Kinetic study and Mechanistic Interpretation of Di-4-Nitrophenyl Phosphate ester via conjugate acid species

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Abstract:

Kinetic study and the hydrolysis ofDi-4- nitrophenyl phosphate ester have been investigated in acid (0.1 to 6.0 mol dm^{-3} HCl) and buffer medium (pH 1.24 to 7.46) at 97 ± 0.5^0C in a 20% aqueous dioxane mixture. Ionic measurements reveal the existence of acid-catalyzed di-ester hydrolysis. Di-ester hydrolyzes through conjugate acid, neutral, and mononegative species; however, we will address just conjugate acid species in this study. The hydrolysis of di-ester involves monoester as an intermediate, which finally hydrolysis into organic phosphate. Since the hydrolysis of monoester is faster, thehydrolysis of the diester could be directly measured by the colorimetricmethod.Allen's modified approach determined the amount of organic phosphate recovered during total hydrolysis. The first-order rate coefficient was determined using an integrate rate equation that matches the rate measured experimentally. The influence of temperature, solvent concentration, and substrate concentration on the involvement of water molecules, bond fission, and molecularity of a reaction have been evaluated.

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Introduction

The recent interest in C-N-P-linked di esters in biochemistry reflects the present emphasis on the acid hydrolysis of a diphosphate ester[1]. Chemical research has entered into new level in this sector resulting in organophosphate insecticides, pesticides and plant hormones [2].As organophosphates havean essential role in the welfare of human life, they are used as fungitoxic, fertilizers, plant hormones, defoliating agents, rodenticides, miticides and aphicides, antiviral medicines, in radioactive traces technique, plasticizers, germicides, flame resistant, anti-wrinkling agents, fuel additive in industries etc [3]. Organophosphate esters have achieved tremendous academic importance also. They are used to determine the various reaction paths of biological changes [4]. Keeping in mind the importance of organophosphate for a living organism, it is essential to have a dynamic and systematic study of all the aspects of the organophosphate reactions[5].

The rate of phosphate ester hydrolysis is generally affected by factors like ionic strength, concentration, temperature, substituents, the polarity of the solvent and catalyst etc.[6]. Bunton and colleagues found that acid-catalyzed hydrolysis [7]. occurs only when electron-withdrawing substituents are present in the aryl component [8]. Hydrolysis of some substituted aryl phosphate shows that the magnitude of acid catalysis decreases with decreasing electron attracting power of the substituents[9]. In most aryl phosphate esters, there have been rate maxima, but maximum protonation is absent. Bunton and colleagues discovered that acid-catalyzed hydrolysis happens only when the aryl portion has an attractive electron substitution[10].

Experimental

The Kinetic research conducted in this manner is presented, together with a discussion of the findings. At 97 degrees Celsius, the insoluble di-ester was investigated in a 20% dioxane water mixture [11]. The di-ester concentration was constant throughout the kinetic runs at 5.0 x 10^{-4} mol.dm^{-3}. The appropriate influence of salt, solvent temperature, and others was used to determine the most likely hydrolysis pathways of C-O-P linkage ester [12]. The influence of ionic strength, pH log rate profile, solvent effect, and substrate concentration has been investigated [13]. The data on ionic strength and assumed pk values were used to create theoretical rates that were very consistent with observed rates [14].

Result and Discussion

Hydrolysis via conjugate acid species

The hydrolysis of Di-4-nitrophenyl phosphate ester demonstrates that it is reactive with neutral, mononegative, and conjugate acid species [15]. The hydrolysis of the di-ester mentioned above was studied kinetically in acid and buffer fluids containing 0.1 to 6.0 mol.dm^{-3}HCl and a pH range of 1.24 to 7.46 at 97 ±0.5^{0}C. Due to dioxane's solubility in water, kinetic runs were conducted in 20% aqueous dioxane. For all kinetic runs, the monophosphate ester concentration was maintained at 5.0x10^{-4} mol.dm^{-3}.

Pseudo First-order rate co-efficient of hydrolysis has been summarized in Table (1) andFigure (1) describes acid and pH log rate profile.

HCl (mol.dm^{-3})	pH	10^5 K_e(mol. dm^{-1}. min^{-1}) observed	5+log K_e Calculated
6.0	-0.778	31.99	1.51
5.0	-0.699	70.08	1.85
4.0	-0.602	134.36	2.13
3.5	-0.544	127.20	2.10
3.0	-0.477	122.24	2.09
2.5	-0.397	116.02	2.06
2.0	-0.300	102.08	2.01
1.5	-0.176	95.82	1.98
1.0	0.000	85.05	1.93
.5	0.301	71.63	1.86
.4	0.400	66.35	1.82
.3	0.520	63.72	1.80
.2	0.700	60.35	1.78
.1	1.00	56.35	1.75
Buffers: Composition of buffers have been mentioned in experimental section	1.24	54.90	1.74
	2.20	46.50	1.66
	3.33	35.24	1.54
	4.17	30.02	1.48
	5.60	8.32	0.92
	6.43	5.90	0.77
	7.46	5.45	0.74

Table – 1

pH-log rate profile of Di-4-nitro phenyl phosphate at 97±0.5 °C

The results indicate that the rate increases with increasing acid concentration up to 4.0 mol.dm^{-3}HCl, which decreases. Whether or not the bend in the pH log rate profile is due to effect may be evaluated by performing constant ionic strength. The reason for the bend may not be the highest possible promotion of esters as a fragilebasicsubstance. Bending may also occur as a result of the action of water activity or ionic strength[16].

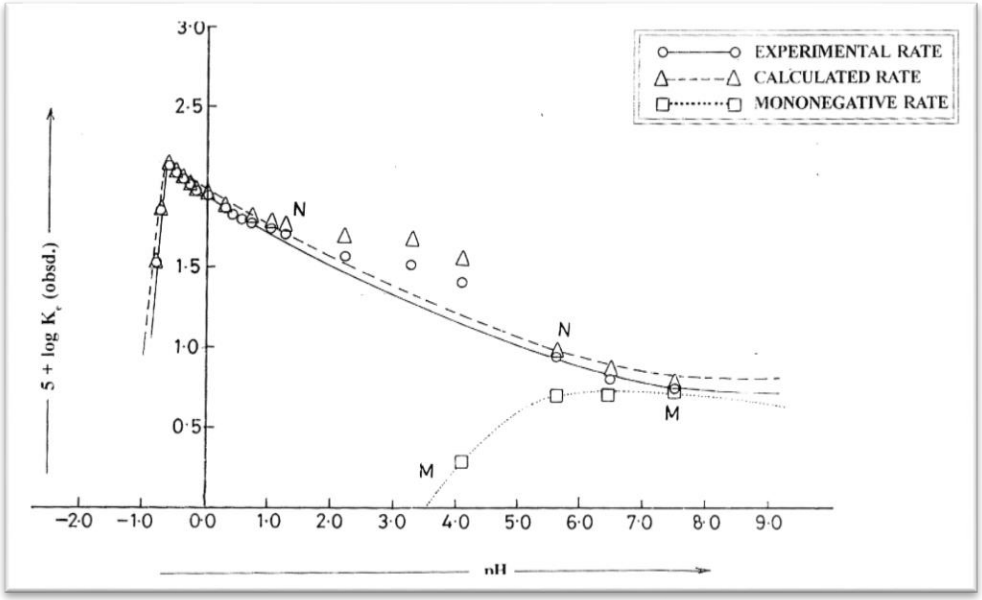


Fig – 1

pH-log rate profile of Di-4-nitro phenyl phosphate at 97±0.5 °C

Ionic Strength (μ) mol.dm^{-3}	Composition HCl (mol.dm^{-3})	Composition KCl (mol.dm^{-3})	10^5K_e mol.dm^{-3} min^{-1} Observed
1.0	0.2	0.8	47.90
1.0	0.4	0.6	55.02
1.0	0.6	0.4	61.51
1.0	0.8	0.2	65.66
1.0	1.0	0.0	85.05
2.0	0.2	1.8	40.02
2.0	0.5	1.5	47.82
2.0	1.0	1.0	60.01
2.0	1.5	0.5	73.30
2.0	2.0	0.0	80.12
3.0	0.5	2.5	102.84
3.0	1.0	2.0	58.86
3.0	1.5	1.5	47.92
3.0	2.0	1.0	56.24
3.0	2.5	0.5	64.50
3.0	3.0	0.0	73.20

Table (2)

$$K_{H^+} = K_{H0^+} \exp. b_{H^+}.\mu$$

$$K_{H^+}.C_H = K_{H0}.C_H \exp. b_{H^+}.\mu$$

$$5+\log K_{H^+}C_{H^+}=5+\log K_{H0}+b_{H^+}\cdot\mu$$

Where K_{H0^+} , $K_{H0^+}$are acid catalyzed rates at specific and zero ionic strength.

$b_{H^+ is}$ constant

μ is ionic strength

$K_{N,} = K_{N,}$ bn and μ "specific neutral rates at that ionic strength at zero ionic strength, respectively".

Equations (3) and (5) may be used to compute the acid-catalyzed, and neutral rate may be represented as

$K_e = K_{H^+}.C_{H^+} + K_N$

The specific acid-catalyzed and specific [K_N] neutral rates for Mono-4-nitrophenyl phosphate hydrolysis at 97± 0.5 ^{0}C.fig 2.

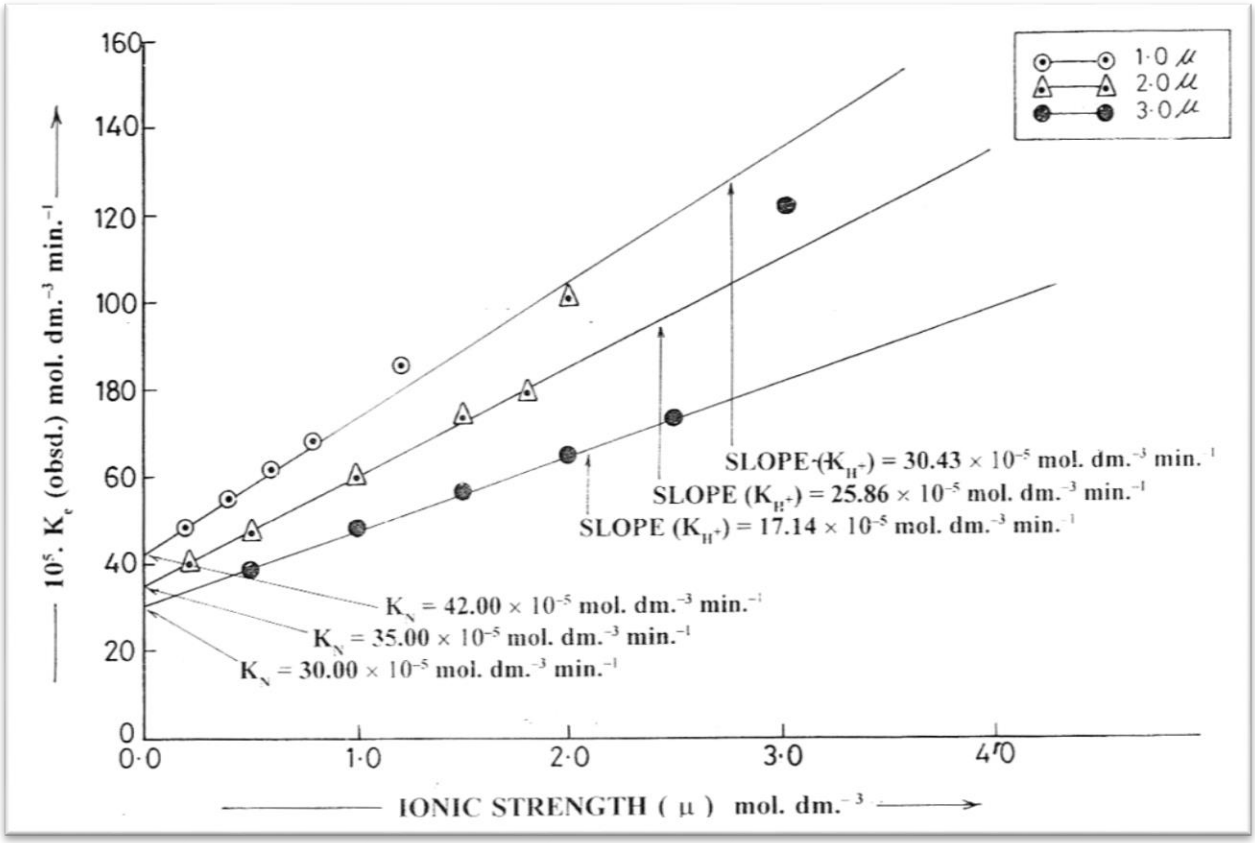
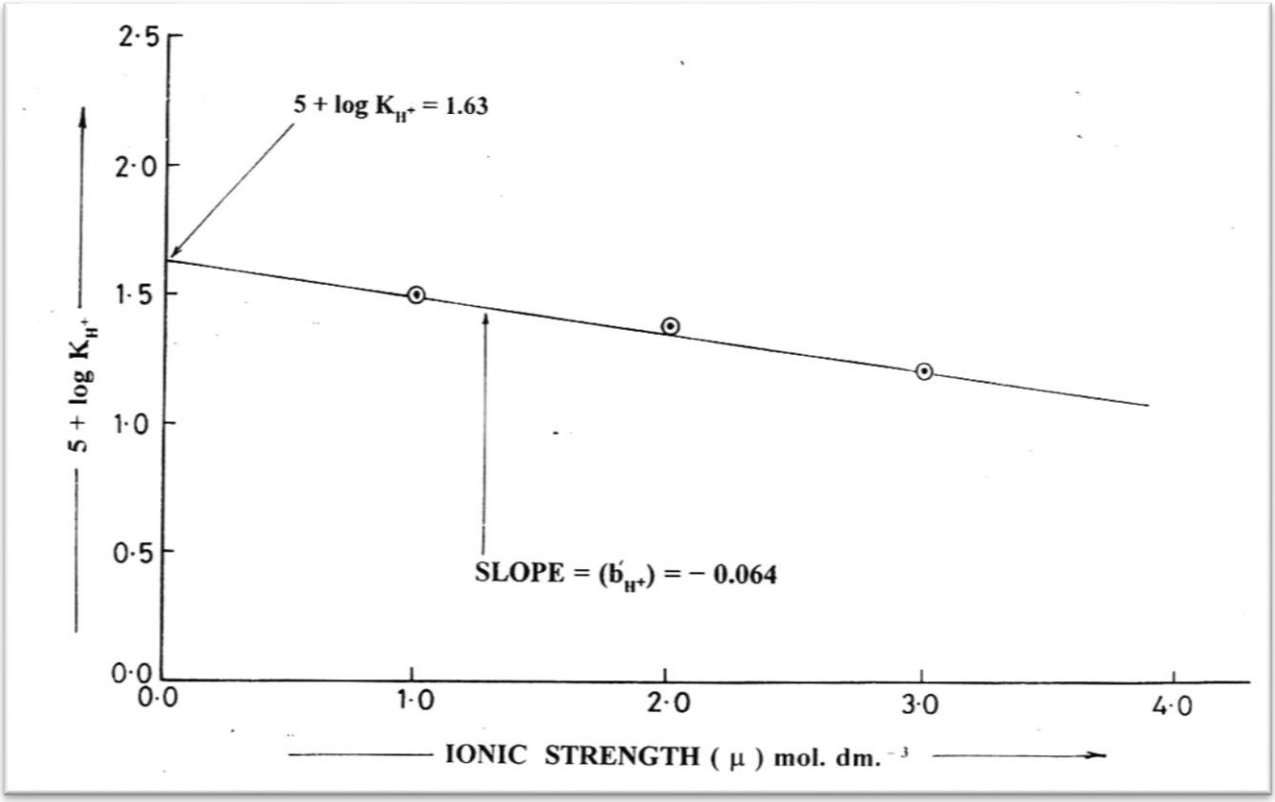


Fig – 2- Hydrolysis of Di-4-Nitropheyyl Phosphate at Constant Ionic Strength at 97±0.5°C

Ionic strenghth(μ)	$10^5 k_H$(mol.dm^{-3} min^{-1})	5+log K_{H0}	10^5. K_N (mol.dm^{-3} min.$^{-1}$)	5+log K_N
1.0	30.43	1.48	42.00	1.62
2.0	25.86	1.41	35.00	1.54
3.0	17.14	1.23	30.00	1.48

Table-(3)

Theoretical rates may be derived using the above equation compared to experimental rates, which exhibit remarkable similarity up to 4.0 mol dm^{-3}HCl.The values of acid-catalyzed rates (5+log K_{H^+} = 1.68) and special neutral rates (5 + logKN_0 =1.60) may be determined from the intercepts on the rate axis, which are b'$_H$ = -0.042 and b'n = -0.027, respectively, as determined by the slope of the figure.



Fig– 3

Hydrolysis of Di-4-Nitrophenyl Phosphate at 97±0.5 °C

(Log specific acid-catalyzed rate Vs ionic strength)

The hydrolysis rates observed and computed in the acid area range from "0.1 to 6.0 mol.dm^{-3} HCl"issummarized in Table (4). The results indicate that the estimated and experimentally observed rates are consistentup to 4.0 mol.dm^{-3}HCl. There is a dramatic decrease in rates, which is assumed to be due to the addition of water molecules as a second reaction. Additionally, the rate is slowed by the negative ionic strength impact. As a result, an agreement between theoretical and experimental rates was sought by adding water activity parameters [17]. Thus, the modified version given by Bronsted-Bjerrum was used to determine both acid-catalyzed and neutral rates [18].

$K_{H.}C_{H^+} = K_{H0^+}.\ exp.b_{H^+}.\ \mu\ (_a H_2O)^n$

And its logarithmic form can be represented as below

$$5+\log K_H.C_H = 5+ \log K_H + \log C_H + b_H.\ \mu + n \log(\ aH_2O)$$

HCl	pH	$10^5.k_N$ (mol $dm^{-3}min^{-1}$)	5+log K_n	$10^5.k_N$ (mol $dm^{-3}min^{-1}$)	$10^5 k_{H.}$ (C_H mol $.dm^{-3}min^{-1}$)	$10^5.K_n$ (mol.$dm^{-3}min^{-1}$)	10^5.Ke (mol.dm-3 min^{-1} Calculated	5+logK_e (mol.dm-3 min^{-1} Calculated	$10^5.K_e$ mol.dm^{-3} min^{-1} Observed
0.1	1.000	54.45	1.74	4.17	----	----	58.62	1.77	53.36
0.2	0.700	53.95	1.73	8.32	----	----	62.27	1.79	60.72
0.5	0.301	52.48	1.72	19.95	----	----	72.43	1.86	71.63
1.0	0.000	52.12	1.70	37.15	----	----	87.27	1.94	85.05
1.5	-0.176	47.86	1.68	51.28	----	----	99.14	2.00	95.82
2.0	-0.300	45.71	1.66	63.09	----	----	108.80	2.04	102.84
2.5	-0.397	43.65	1.64	74.13	----	----	117.78	2.07	116.02
3.0	-0.477	41.69	1.62	83.17	----	----	124.86	2.09	122.24
3.5	0.544	39.81	1.60	89.12	----	----	128.26	2.11	127.20
4.0	0.602	38.82	1.58	95.50	----	----	133.52	2.13	134.36
5.0	0.699	34.67	1.54	102.33	50.18	16.98	67.16	1.83	70.08
6.0	0.788	31.62	1.50	104.70	24.55	7.36	31.91	1.50	31.99

Table – (4)

Table 4 Calculated and observed rate for the hydrolysis of mono-4- Nitrophenyl phosphate at 97±0.5 ^{0}C.

Where n=0 for 1.0 to 4.0 mol.dm^{-3}HCl n=2 and 3 for 5.0 and 6.0 mol.dm^{-3}HCl respectively.

Neutral rates at higher concentrations are as follows

$$Kn = K_n\ exp.\ b_N\mu\ (aH_2O)^n$$

and its logarithmic form can be represented as

$$5 + \log Kn = 5+\log Kn + b'_N + b'_N\ \mu + n\ \log\ aH_2O \text{ where } (aH_2O)$$

is water activity, and n is an integer.

Table (5) summarizesthe Arrhenius parameter of monoester at 3.0 and 5.0 mol dm^{-3}HCl. The value shows the similarity of these acidities' mechanisms and indicates the bimolecular nature of hydrolysis[19]. Arrhenius parameter for the rate of hydrolysis of Di-4-nitrophenyl phosphate ester via conjugate acid species.

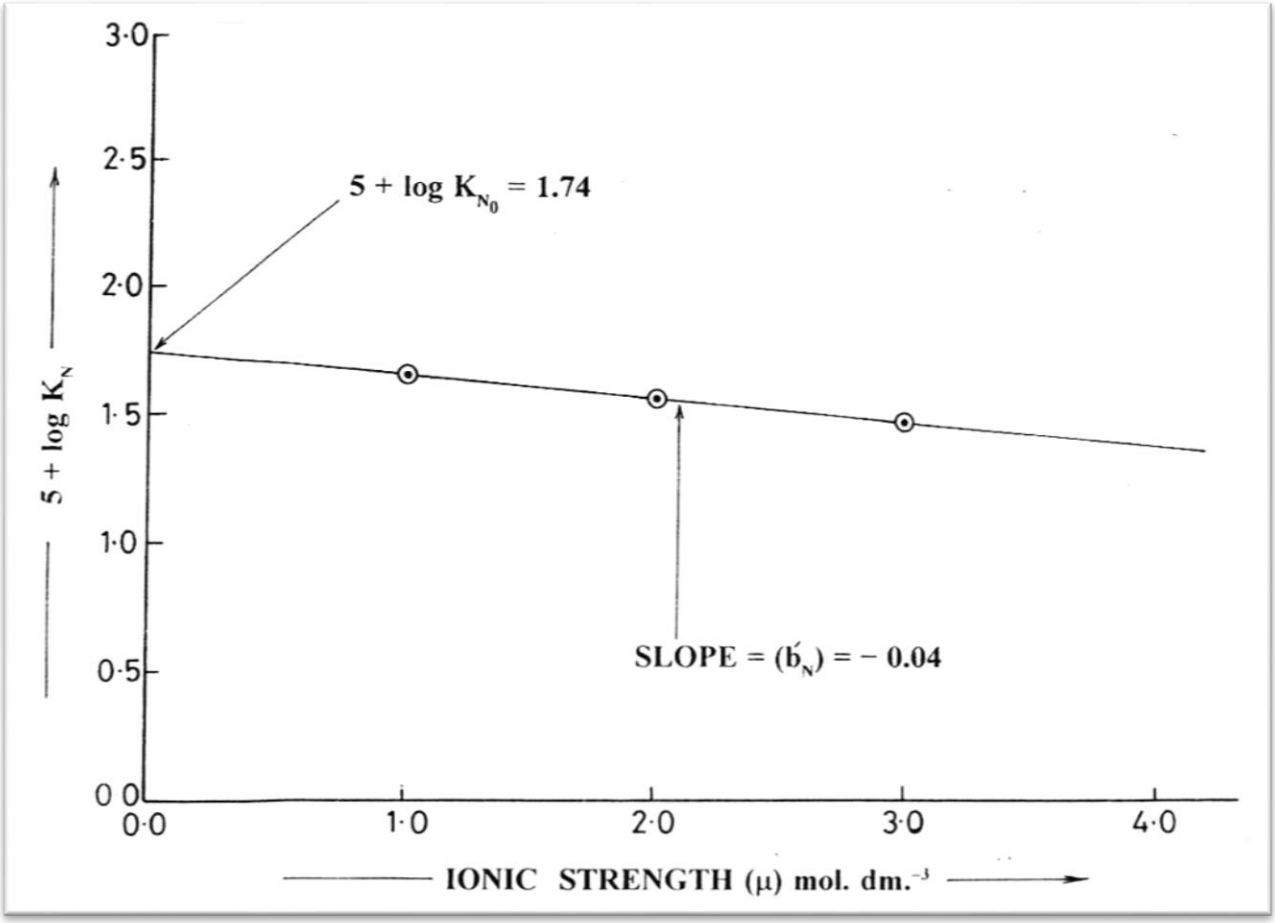


Fig – 4

Hydrolysis of Di-4-Nitrophenyl Phosphate at 97±0.5 °C

(Log specific neutral rate Vs ionic strength)

HCl (mol.dm^{-3})	Energy of activation (Ea) (K.cal.mol)	Frequency factor (A)	Entropy $-\Delta S^{\#}$
3.0	21.05	5.50×10^7	25.53
5.0	29.97	10.96×10^7	24.16

Table (5)

The comparative isokinetic rate statistics for other similarly substituted aryl phosphates that have been recently discovered to undergo hydrolysis by P-O bond fission are summarized in Table(6)[20]. Fig. 6 depicts the isokinetic curve for Di-4-nitrophenyl phosphate hydrolysis. The linearity of the figure indicates that the process of acid-catalyzed Di-ester hydrolysis is comparable. On this basis, it is reasonable to consider the current Di-ester's P-O bond fission [21]. Table(6) summarizes the comparative isokinetic data for many phosphate monoesters.The isokinetic rates of hydrolysis of numerous phosphate Di-esters through their conjugate acid species are compared.

S.No	Phosphate di-ester	Activation energy (K.Cal.mol.$^{-1}$)	-ΔS$^{\#}$ (e.u)	Bond Fission
1.	2,3- Methoxyphenyl	31.56	2.57	P-O
2.	2,4,6-trichlorophenyl	24.41	11.87	P-O
3.	Penta-bromophenyl	24.44	15.02	P-O
4.	4-Chloro-3,5-diethylphenyl	23.33	19.14	P-O
5.	2,6-dimethyl	21.04	26.89	P-O
6.	4-chlorophenyl	18.20	29.96	P-O
7.	2,4-Dichlorophenyl	16.60	33.90	P-O
8	4-chloro-3-methyl phenyl	11.00	42.60	P-O
9.	MeO-methylphenyl	11.69	44.17	P-O
10.	diethyldithiophenyl	11.44	50.82	P-O
11.	4-nitrophenylPhosphate	21.05	25.36	P-O*
12.	4-nitrophenylphosphate	21.97	23.87	P-O*

Table (6)

Here P-O* Bond fission assumed for the present work.

The mechanism of Di-4-nitrophenyl phosphate hydrolysis, based on empirically reported rates and all those mentioned above via- conjugate acid species, may be stated as follows: Conjugate acid species are formed by rapid pre-equilibrium proton transfer[22].

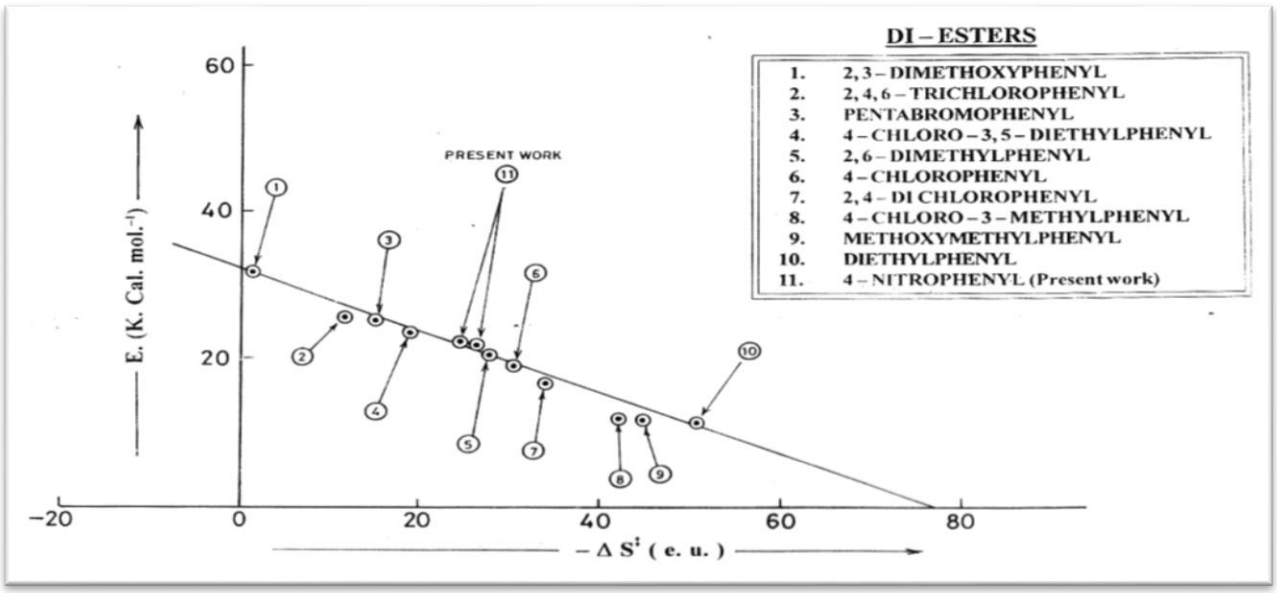
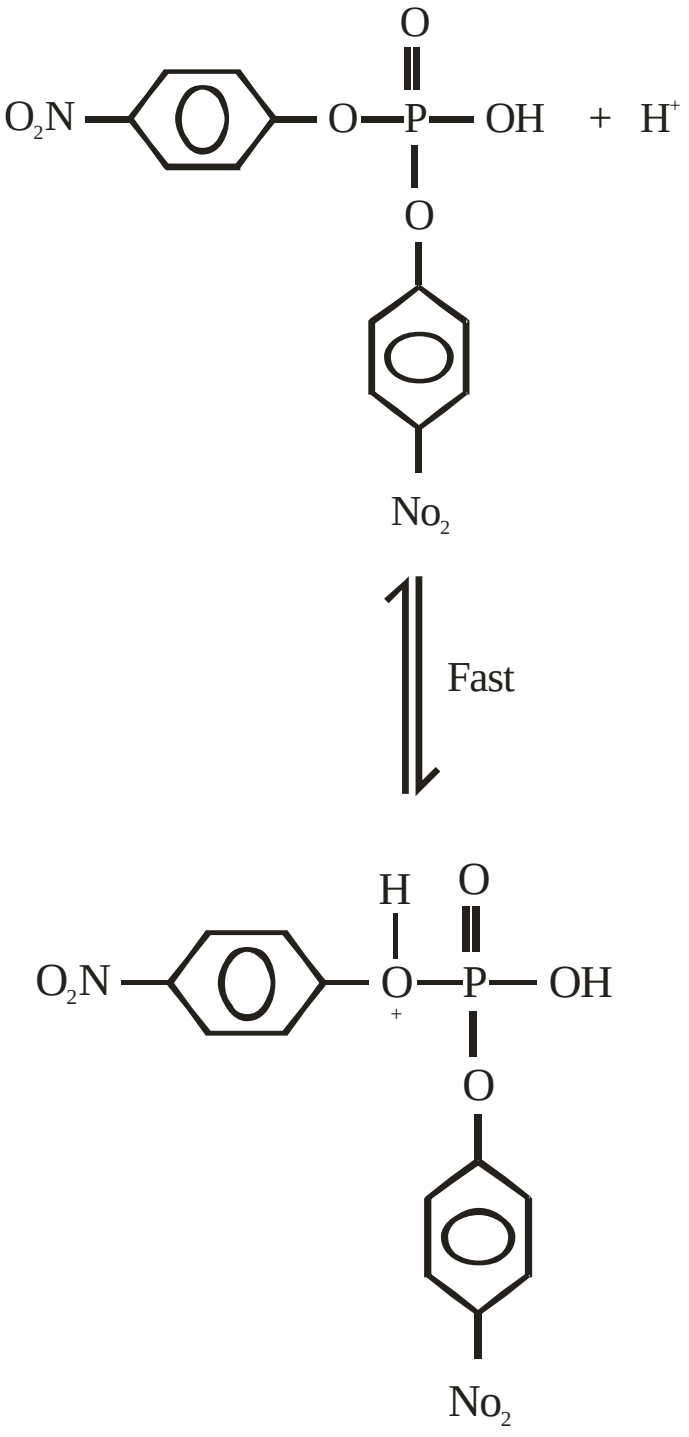
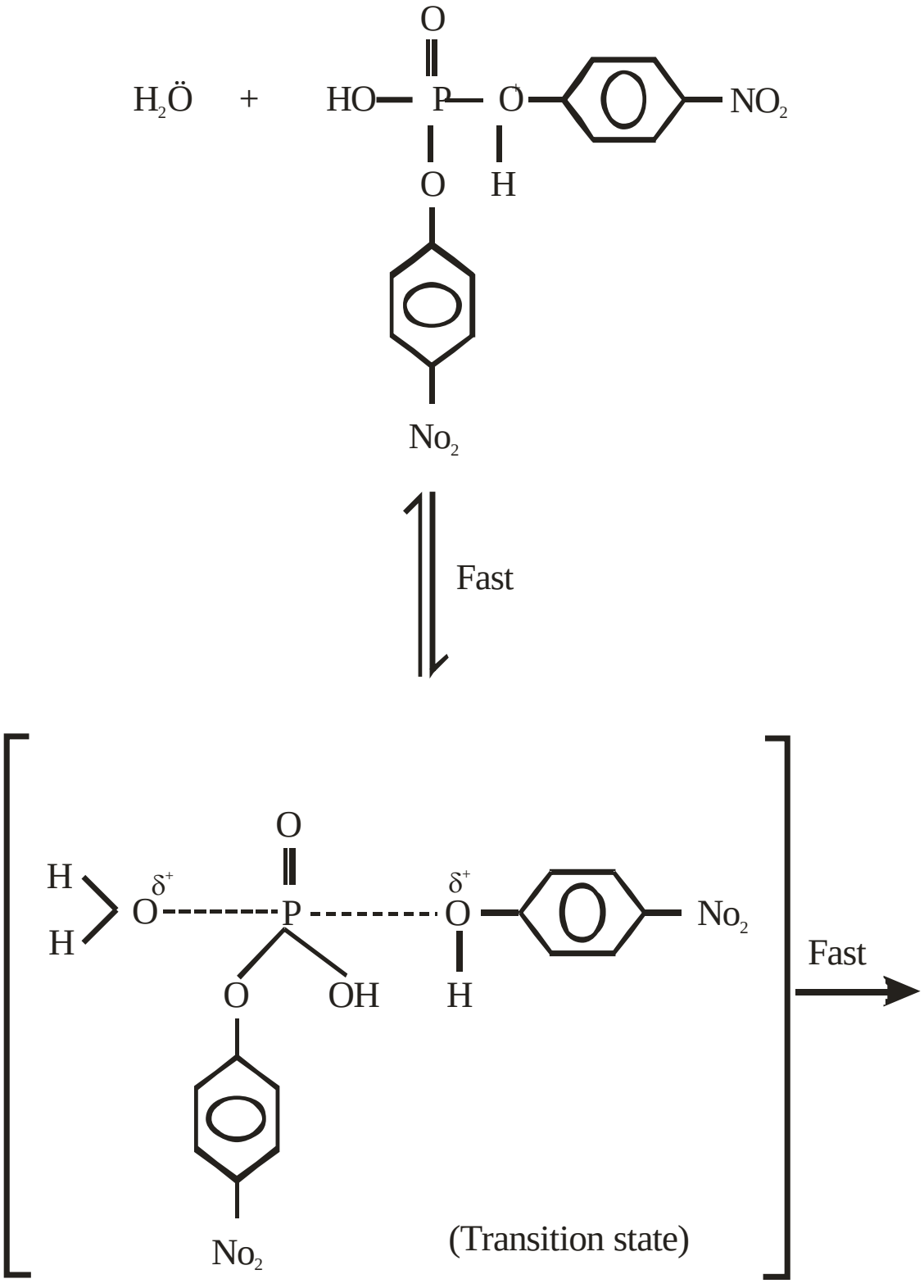


Fig – (5)

Isokinetic Relationship Plot for the Hydrolysis of some Phosphate DI-Esters via Their Conjugate Acid Species



Conjugate acid species)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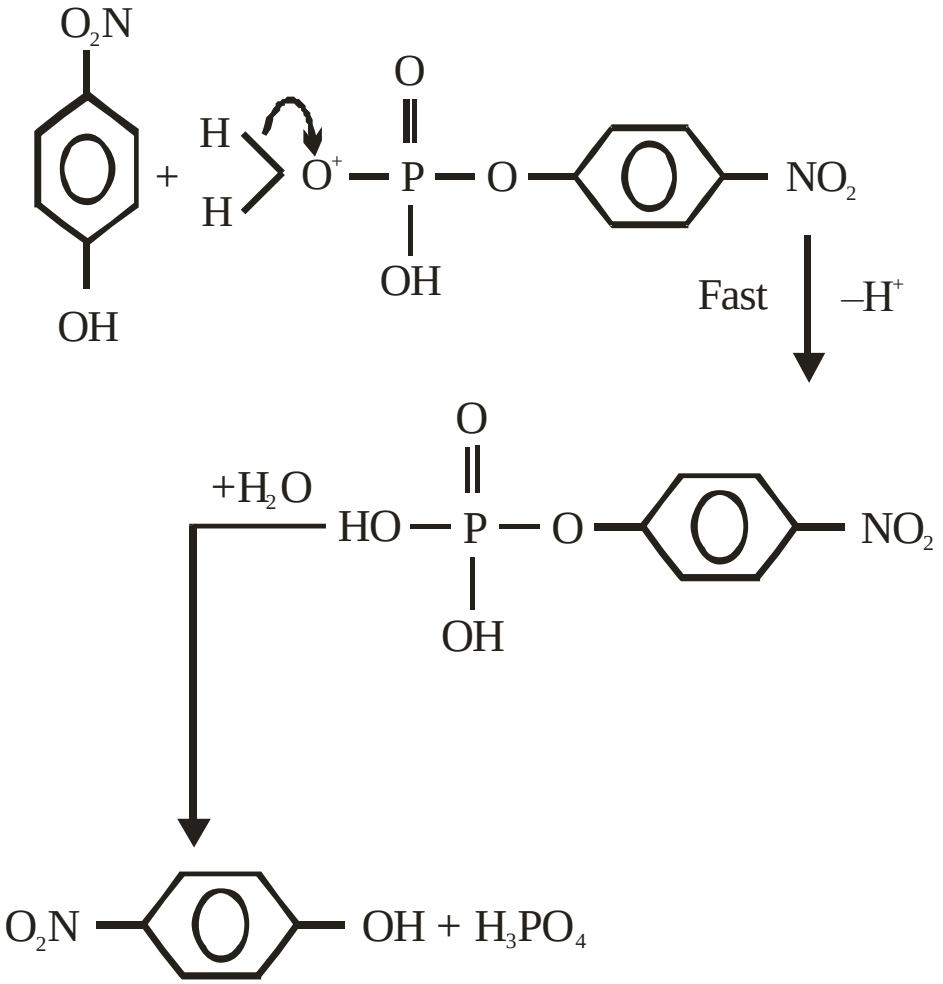

Conclusion

The kinetic investigation of Di-4-Nitrophanyl phosphate ester through conjugate acid species revealed that the rate rises with increasing acid molar concentration up to 4.0-mol dm^{-3}HCl and then abruptly decreases with increasing acid concentration. The acid log rate profile bend is due to water activity, not maximum protonation. Thus, it is established that conjugate acid species developed by rapid proton transfer between conjugated and neutral species. The acid-catalyzed rate is retarded by a negative salt effect, also known as ionic retardation[23].The solvent effect results favour the formation of the transition state. Water molecules attack the conjugated species at the P-O bond-forming the parent compound via a transition state[24].This way, the reaction follows first-order kinetics and bimolecular mechanism.The order of the hydrolytic reaction is pseudo-first-order[25].

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