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Kinetic and Mechanism of Acid Hydrolysis of Di-4-Hydroxybi Phenyl Phosphate Ester

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KEYWORDS :

The acid hydrolysis of di-4- hydroxy bi phenyl phosphate ($5.0X10^{-5}$ mol . dm^{-3} HCl at 97 ± 05^0C) has been carried out in 20% v/v aqueous dioxin mixture. The inorganic phosphate obtained during hydrolysis has been estimated colorimetrically . The pseudo first order rate constants have been calculated by using Debye-Huckle equation[1].

Experimental – The 4-hydroxy biphenyl phosphate ester has been synthesized by general method[2]. 200ml benzene and 9.0 ml $POCl_3$ was refluxed for about 48 hours and distilled at reduced pressure, the white residue after treatment 5.0 N NaOH solution and dilute HCl was recrystalized in absolute alcohol.

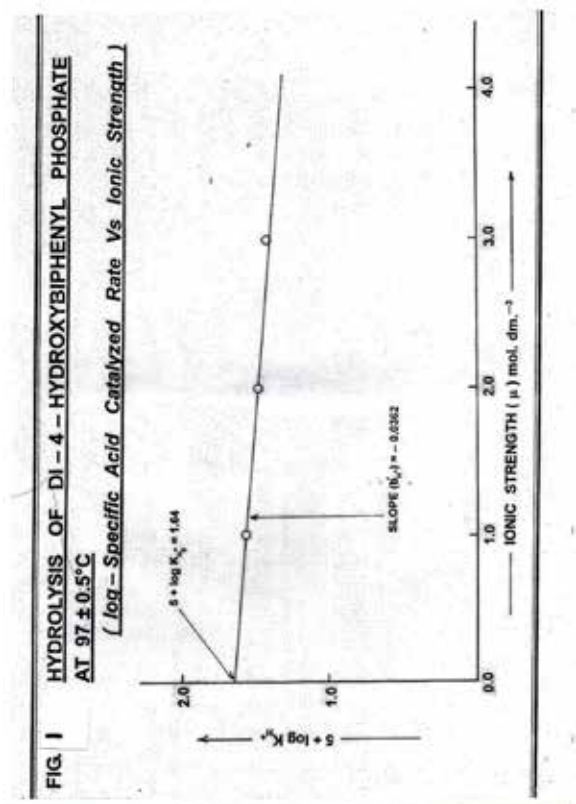
M.P= 210^0C, Observed percentage of 'P' = 8.88%, Theoretical % of 'P'=7.71%

Further the compound is characterized by IR Spectrum

-OH = 3500-3265cm^{-1}, -CH =3091-2983cm^{-1}, -C=C- =1500-1450cm^{-1}, -P =O =1200-1120cm^{-1}, C-O-P =1109-1070cm^{-1}, substituted aromatic ring = 800-760cm^{-1}. Thus it confirms the structure of 4-hydroxy biphenyl phosphate .

Result and Discussion- The pseudo first order rate coefficient for the hydrolysis of di-esters show that the rate decreases with the increase in acid concentration form 0.1 to 4.0 mol.dm^{-3}.HCl. Further rising acidity brings about lowering in rates (>0.1mol.dm^{-3}.HCl) maxima in the hydrolysis of phosphate ester has been found due to ionic strength effect [3]and water activity and not due to the maximum protonation as in case of amides [4]. This has been confirmed by carrying out kinetic runs , before and after the maximum, the participation of water activity and effect of ionic strength have been determined by carrying out kinetic runs at different constant ionic strengths using appropriate mixture of KCl and HCl. Under these experimental conditions a plot of log rate profile Vs acid concentration has three linear curves to be found (fig not shown). The di-ester is not very sensitive due to the change in ionic strength, so that the linear curves lie close to each other .

Three linear curves make an intercept on the rate axis, the slope of the curve represents the (K_H+) specific acid catalyzed[5] rates and the intercepts on the rate axis the specific neutral rates (K_{N0}) at the ionic strength which decrease with the increase in ionic strength, consequently both the acid catalyzed rates and neutral rates are subject to negative effects of ionic strengths.



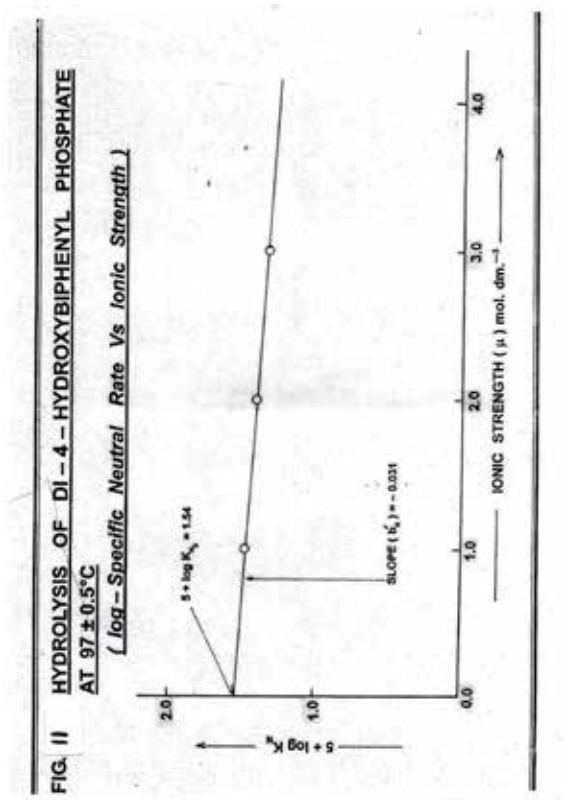


Table 1
SPECIFIC ACID CATALYZED AND SPECIFIC NEUTRAL RATES FOR THE HYDROLYSIS OF DI-4-HYDROXY BI PHENYL PHOSPHATE AT DIFFERENT IONIC STRENGTH AT 97± 0.5°C

Ionic Strength μ	$10^5.K_H+$(mol. $dm^{-3}.min^{-1}$)	$5+\log K_H+$	$10^5.K_N$(mol. $dm^{-3}.min^{-1}$)	$5+\log K_N$
1.0	35.71	1.55	30.00	1.48
2.0	30.00	1.48	26.00	1.41
3.0	27.27	1.44	22.0	1.34

The negative slope of the linear curves represent the constant b^*_H+ and b^*_N while the intercepts on the log-rate axis represents the specific catalyzed ($K_{H0}+$) and specific neutral (K_{N0}) rates at zero ionic strength. The values are used to calculate acid catalysis and neutral rates.

Acid Catalyzed Rates –

$$\text{Log } (K_H+.C_H+) = \log K_{H0}+ + \log C_{H+} + b^*_H+.\mu \text{----------(1)}$$

Neutral rates –

$$\text{Log } K_N = \log K_{N0} + b^*_N.\mu \text{ ----------(2)}$$

Where, K_H+, $K_{H0}+$, K_N, K_{N0} in the abo-ve equations are specific acid catalyzed rate at zero ionic strength, neutral rate at zero ionic strength respectively and also b^* =b/2.303. On the basis of these calculated rate of both the specifies, the over all rates of hydrolysis may be obtained by applying the following equation

$$Ke = K_H+.C_H+ + K_N \text{----------(3)}$$

These calculated fairly resemble with Ke (obsd) upto 4.0 mol.dm^{-3}. HCl. The rate above 4.0 mol.dm^{-3}.HCl however deviate from the normal value which is attributed to (1) decrease in the reactivity of the neutral form (2) negative ionic strength effect (3) decrease in water activity. Thus the rate beyond 4.0 mol.dm^{-3}.HCl has been calculated by introducing water activity parameter.

In Acid Rates

$$5+\log K_H+.C_H+ = 5+\log K_{H0}+ + \log C_H+ + b^*_H+.\mu + n\log (aH_2O) \text{----------(4)}$$

In Neutral Rates

$$5+\log K_N = 5+\log K_{N0} + b^*_N.\mu + n\log (aH_2O) \text{---------(5)}$$

Where, (aH_2O) represent water activity and 'n' is an integer . The value of n at 5.0 and 6.0 mol.dm^{-3}.HCl has been found 2.0 and 3.0 for acid and neutral rates.

Table-2 summarizes the calculated and observed rate coefficient for the hydrolysis of 4-hydroxy bi phenyl phosphate.

Table.2
CALCULATED AND OBSERVED RATES FOR THE HYDROLYSIS OF DI-4-HYDROXY BIPHENYL PHOSPHATE AT 97± 0.5°C

HCl (mol. dm-3)	pH	105. K_N(mol. dm^{-3}. min^{-1}.)	$5+\log K_N$	$105.K_H+.C_H+$ (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}) (Calcd.)	5+logKe (calcd)	10^5. Ke(mol. dm^{-3}. min^{-1}.) (obsd.)
0.1	1.000	34.43	1.54	4.33	-	-	38.76	1.59	40.02
0.2	0.700	34.18	1.53	8.57	-	-	42.75	1.63	46.15
0.5	0.301	33.46	1.52	20.94	-	-	54.40	1.74	50.28
1.0	0.000	32.28	1.51	40.16	-	-	72.44	1.86	75.60
1.5	-o-176	31.15	1.49	57.77	-	-	88.92	1.95	91.01
2.0	-0.300	30.06	1.48	73.72	-	-	103.78	2.02	95.62
2.5	-0.397	29.01	1.46	88.41	-	-	117.42	2.07	112.82
3.0	-0.477	27.99	1.45	101.95	-	-	129.94	2.11	118.43
3.5	-0.544	27.01	1.43	114.10	-	-	141.11	2.15	134.86
4.0	-0.602	26.02	1.42	125.08	-	-	151.14	2.18	148.25
5.0	-0.699	24.27	1.39	143.88	70.47*	11.89*	82.36	1.92	77.42
6.0	-0.778	22.59	1.35	158.78	36.97*	5.26*	42.23	1.63	38.88

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

The validity of above computed specific neutral rates (K_{N0}=34.67X10^{-5} mol.dm^{-3}.HCl) from ionic strength data which is approximately equal to the specific neutral rates calculated from pK values (K_{N0}=35.76X10^{-5} mol.dm^{-3}.HCl).

Various correlation plot like Hammett plot[6] (0.25), Zucker-Hammett plot[7] (0.67), Bunnet plot (9.0 &5.33) and Bunnet-Olsen plot[8] (1.75). Postulate a bimolecular rates of hydrolysis with the involvement of a water molecule as a second reaction partner.

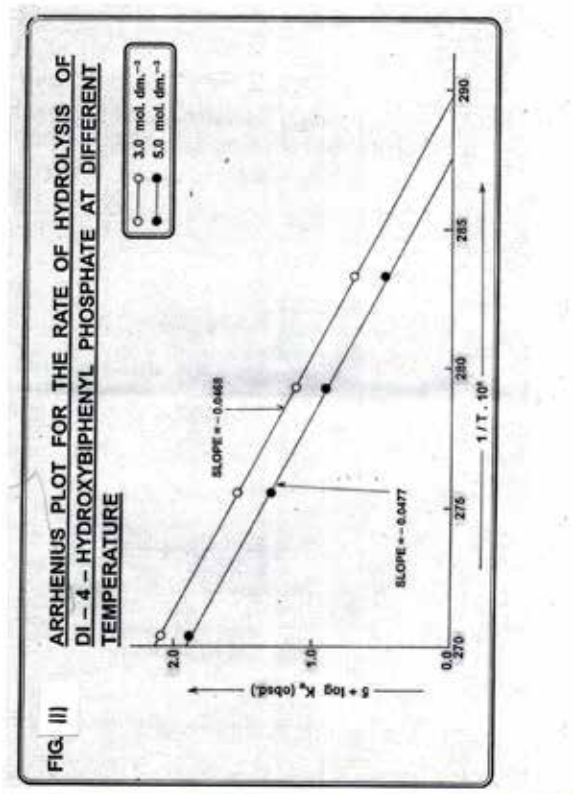
Solvent effect has been studied for both reactive forms at 3.0 and 5.0 mol.dm^{-3}.HCl. The neutral species and conjugate acid species passes through a transition state with the creation of changes in both the moles of hydrolysis since the rates increases with increase in concentration of dioxin.

Table.3
EFFECT OF SOLVENT ON THE HYDROLYSIS OF DI-4-HYDROXY BIPHENYL PHOSPHATE AT 97± 0.5°C

HCl mol.dm^{-3}	Water Percentage (v/v)	Dioxin Percentage (v/v)	10^5.Ke (mol. $dm^{-3}.min^{-1}$.)(Obsd)
3.0	100.00	0.00	118.43
3.0	60.00	40.00	130.73
3.0	40.00	60.00	134.96
5.0	100.00	0.00	77.42
5.0	60.00	40.00	85.99
5.0	40.00	60.00	102.34

It has been shown that the rate of reaction is influenced by the nature of solvent. Solvent effect has been used as one of the criteria to determine the mechanism of hydrolysis of alkylhalides .

The kinetic runs for the hydrolysis of di- ester were performed at 3.0 and 5.0 mol.dm^{-3}.HCl at different temperature. Table 4 and figure III describes Arrhenius plot between log rate co- efficients and reciprocal of absolute temperature.



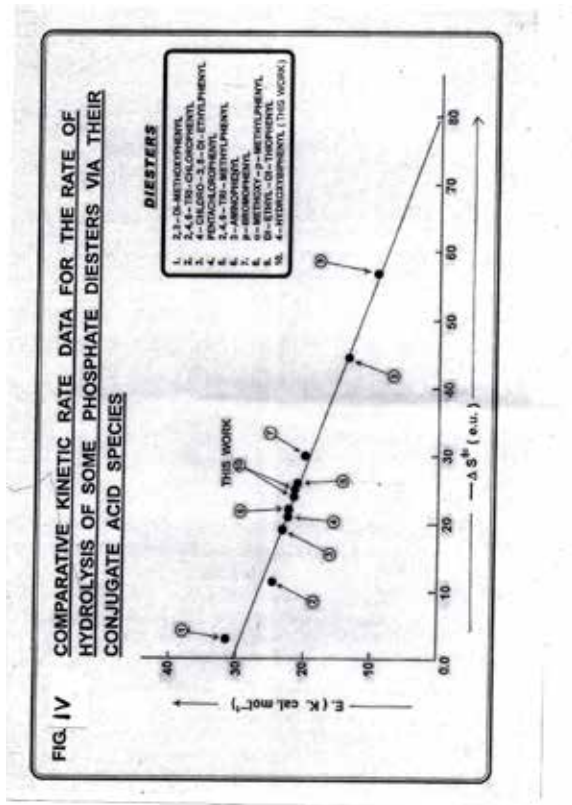


Table. 4
ARRHENIUS PLOT DATA FOR THE RATE OF HYDROLYSIS OF DI-4-HYDROXY BIPHENYL PHOSPHATE AT DIFFERENT TEMPERATURE.

HCl (mol. dm^{-3})	T^0C	T.K (abs)	10^5.1/T	10^5. Ke(mol. dm^{-3}.min^{-1}.)(obsd)	5+logKe
3.0	97	370	270.3	118.43	2.07
3.0	90	363	275.5	35.79	1.55
3.0	85	358	279.3	13.42	1.13
3.0	80	353	283.3	5.15	0.71
5.0	97	317	270.3	77.42	1.89
5.0	90	363	275.5	20.40	1.31
5.0	85	358	279.3	8.00	0.90
5.0	80	353	283.3	3.05	0.48

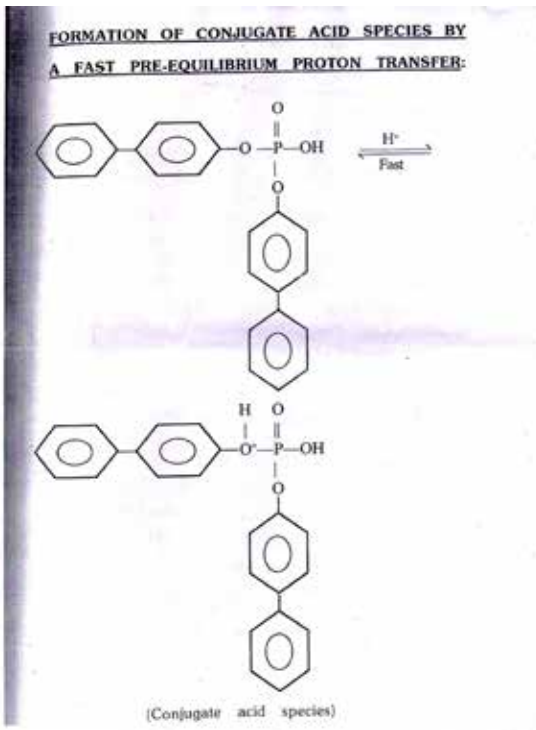
The Arrhenius parameters [9] at 3.0 M, Δ E= 21.42 K cal/ mol, frequency factor (A) (Sec^{-1})=8.8X10^{-7}, $\Delta S^{\neq}$ = 21.43 e.u and at 5.0 M, Δ E=21.83 Kcal/mol, A=10.0 X10^{-7} $\Delta S^{\neq}$ = 24.34 e.u has been found.

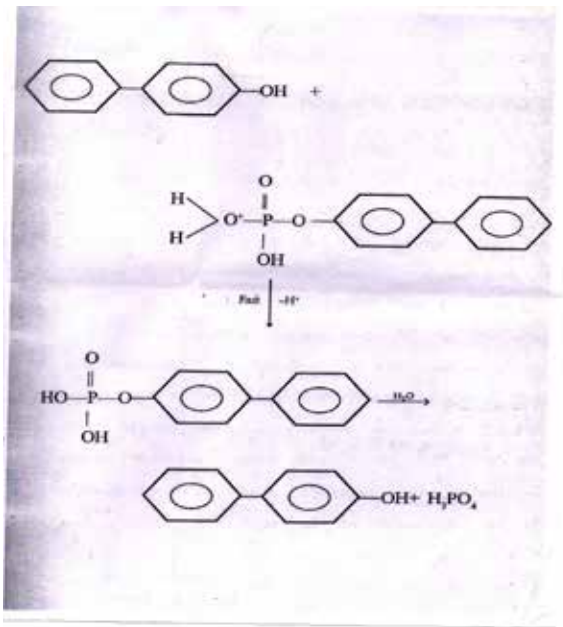
These parameters fall in the range of bimolecular hydrolysis involving P-O bond fission as supported by the isokinetic relationship. Table-5 summaries the comparative isokinetic rate data of di-esters and figure-4 describes the isokinetic relationship plot, which shows the point of 4-hydroxybiphenyl phosphate di-ester undergoes hydrolysis via P-O bond fission.

Table 5
COMPARATIVE ISOKINETIC RATE DATA FOR THE HYDROLYSIS OF SOME PHOSPHATE MONO ESTERS VIA THEIR CONJUGATE ACID SPECIES

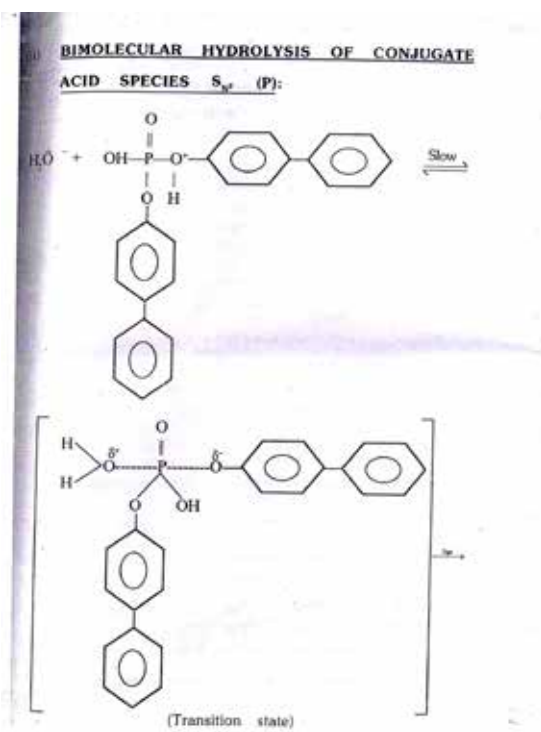
S NO.	Phosphate Esters	E.k cals/ mole	- $\Delta S^{\neq}$ (e.u)	Bond fission	Ref.
1	2,3-dimethoxy phenyl	31.56	2.57	P-O	10
2	2,4,6-trichlorophenyl	24.41	11.87	P-O	11
3	4-chloro-3,5-diethylphenyl	23.33	19.14	P-O	12
4	Pentachlorophenyl	22.40	21.43	P-O	13
5	2,4,6-trimethylphenyl	21.08	25.46	P-O	14
6	3-aminophenyl	21.96	22.51	P-O	15
7	p-bromophenyl	20.14	30.00	P-O	16
8	o-methoxy-p-methylphenyl	13.63	44.15	P-O	17
9	di-ethyl-dithiophenyl	11.44	56.82	P-O	18
10	4-hydroxybiphenyl	21.42 21.83	24.61 24.34	P-O	This work

Mechanism-Thus the mechanism of hydrolysis of di-4-hyroxybiphenyl phosphate in the region involves bimolecular attack of water on phosphorous of neutral species gives finally parent phenol and phosphoric acid.





The hydrolysis of 4-hydroxybiphenyl phosphate diester involve P-O bond fission in the transition state formed due to bimolecular nucleophilic attack of water molecule.Therefore, the isokinetic relationship has been examined with the similarity of substituted phenyl phosphate diester which proceeds similar mechanism under the similar experimental conditions.



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