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Mechanistic and Kinetic approach to the Hydrolysis of Mono-*p*-nitro-Thiophenyl Phosphate in Acidic Media

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Investigation of *p*-nitro-thiophenyl phosphate was carried out, by using "Allen's" modified method of colorimetry, in aqueous medium from 0.1 to 7.0 mol dm^3 HCl at 65°C. pH log rate profile has a rate maximum at 4.0 mol dm^3 HCl. Here mainly contribution of conjugate acid species of mono-thioate is involved in hydrolysis. Ionic-strength, temperature, solvent and concentration's kinetic studies provided to identify the reactive species and molecularity. Molecularity and bond-fission is also discussed in terms of Zücker-Hammett hypthesis, Hammett acidity founctions, Bunett and Bunett-Olsen parameters, isokinetic relationships and effect of temperature and solvent etc.

INTRODUCTION

Despite the fact the C—S—P forms of phosphate esters are having vast-significance as fungicides and insecticides[1] as thiol forms is activated by oxidation at ease. The 'ATP' era of biochemical development is all of due to the adenosine triphosphate involved in the numerous biological activities. Beside these biochemical, industrial[2] applications of the phosphate esters are of great academic interest with this view in mind the kinetic study of hydrolysis of mono-*p*-nitro-thiophenyl phosphate is investigated.

EXPERIMENTAL

Mono-*p*-nitro-thiophenyl phosphate was prepared by the method of $POCl_3$[3, 4] by phosphorylation of *p*-nitro-thiophenol in the mixture of pyridine and benzene. The reactions were carried out at 65 ± 0.05°C employing 0.005 mol dm^3 solution of mono-ester which was subsequently followed by the Allen's[5] modified method of colorimetric estimation of organic phosphate in aqueous media maintaining constant ionic-strength by means of HCl and NaCl. All the chemicals used were of B.D.H. quality.

RESULTS AND DISCUSSION

In aqueous medium hydrolysis of mono-*p*-nitro-phenyl phosphate was studied in HCl from (0.1 mol dm^3 to 7.0 mol dm^3 HCl) at 65°C. In Table 1 the pseudo-first order rate constants are summarised, from which it is quite clear that rate of reaction increases upto 4.0 mol dm^3 but further increase in acid molarity really decreases the rate as it can be attributed to the complete conversion of the ester (basic) molecule into their respective conjugate acid species with the lowering of concentration of a nucleophile (water), which plays its role in rate determining step of bimolecular hydrolytic reaction.

TABLE–1
RATE OF HYDROLYSIS OF MONO-*p*-NITROTHIOPHENYL PHOSPHATE ESTER AT 65°C

S. No.	HCl (mol dm^3)	$10^8 K_e$ (experimental) (min^{-1})	$2 + \log K_e$
1.	0.1	2.92	0.4653
2.	0.2	3.25	0.5118
3.	0.5	4.28	0.6314
4.	1.0	6.41	0.8068
5.	2.0	12.46	1.0955
6.	3.0	20.33	1.3081
7.	4.0	33.76	1.5200
8.	5.0	10.65	1.0273
9.	6.0	6.50	0.8129
10.	7.0	3.75	0.5740

The hydrolysis at each ionic strength can be governed by the equation[6], as,

$$K_e = K_H^+ \cdot C_H^+ + K_N \tag{1}$$

where, K_e and K_H^+ are experimental and specific rate constants, C_H^+ is the concentration of H^+ ions and K_N is the neutral rate.

TABLE–2
EXPERIMENTAL AND ESTIMATED RATES FOR THE HYDROLYSIS OF MONO -*p*-NITRO-THIOPHENYL PHOSPHATE ESTER AT 65°C

HCl mol dm^3	$K_H^+ \cdot C_H^+ \times 10^2$ (min^{-1})	$K_N \times 10^2$ (min^{-1})	$K_e \times 10^2$ (min^{-1}) estimated	$-\log a(H_2O)^n$ water activity	$K_e \times 10^2$ (min^{-1}) estimated	$K_e \times 10^2$ (min^{-1}) experimental
0.1	0.3236	2.5	2.82	—	2.82	2.92
0.2	0.6622	2.5	3.16	—	3.16	3.25
0.5	1.7740	2.5	4.27	—	4.27	4.28
1.0	3.9810	2.5	6.48	—	6.48	6.41
2.0	10.2	2.5	12.52	—	12.52	12.46
3.0	18.92	2.5	21.45	—	21.45	20.33
4.0	31.78	2.5	34.48	—	34.38	33.76
5.0	50.00	2.5	52.50	$(0.155)^5$	10.89	10.65
6.0	77.54	2.5	80.40	$(0.211)^6$	6.59	6.50
7.0	109.94	2.5	111.94	$(0.279)^7$	3.73	3.75

According to the empirical equation of Debye-Hückel[6]

$$K_e = K_H^+ \cdot C_H^+ = K_{HO} \cdot C_H^+ \exp b_H^+ \cdot \mu \tag{2}$$

where K_H^+, K_{HO} and b_H^+ are specific acid catalysed rates at that ionic strength, specific acid catalysed rate at zero ionic strength and slope of the linear curve constant ($b_H^+/2.303$) respectively. From the above equations (1) and (2) the acid and neutral rates can be written as follows,

For Acid rate

$$\log K_H^+ \cdot C_H^+ = \log K_{HO}^+ + \log C_H^+ b'_H \cdot \mu \qquad (3)$$

For protonated neutral rate

$$\log K_N^+ = b'_N \cdot \mu + \log K_{NO} \qquad (4)$$

(where $b'_N = b/2.303$)

The hydrolysis of present monoester can be represented by the equation.

K_e = Acid rate + Neutral rate equation

From equation (3) and (4)

$$K_e \text{ (estimated)} = K_H^+ \cdot C_H^+ + K_N \qquad (5)$$

This equation (5) is used to estimate theoretical rates which are then compared with experimental rates.

It can be seen that there is close agreement in theoretically calculated and experimentally observed rates for the region 0.1 to 4.0 mol dm^3 HCl. But for higher molarity *i.e.*, after 4.0 mol dm^3 the equation will change by including water-activity as an additional parameter, which is also shown by Bunnett parameters, in the hydrolysis of both conjugate acid species and neutral species. Both acid catalysed and neutral rates are subjected to positive effect of ionic-strength. The w and w* are associated with a slow proton transfer with the values as 9.37 and 4.0 respectively supporting the bimolecular nature of mechanism.

TABLE–3
ESTIMATED ARRHENIUS PARAMETERS

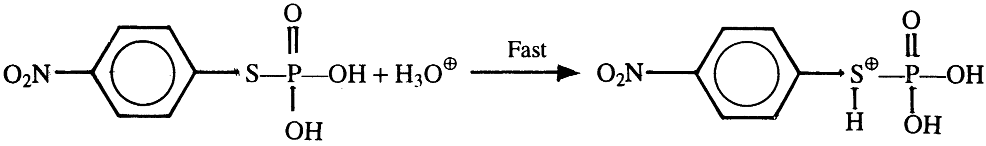
Acid mol dm^3	Temp. (°C)	10^3K_e (experimental)	E K.cal/mol	$A \times 10^2\ Sec^{-1}$	$-\Delta S \neq$ e.u
3.0	75	24.60			
3.0	65	20.33	4.759	3.9770	–58.03
3.0	55	16.46			
5.0	7	12.63			
5.0	65	10.65	4.209	0.9243	–60.10
5.0	55	8.65			

Bunnett-Olsen parameter[7, 8] $\phi = 1.92$ (>0.58) shows that the water involved as proton transfer agent in rate determining step in this present monoester. Arrhenius parameters[9] determined for the hydrolysis at 3.0 and 5.0 mol dm^3 HCl (Table–3). The magnitudes of Arrhenius parameters[9] fall in the range of bimolecular reaction. Since dioxane-water[10, 11] is a better (proton-donor) donating medium, therefore, solvent effect studies from Table (not shwon) suggests that rate increases with increase in dioxane contents as it increases the concentration of conjugate acid species, so on the ground of qualitative theory, the transition state formed out of conjugate acid species and water brings about dispersion of positive charge, which is in accord with Chanley's observtation[12]. Here the effect of concentration of ester on rate also confirms the order of reaction to be one with respect to the ester by reducing either half ($K = 33.16 \times 10^{-3}\ min^{-1}$) or double ($K = 33.70 \times 10^{-3}\ min^{-1}$) the normal concentration at 4.0 mol dm^3.

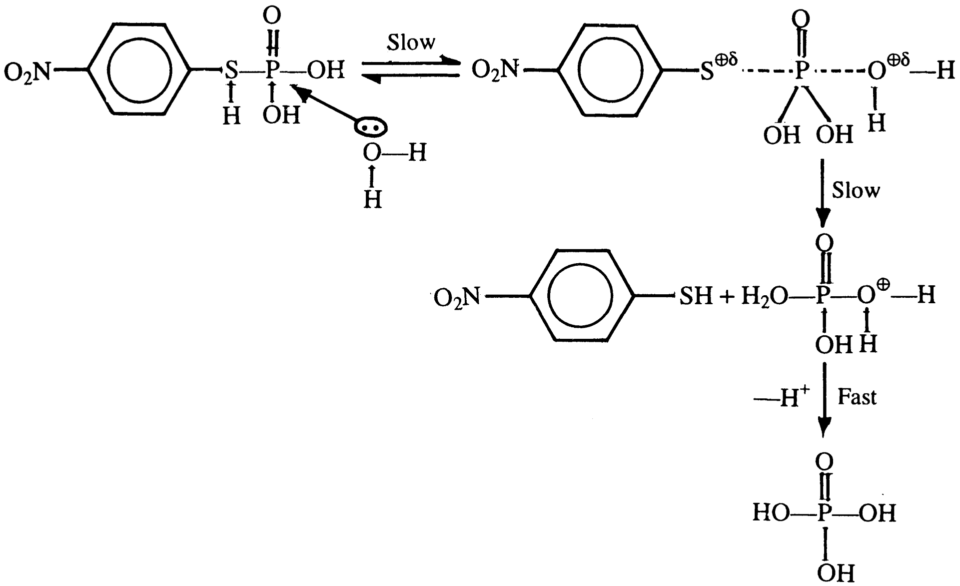
A comparative kinetic data[13] (not shown) also support the bi-molecular nature of the hydrolysis involving P—S bond fission. Therefore, acid-hydrolysis of mono-*p*-nitrothiophenyl phosphate involves bimolecular attack as shown by iso-kinetic relationship data shows a linear plot suggesting a mechanism of hydrolysis with P—S bond fission.

Mechanism

1. Formation of conjugate acid species:



2. Bimolecular nucleophilic attack of water on the phosphorus of the conjugate acid-species $(S_N^2)P$:



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