^{0}C

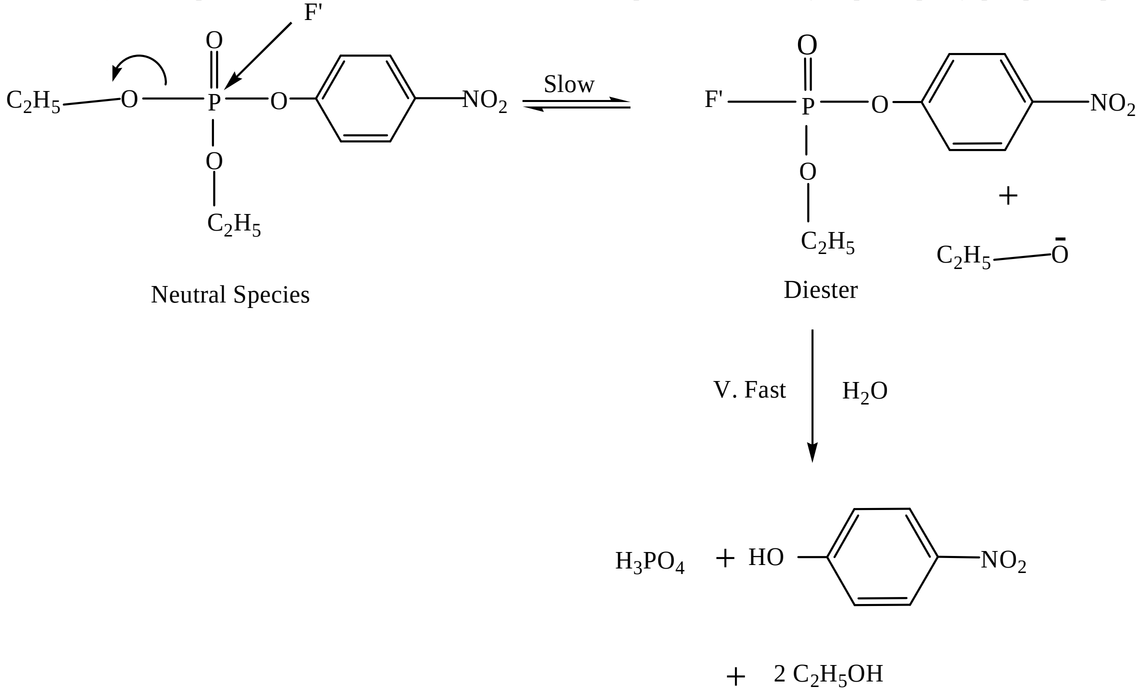


Scheme-1:S_N2(P)-Hydrolysis of the Neutral species (pH 1.24 to 7.46) of O, O-diethyl O-p-NO_2-phenyl phosphate, bimolecularly with P-O bond fission



Diester undergoes complete hydrolysis via. monoester to form inorganic Phospahte H_3PO_4

Scheme-2: S_E2(P)-Nucleophilic attack of the Fluoride ions on the Neutral Species of O, O-diethyl O-p-NO_2-phenyl phosphate at pH 1.24



CONCLUSION

From all the above information, conclusion may be made that O, O-diethyl O-p-NO_2-phenyl phosphate undergoes buffer media hydrolysis via the neutral species and the reaction follows S_N2(P) mechanism (Scheme-1). Scheme-2 indicates S_E2(P) mechanism via the attack of fluoride ions. The two routes clearly shows that the triester is converted into diester and then to monoester and finally determined as the inorganic phosphoric acid. There is always a possibility that a simultaneous cleavage of all the three C-O-P linkages leaving behind the phosphoric acid only. The above study reveals that the hydrolysis of the present phosphate triester undergoes pseudo first-order reaction.

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