

## Kinetics of Hydrolysis of Mono-*p*-toluidine Phosphate Catalyzed by Hydrochloric Acid

PRAGYA AWADHIYA and S.A. BHOITE\*

School of Studies in Chemistry, Pt. Ravi Shankar Shukla University, Raipur-492 010, India

E-mail: sa\_bhoite@rediffmail.com; p\_awadhya@rediffmail.com

Kinetic study of the hydrolysis of mono-*p*-toluidine phosphate has been carried out in 0.1 to 7.0 M HCl at  $50 \pm 0.5$  °C. The rate of hydrolysis increases with increase in acid molarity up to 4 M HCl and after that it decreases. The lowering of rates after 4 M HCl has been attributed to the effect of water activity. Rate data at constant ionic strength is used to identify reactive species and to determine theoretical rates. Hydrolysis of monoester *via* conjugate acid species has been assigned the bimolecularity of the reaction on the basis of Arrhenius parameters, Zucker-Hammett hypothesis and Bunnett & Bunnett-Oleson's parameters. Solvent effect has been found to indicate the formation of a transition state in which charge dispersion occurs. Kinetic rate data and isokinetic relationship have been used to propose the probable bond fission.

**Key Words:** Kinetics, Hydrolysis, Mono-*p*-toluidine phosphate, Hydrochloric acid.

### INTRODUCTION

The importance of kinetic study of phosphate esters have been well recognized. Much work has been done on the phosphate esters of C-O-P linkages<sup>1</sup> and some of their reaction paths have been understood. Phosphate esters having C-N-P linkages have been less studied, even though the comparisons of hydrolytic reactions of phosphates having C-O-P and C-N-P linkages are of great academic importance. The phosphate esters having C-N-P linkages are used as insecticides<sup>2</sup>, pesticides<sup>3</sup>, cancer chemotherapeutic agent<sup>4</sup>, plasticizers<sup>5</sup>, smoke generation<sup>6</sup>, additives for fire-retardant<sup>7</sup>, petroleum and corrosion inhibitors<sup>8</sup>, *etc.* For research point of view, the kinetic study of the hydrolysis of mono-*p*-toluidine phosphate ester is of great interest.

### EXPERIMENTAL

Mono-*p*-toluidine phosphate (barium salt) has been prepared from *p*-toluidine and phosphorus pentoxide by the method described earlier<sup>9</sup>. Inorganic phosphate produced during hydrolysis has been determined spectrophotometrically by Allen's modified method<sup>10</sup>. All the reactions have been carried out at the  $50 \pm 0.05$  °C employing  $5 \times 10^{-4}$  M solution of the monoester in aqueous medium. The constant

ionic strengths were maintained by using mixture of HCl and NaCl. All the chemicals used were of AR grade. Confirmations of the compound have been done by: Elemental analysis (%) calcd. (found): C 26.05 (27.81), H 2.48 (2.17), N 4.34 (3.45), P 9.61 (8.76). IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3286, 2939, 1087, 948, 844 (P-N).

## RESULTS AND DISCUSSION

Hydrolysis of mono-*p*-toluidine phosphate ester has been studied at  $50 \pm 0.5$  °C, in the region from 0.1 to 7.0 M HCl. Pseudo first order rate coefficients obtained are summarized in the Table-1.

TABLE-1  
RATE OF HYDROLYSIS OF MONO-*p*-TOLUIDINE PHOSPHATE  
IN HYDROCHLORIC ACID AT 50 °C

HCl (M)	$k \times 10^{-3}$ ( $\text{min}^{-1}$ )		$3 + \log k$	
	Experimental	Estimated	Experimental	Estimated
0.1	6.00	4.55	0.78	0.65
0.2	8.34	5.10	0.92	0.71
0.5	10.24	7.71	1.01	0.89
1.0	14.98	13.15	1.17	1.12
2.0	29.62	29.47	1.47	1.47
3.0	56.94	55.78	1.76	1.75
4.0	97.47	97.40	1.98	1.99
5.0	83.02	78.61	1.92	1.89
6.0	62.81	60.64	1.80	1.78
7.0	29.08	31.83	1.46	1.49

The rate of hydrolysis increases with the rise in acid molarity up to 4.0 M and further rise in acid molarity decreases the rate as shown in Fig. 1.

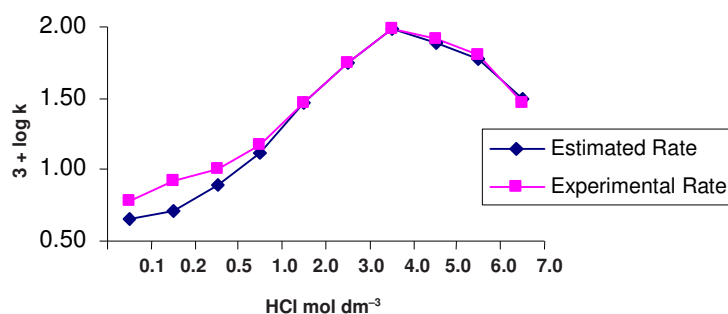


Fig. 1. Acid molarity vs.  $\log k$  for the hydrolysis of mono-*p*-toluidine phosphate at  $50 \pm 0.5$  °C

The result of studies at different ionic strengths (Fig. 2) shows that (a) each linear curve makes the positive slope with acid axis, hydrolysis is subjected to acid catalyzed at each ionic strength. (b) Curves meet at a point on the rate axis indicating the participation of neutral species is constant and independent of the influence of ionic strength.

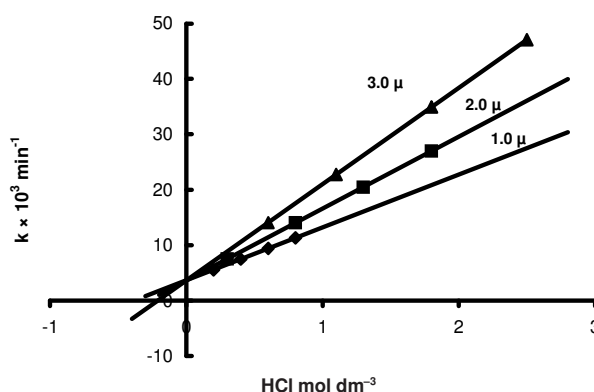


Fig. 2. Acid hydrolysis of mono-*p*-toluidine phosphate at constant ionic strength at  $50 \pm 0.5$  °C

The overall rate of hydrolysis of the reaction may be represented as:

$$k_e = k_H^+ \cdot C_H^+ \quad (1)$$

where  $k_e$ ,  $k_H^+$  and  $C_H^+$  are the experimental rate coefficients, specific acid catalyzed rate at ionic strength and concentrations of  $H^+$ .

Since the slope of the linear plot increases with increase in ionic strength, hydrolysis is subjected to the positive effect of ionic strength. Specific acid catalyzed rates ( $k_H^+$ ) were then converted to acid rates ( $k_H^+ \cdot C_H^+$ ) as:

$$k_H^+ \cdot C_H^+ = k_{H_0} + C_H + \exp. b_H^+ \cdot \mu \quad (2)$$

where for HCl,  $\mu$  and  $C_H^+$  are of the same value. The slope of the linear curve is  $b_H^+$ , which is equal to  $b_H^+/2.303$  and intercept on log rate axis is  $3 + \log k_{H_0}^+$  (Fig not shown). It is seen that there is an agreement between theoretical and experimental rates in the acid region up to 4.0 M HCl, while at the lower (0.1 M and 1.0 M) HCl as well as at higher (above 4.0 M) acid molarities the agreement between theoretical and experimental rates does not exist. At lower acidities disagreement may be due to incursion of neutral species. Disagreement between rates 5.0 to 7.0 M HCl has been found to be due to the incursion of water activity parameter. Rate estimated by equation (3) agree with the experimental rates.

$$k_H^+ \cdot C_H^+ = k_{H_0} + C_H \exp. b_H^+ \cdot \mu (a_{H_2O})^n \quad (3)$$

where  $n$  is an integer and  $a_{H_2O}$  is water activity.

Arrhenius parameters (figure not shown) determined for the hydrolysis at 4.0 M HCl are given as:  $E = 11.89$  Kcal/mol,  $A = 1.08 \times 10^7$  s<sup>-1</sup>,  $\Delta S^\ddagger = -28.45$  e.u.

Magnitude of the Arrhenius parameters fall in the range of bimolecular nature of the reaction<sup>11</sup>. The slope of Zucker-Hammett hypothesis<sup>12</sup> is 1.64 which clearly indicates the bimolecularity of the reaction (fig not shown). Slope slightly greater than unit is due to positive salt effect. Dependence of rate on water activity is supported by Bunnett and Bunnett-Olsen's plot<sup>13</sup> (fig not shown). The parameters  $w$ ,  $w^*$  and  $\phi$  are 8.5, 2.3 and 1.15, respectively.

A change over from water to 30 % aqueous dioxane (v/v) increases the rate of hydrolysis (Table-2) indicates the formation of a transition state in which charge is dispersed<sup>14</sup>.

TABLE-2  
EFFECT OF CHANGES IN SOLVENT PROPORTIONS ON THE RATE OF  
ACID HYDROLYSIS OF MONO-*p*-TOLUIDINE PHOSPHATE AT 50 °C

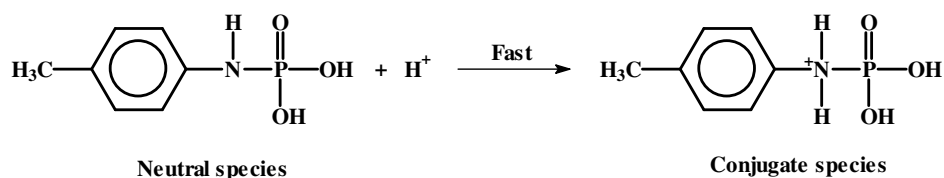
HCl (M)	Percentage of dioxane (v/v)	$k \times 10^{-3}$ (min <sup>-1</sup> )
4.0	0.00	97.47
	10.00	99.08
	20.00	102.27
	30.00	105.33

Mono-*p*-toluidine phosphate may undergo hydrolysis either by P-N or C-N bond fission. Table-3 summarizes comparative rate data<sup>15</sup> for the hydrolysis of other monoesters studied kinetically shows isokinetic relationship. The point of mono-*p*-toluidine phosphate lies on the linear curve of those monoesters which are known to undergo hydrolysis *via* P-N bond fission (fig. not shown). Thus P-N rather than C-N bond fission appears to be more likely.

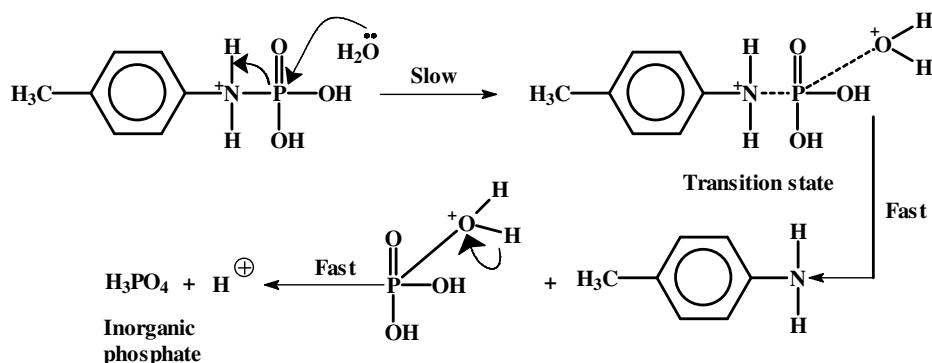
TABLE-3  
COMPARATIVE KINETIC RATE DATA FOR THE HYDROLYSIS OF SOME  
PHOSPHATE MONOESTERS *via* CONJUGATE ACID SPECIES

Phosphate monoesters	Medium HCl (mol dm <sup>-3</sup> )	E (Kcal/mol)	$-\Delta S^\ddagger$ e.u.	Molecularity	Fission
2-Nitro 4-methoxy aniline	4.0	6.61	54.80	2	P-N
<i>p</i> -Nitro aniline	3.0	15.25	9.50	2	P-N
Diethyl amine	4.0	6.61	60.65	2	P-N
<i>p</i> -Butyl aniline	3.0	11.12	45.77	2	P-N
Mono <i>p</i> -toluidine phosphate	4.0	11.89	28.48	2	This work

The bimolecular hydrolysis with P-N bond fission of the conjugate acid species has been proposed as below:



Formation of conjugate acid species by fast pre-equilibrium proton transfer



Bimolecular nucleophilic attack of water on phosphorous atom of conjugate acid species

### ACKNOWLEDGEMENT

The authors are thankful to the Head, School of Studies in Chemistry, Pt. Ravi Shankar Shukla University, Raipur for providing research facilities.

### REFERENCES

1. C.A. Vernon, The Chemical Society of London, Special Publication No. 8, p. 17 (1957).
2. J.F. Cavalier, F. Fotiadu, R. Verger and G. Bueno, *Synlett.*, 73 (1998).
3. T.C. Kwong, *Ther. Drug Monit.*, **24**, 144 (2002).
4. B.T. Burlingham and T.S. Widlanski, *J. Org. Chem.*, **23**, 7561 (2001).
5. Y. Tonaka, S. Kano and K. Odawara, Nipponsoda Co. Ltd., D.O.S. 2.416.178 (1974).
6. R.A. Moss and H.R. Morales, *J. Am. Chem. Soc.*, **123**, 7457 (2001).
7. M. Paul, *J. Vinyl Additive Technol.*, **10**, 187 (2004).
8. L.D. Quin, A Guide to Organophosphorus Chemistry, John Wiley & Sons Inc. New York, p. 2, 375 (2000).
9. J. Cavalier, *Bull. Soc. Chem. (France)*, **13**, 885 (1895).
10. R.J.L. Allen, *Biochem. J.*, **34**, 858, (1940).
11. F.A. Long, J.G. Pritchard and S.E. Stafford, *J. Am. Chem. Soc.*, **79**, 2365 (1957).
12. L. Zucker and L.P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939).
13. J.F. Bunnett and F.F. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).
14. J.D. Chanley and E. Feageson, *J. Am. Chem. Soc.*, **77**, 4002 (1955).
15. J.S. Chauhan, Ph.D. Thesis, Jiwaji University, Gwalior, India (1995).