Effect of Temperature and Nature of Bond Fission involved in the Hydrolysis of Tri-3,4-Dichloro Aniline Phosphate Ester

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Kinetic study of the hydrolysis of 3,4-dichloro aniline phosphate triester have been investigated in 30% aqueous dioxan medium by performing kinetic runs in buffer solution from pH 1.24 to 7.46 at (97±0.5)°C temperature. Neutral species of the triester have been found to be reactive in this region.

Effect of temperature on the rate of hydrolysis of the triester have been studied to know the molecularity of the reaction. Comparative kinetic rate data and isokinetic relationship plot of some other phosphate triesters of known mechanism were considered to decide whether the hydrolysis of the present triester proceed with P-N or C-N bond fission.

Keywords: Hydrolysis, Dioxan medium, Triester.

1. INTRODUCTION

Organic phosphate esters are physiologically necessary, biologically essential [1] and also play a vital role in nature as well. Thus organic phosphates esters are studied and used in various branches of chemistry.

These organophosphate esters have significant physical, chemical and biological properties. Phosphate esters transformation being metabolic process, thus appreciated by biochemists as well as physio-organic chemists to study the complexity and variety of mechanistic aspects of the ester reaction. Due to significant role of the phosphate esters in establishing human race development, scientists put their efforts in studying the kinetics and mechanism of the phosphate esters.

Due to their efforts a very vast literature of kinetic investigations of phosphate esters having C-O-P, C-S-P and C-N-P [1-14] linkages is available today. The kinetic study of 3,4-dichloro aniline phosphate triester is also one of the effort to know the effect of temperature and the bond fission involved in the hydrolysis of the present triester via its neutral species.

2. HYDROLYSIS OF PHOSPHATE TRIESTER VIA NEUTRAL SPECIES

Kinetic study of the hydrolysis of 3,4-dichloro aniline phosphate triester have been made in buffer solution ranges from pH 1.24 to 7.46 in 30% aqueous dioxan at a temperature of $(97 \pm 0.5)°C$. Pseudo first order rate constant have been summarised in Table 1.

Table 1: pH log rate profile of tri- 3,4-di chloroaniline phosphate at $(97 \pm 0.5)°c$

pH	$10^5 \times K_e$ (mol.dm.$^{-3}$ min.$^{-1}$) (Obsd.)	$5+\log K_e$
1.24	31.69	1.50
2.20	19.68	1.29
3.33	11.45	1.05
4.17	9.39	0.97
5.60	8.63	0.93
6.43	8.16	0.91
7.46	7.85	0.89

It is clear from Table 1 that in the entire pH region the rates are nearly constant and thus the bulk species solely working is neutral species rather than conjugate acid species. Thus, hydrolysis of triester is due to neutral species in the entire pH region from 1.24 to 7.46.

3. EFFECT OF TEMPERAURE

Kinetic runs have been performed at 97°, 90°, 85° and 80°C at pH 1.24 in order to determine Arrhenius plot data for the hydrolysis of 3,4-dichloroaniline phosphate triester to study of effect of temperature on the rate of hydrolysis. Rate coefficients have been summarised in Table 2.

Table 2: Arrhenius plot data for the hydrolysis of tri-3,4-dichloroaniline phosphate via neutral species.

pH	t°C	T°K (Obsd.)	$10^5 \times (1/T)$	$10^5 \times K_e$ (mol.dm.$^{-3}$ min.$^{-1}$) (Obsd.)	$5+\log K_e$
1.24	97	370	270.2	31.69	1.50
1.24	90	363	275.4	10.59	1.02
1.24	85	358	279.3	4.56	0.65
1.24	80	353	283.2	1.73	0.23

To observe the validity of Arrhenius parameters of the hydrolysis, a plot between log rate constant and the reciprocal of the absolute temperature is drawn as shown in Figure 1.
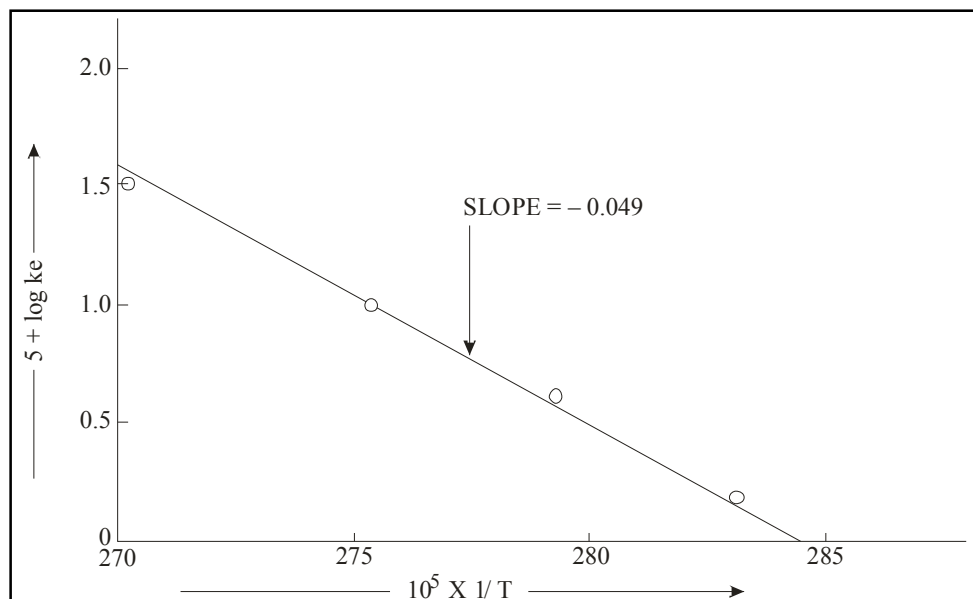
Fig. 1: Arrhenius plot data for the hydrolysis of tri-3,4-dichloroaniline phosphate via neutral species at 1.24 pH.

The linear curve obtained shows the validity of Arrhenius equation for the hydrolysis of triester.

This plot has been used to determine the Arrhenius parameters, which give an evidence about the molecularity of the reaction. The magnitude of Arrhenius parameter calculated from the above plot are summarized in Table 3

Table 3: Arrhenius parameters for the hydrolysis of tri-3,4-dichloroaniline phosphate via neutral species.

pH	Parameter		Entropy ($-\Delta S^{\#}$) e.u.
	Energy of activation (E) Kcal/mol	Frequency factor (A) Sec^{-1}	
1.24	22.42	9.24×10^{7}	24.49

It may be concluded from the results obtained from Table 3 that the magnitude of Arrhenius parameters fall in range of bimolecular reaction. The value of Activation energy is very low, the value of entropy of reaction is a negative value and the frequency factor value has power less than 12. Thus hydrolysis of triester may be expected to proceed with the formation of highly charged transition state.
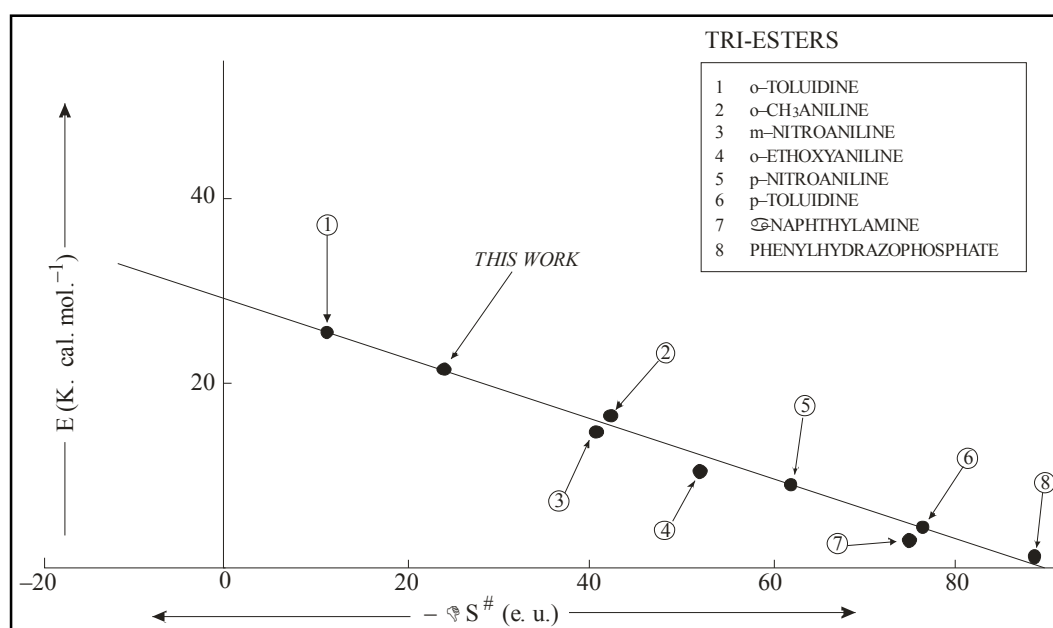
4. BOND FISSION

From Arrhenius parameters, it is clear that hydrolysis via neutral species is governed by the attack of water (nucleophile) on the phosphorus of the triester. To decide the exact path of mechanism i.e. total number of steps involved in the hydrolysis it is necessary to know about the bond fission. The possibility of Phosphorus-Nitrogen (P-N) bond fission is more than that of Carbon-Nitrogen (C-N) bond fission, because the nucleophilic attack of water on phosphorus of neutral species, passing through transition state in which the developed charges causes P-N bond fission.

The probable mechanism is further supported by comparative isokinetic rate data of similarly substituted aryl phosphate trimesters as in Table 4. The neutral species of these triesters have been found to hydrolyse bimolecularly with P-N bond fission.

Table 4: comparative kinetic rate data for the hydrolysis of some phosphate tri-esters via neutral species.

| S.No.	Phosphate triesters	Temp. °C	Medium	E. (Kcal/mol)	$-\Delta S^{\neq}$ (e.u)	Bond Fission	Ref.
1.	o-toludine	80	1.22	26.91	11.91	P—N	15
2.	o-CH_3 aniline	98	1.24	15.08	41.77	P—N	16
3.	m-nitroaniline	98	4.17	17.11	42.42	P—N	17
4.	o-ethoxy aniline	98	4.17	10.06	52.13	P—N	16
5.	p-nitroaniline	98	4.17	10.07	62.37	P—N	18
6.	p-toluidine	50	4.11	5.02	76.40	P—N	19
7.	α-Napthyl amine	98	1.24	3.66	75.34	P—N	19
8.	Phenylhydrazophosphate	98	1.24	1.92	89.47	P—N	20
9.	3,4-dichloroaniline	97	1.24	22.42	24.49	P—N*	This work

On the basis of the above isokinetic rate data, a plot is drawn between energy of activation (E) and entropy of reaction ($-\Delta s^{\neq}$). Since in the isokinetic relationship plot in Figure 2, the point of 3,4-dichloro aniline phosphate triester lies on the same straight line of other similarly substituted aryl phosphate triesters which undergoes P-N bond fission shows that this triester also undergoes P-N bond fission with SN^2 mechanism and also the range of Arrhenius parameters in Table 4 supports P-N bond fission.

TRI-ESTERS

1	o–TOLUIDINE
2	o–CH₃ANILINE
3	m–NITROANILINE
4	o–ETHOXYANILINE
5	p–NITROANILINE
6	p–TOLUIDINE
7	ᴕNAPHTHYLAMINE
8	PHENYLHYDRAZOPHOSPHATE

*THIS WORK*

E (K. cal. mol.⁻¹)

$- S^{\#}$ (e. u.)

Fig. 2: Isokinetic relationship plot for the hydrolysis of some phosphate trimesters via neutral species.

5. MECHANISM

From the above kinetic study of neutral species, the mechanism of the hydrolysis of 3,4-dichloro aniline phosphate triester in the buffer region involved biomolecular nucleophilic attack of water on phosphorous of the neutral species, passing through a transition state in which the developed charges causes P-N bond fission and then liberate a proton by fast step giving the parent amine & and phosphoric acid.

(Transition state)
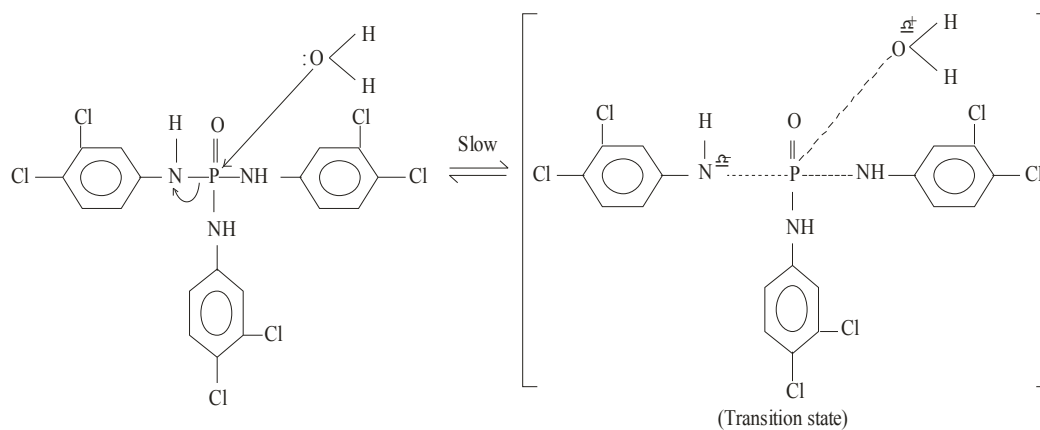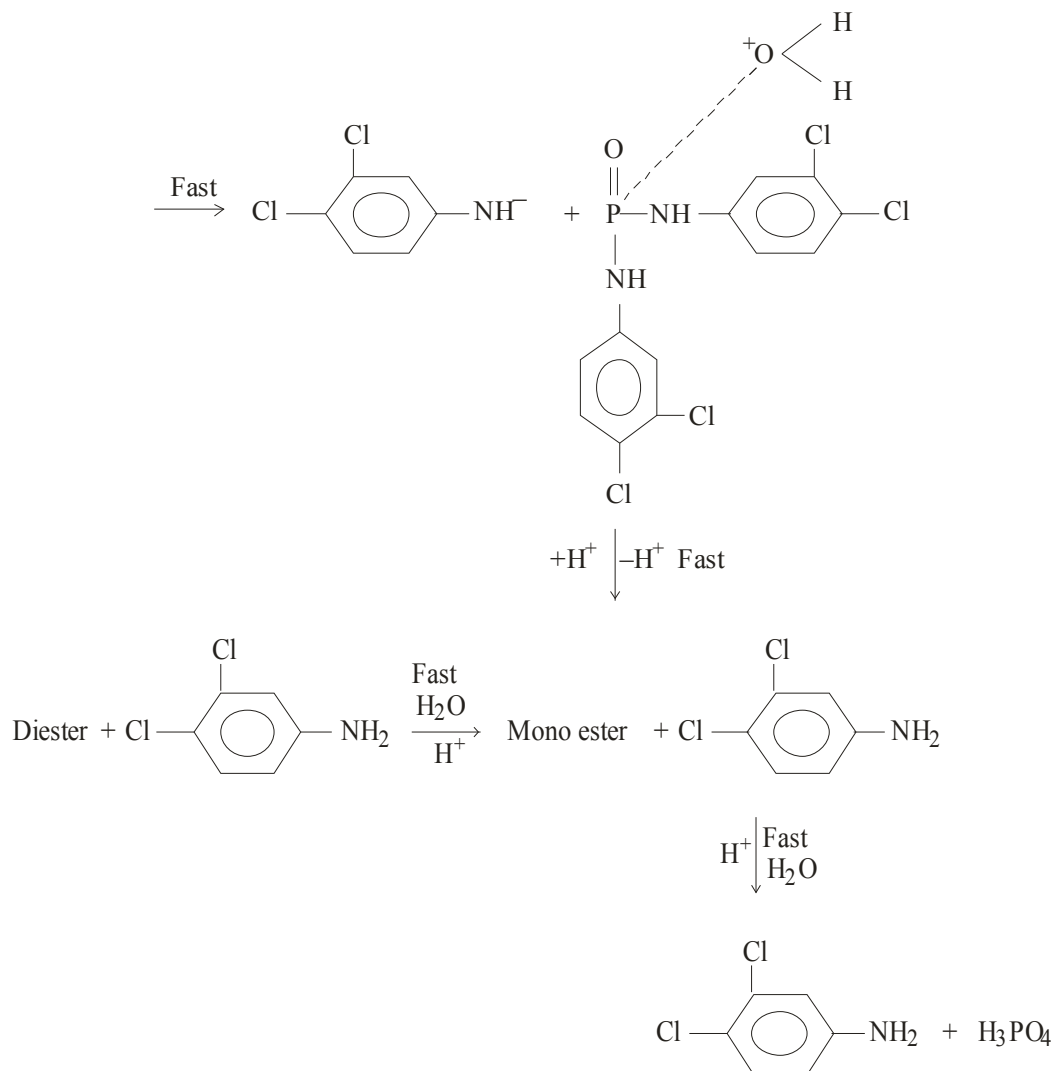
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