

## Kinetic Study and Mechanism of Mono Phenyl Hydrazo Phosphate (Ba-Salt) via Its Conjugate Acid Species

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Hydrolysis of mono phenyl hydrazo phosphate (Ba-salt) was carried out in the acid region ( $0.1-7.0 \text{ mol dm}^{-3}$ ) at  $98^\circ\text{C}$  in aqueous media. The acid-log rate profile has a rate maxima at  $4.0 \text{ mol dm}^{-3}$ . Here mainly contribution of mono phenyl hydrazo phosphate (Ba-salt) is involved in hydrolysis. The participation of conjugate acid species and determination of theoretical rates has been exhibited by ionic strength data. The observed rates were also found in close agreement with the estimated theoretical rates derived from the 2nd empirical term of Debye-Hückel equation. By molecularity data the bimolecular nature of reaction is detected and P—N bond fission has been strengthened by isokinetic relationship.

### INTRODUCTION

The phosphate esters with C—N—P linkages have also been used as plasticisers<sup>1</sup>, polymeric substances<sup>2</sup>, synthetic lubricants<sup>3</sup>, and hydraulic brake fluid<sup>4</sup>. Particularly cyclic amino phosphate in combination with phosphoramidic acid and sulphur drugs are very important for their pharmaceutical and medicinal value<sup>5</sup> and as cancer chemotherapeutic agents<sup>1</sup>. The present work is an extension of the previous work<sup>6</sup>.

### EXPERIMENTAL

Mono phenyl hydrazo phosphate (Ba-salt) was prepared by the  $\text{H}_3\text{PO}_4$  method by phosphorylation of phenyl hydrazine hydrochloride in the mixture of benzene and pyridine. The reactions were carried out at  $98^\circ\text{C}$  employing ( $5 \times 10^{-4} \text{ mol dm}^{-3}$ ) solution of the compound, which was followed by colorimetric estimation by Allen's<sup>7</sup> modified method in aqueous media, while constant ionic strengths were maintained using appropriate mixture of NaCl and HCl.

### RESULTS AND DISCUSSION

#### Hydrolysis via conjugate acid species

Investigation was carried out at  $98^\circ\text{C}$  in the range of  $0.1-7.0 \text{ mol dm}^{-3}$  in aqueous media and it was found that the pseudo-first order rate co-efficients increase with the subsequent increase in acid molarity<sup>7,8</sup> upto  $4.0 \text{ mol dm}^{-3}$

(Table-1) and then on further rise in molarity decrease in rate co-efficients has been found which can be attributed to the complete conversion of the basic (ester) molecules into respective conjugate acid species with simultaneous lowering in concentration of nucleophile (water) playing an important role in the rate determining step of bimolecular reactions.

Hydrolysis at each ionic strength (1, 2 and 3  $\mu$ ) is denoted by linear curve; the increase in rates with the increase in acid concentration at each ionic strength (1, 2 and 3  $\mu$ ) indicates specific acid catalysis. Here the neutral rates are subjected to a +ve ionic strength effect, since increase in intercepts with increase in  $\mu$  has been observed. The slopes of the linear curves suggest a +ve contribution of ionic strength effect to the acid catalysed species.

By the 2nd empirical term of the Debye-Hückel<sup>9</sup> equation the total rates contributed by conjugate acid, neutral forms, can be estimated as

$$K_e = K_H^+ \cdot C_H^+ + K_N \quad (I)$$

From the above equation (I) the acid and the neutral rates contributing to the experimental rate constants can be written as follows:

**(A) For Acid-rate<sup>10</sup>**

$$\log K_H^+ \cdot C_H^+ = \log K_{H_0}^+ + \log C_H^+ b_{H^+} \cdot \mu \quad (II)$$

**(B) For Protonated Neutral-rate<sup>10</sup>**

$$\log K_N = b_N' \cdot \mu + \log K_{N_0} \quad (III)$$

where  $b_N' = b/2.303$ .

Now the hydrolysis of present monoester can be governed by the following equation

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

The equation (IV) gives the estimated rates which are then compared with the experimental rates.

Arrhenius parameters<sup>11</sup> are determined for the hydrolysis at 4.0 and 5.0 mol dm<sup>3</sup> HCl. The magnitudes of Arrhenius parameters fall in the range of bimolecular reaction.

Bimolecular nature is further supported by Hammett<sup>12</sup> (0.30), Zucker-Hammett<sup>13</sup> (1.00), Bunnett<sup>6</sup> ( $W = 7.5$ ,  $W^* = 2.0$ ) plots. Arrhenius parameters at 4.0 and 5.0 mol dm<sup>3</sup> are: E (kcal mole<sup>-1</sup>) is 1.0067 and 1.0433 respectively,  $A \times 10^{-4}$  (sec<sup>-1</sup>) is 3.51 and 3.37 respectively,  $-\Delta S^\ddagger$  (e.u.) is 76.79 and 76.87 respectively.

Bunnett-Olsen<sup>14</sup> ( $\phi = 0.92$ ) suggests that water is involved as a proton transfer agent in the rate determining step.

The effect of solvent (Table-1) shows a significant rise in rates. Dioxane<sup>15</sup> being a better proton donor than water increases the concentration of conjugate acid species resulting in the increase in rates. Similar results were observed in tri-,2,4,6-tribromothiophenyl phosphate<sup>16</sup>. This is in accord with Chanley's<sup>17</sup> observation that indicates dispersion of charge in the transition state formed.

TABLE-I

HCl (mol dm <sup>3</sup> )	$K_H^+ \cdot C_H^+ \times 10^5$ (min <sup>-1</sup> )	$K_N \times 10^5$ (min <sup>-1</sup> )	$K_e \times 10^5$ (estimated rates)	$K_e \times 10^5$ (experimental rates)
0.1	5.393	150.31	155.703	158.91
0.2	10.833	152.75	163.583	165.79
0.5	27.435	160.32	187.755	192.72
1.0	56.066	173.78	229.846	229.92
2.0	117.065	204.17	321.235	322.27
3.0	183.324	239.88	423.204	427.23
			423.23 <sup>d</sup>	
			428.72 <sup>e</sup>	
			430.34 <sup>f</sup>	
4.0	255.187	281.83	537.017	538.84
				509.03 <sup>a</sup>
				441.67 <sup>b</sup>
5.0	163.07	331.13	494.20	492.33
			492.83 <sup>d</sup>	460.14 <sup>a</sup>
			494.45 <sup>a</sup>	401.79 <sup>b</sup>
			497.22 <sup>f</sup>	
6.0	59.88	389.04	448.92	449.36
7.0	38.89	365.04	403.93	403.11

a, b are temperature effect data at 90° and 50°C respectively.

d, e and f are solvent effect data of 10%, 20% and 30% dioxane respectively.

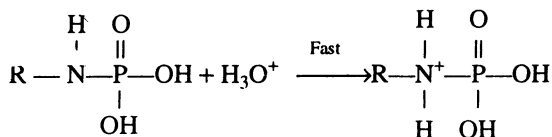
The concentration effect of the present ester confirms the order of reaction to be one with respect to the present ester by reducing either half ( $K_e = 538.52 \times 10^{-5} \text{ min}^{-1}$ ) or double ( $K_e = 538.55 \times 10^{-5} \text{ min}^{-1}$ ) and the normal concentration ( $K_e = 538.84 \times 10^{-5} \text{ min}^{-1}$ ) at 4.0 mol dm<sup>3</sup> hydrochloric acid.

P—N bond fission has been supported by the comparative kinetic rate data<sup>9</sup> (not shown).

By considering all the above data we conclude that acid hydrolysis of monophenyl hydrazo phosphate (Ba-salt) undergoes bimolecular P—N bond fission with fast pre-equilibrium proton transfer.

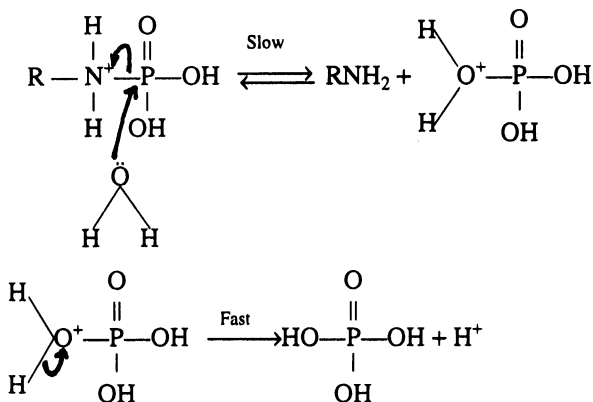
### Mechanism of Hydrolysis

#### (a) Formation of conjugate acid species:



where R = C<sub>6</sub>H<sub>5</sub>NH—

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



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(Received: 29 March 1995; Accepted: 25 September 1995)

AJC-1018