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Kinetics and Mechanism of Hydrolysis of Mono–2,4,6– Tribromothiophenyl Phosphate via Conjugate Acid Species

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Kinetic Study of mono–2,4,6–tribromothiophenyl phosphate has been made in acid region (0.1 to 8.0 mol dm^{-3}) at 50°C. Acid log rate profile has a rate maximum at 7.0 mol dm^{-3}. Ionic strength data up to 3.0 μ requires the participation of conjugate acid species and to determine theoretical rates. Theoretical rates, estimated from second empirical term of Debye-Hückel equation, have been found in close agreement with experimental rates. Bimolecular behaviour has been decided by the Arrhenius parameters and by the analysis of molecularity data. The monoester involves P–S bond fission which is strengthened by comparative kinetic data.

INTRODUCTION

Phosphate having C–S–P linkages are of great importance. They are used for antiviral activity[1], insecticidal activity[2], radioactive tracer techniques[3], for biological investigations and textile commodities[4], with such a broad spectrum biological activity of thiophosphates the knowledge regarding their bond cleavages and their stabilities are important. Keeping this in view, the hydrolytic bond cleavages of mono–2,4,6– tribromothiophenyl phosphate has been investigated.

EXPERIMENTAL

Mono– 2,4,6– tribromothiophenyl phosphate was prepared by treating 2,4,6–tribromothiophenol with $POCl_3$[5,6] in pyridine which is used as a solvent. (Found:- C–8.96, H–0.24, S, 4.01, P–3.85, Br–59.9%, Calcd:- C–8.98, H–0.25, S–3.99, P–3.86, Br–59.8%.)

The hydrolysis of mono– 2,4,6– tribromothiophenyl phosphate (0.0005 mol dm^{-3}) was followed by colorimetric estimation of Allen[7]. The constant ionic strengths were maintained using mixtures of HCl and NaCl.

RESULTS AND DISCUSSION

The pseudo first order rate coefficients for the hydrolysis of the present mono ester in the range of 0.1 to 8.0 mol dm^{-3} HCl are found to increase with the increase in acid molarity upto 7.0 mol dm^{-3} (Table-1) further rise in acidity decreases the rate constants.

In order to determine whether or not there in effect of ionic strength or the presence of acid catalysis, kinetic runs were made at three different ionic strengths (1,2 and 3μ) which were maintained by adequate mixture of NaCl and HCl.

Hydrolysis at each ionic strength is denoted by a linear curve that mades a +ve slope with the acid axis, indicating the presence of acid catalysis. Since the slopes ($K_{H^+} = 0.765$, 0.829 and 0.912 for 1,2 and 3μ respectively) increases with increase in ionic strength, acid catalysed is subjected to positive effect of ionic strength. These curves make intercept on the rate axis, indicating the presence of side reaction of the neutral species. Ionic strength data shows that maximum at 7.0 mol dm^{-3} HCl is due to salt effect.

TABLE 1
RATE OF HYDROLYSIS OF MONO–2,4,6– TRIBROMOTHIOPHENYL PHOSPHATE (BARIUM SALT) AT 50°C.

HCl (mol dm^{-3})	$10^3 K_{H^+} \cdot C_{H^+}$ (min^{-1})	$10^3 K_N$ (min^{-1})	$10^3 K_{calc.}$ (min^{-1}) from eqn (1)	$10^3 K_{obsd}$ (min^{-1})
0.1	0.501	5.662	6.161	6.210
0.2	1.023	5.834	6.857	6.756
0.5	2.685	6.383	9.068	9.120
1.0	5.754	7.413	13.16	13.20
2.0	13.21	10.00	23.21	23.22, 27.90[a] 31.35[b], 40.25
3.0	22.75	13.49	36.24	36.30
4.0	34.83	18.20	53.03	53.13, 57.85[a] 60.32[b], 65.33[c]
5.0	50.00	24.55	74.55	74.60
6.0	68.87	33.11	101.9	101.9
7.0	92.26	44.67	136.9	136.8

a = 10% dioxane, b = 20%, dioxane, c = 30% dioxane,

From the study of ionic strength effect, the total rates contributed by conjugate acid neutral forms can be calculated by the following 2nd empirical term of Debye-Hückel[8] equation.

$$Ke = K_{H^+} \cdot C_{H^+} \cdot K_N \qquad (1)$$

In the above eqn the terms Ke, K_{H^+} and K_N are the observed rate constants, the specific acid catalysed and specific neutral rate at that ionic strength respectively. The sum of neutral and acid rates agree well with the experimentally observed rates (Table 1).

The rate law may therefore be formulated as:

$$K_e = 5.012 \times 10^{-3} \cdot C_{H^+} \cdot \text{Exp}\,(2.303 \times 0.066)\mu + 5.495 \times 10^{-3} \cdot \text{Exp}\,(2.303 \times 0.135)\mu$$

Arrhenius parameters[9] determined for the hydrolysis at 3.0 and 5.0 mol dm^{-3} HCl (Table 2). The magnitudes of Arrhenius parameters fall in the range of bi-molecular reaction[10]. Bi-molecular nature of reaction is further supported by Zücker-Hammett[11] (0.95), Hammett (0.43) and Bunnett ($W = 4.03$, $W^* = -1.029$) plots (not shown).

TABLE 2
CALCULATED ARRHENIUS PARAMETERS

HCl mol dm^{-3}	Temp t°C	10^3 Ke(Obsd) (min^{-1})	E K.Cal $mole^{-1}$	A × 10^2 Sec^{-1}	$-\Delta s^{\neq}$ e.u
3.0	40	10.52			
3.0	50	36.30	1.868	1.258	54.86
3.0	60	115.3			
3.0	70	380.2			
5.0	40	29.58			
5.0	50	74.60			
5.0	60	167.60	1.830	2.432	49.69
5.0	70	380.2			

Bunnet-Olsen[12] parameter ($\phi = 0.769$, which is greater than 0.58) 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 being a better proton donor than water increases the concentration of conjugate acid species resulting in the increase in rates. Effect of solvent on the rate of hydrolysis may therefore by taken to indicate the formation of transition state in which charge is dispersed.

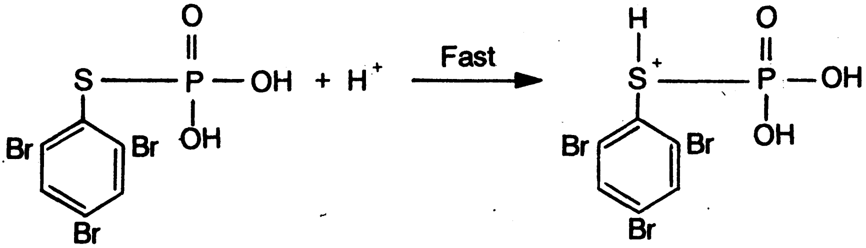
The effect of concentration of monoester on the rate of hydrolysis also confirms the order of reaction to be one with respect to the mono-ester by reducing either half ($Ke = 53.10 \times 10^{-3}$ min^{-1}) or double ($Ke = 53.11 \times 10^{-3}$ min^{-1}) the normal concentration ($Ke = 53.13 \times 10^{-3}$ min^{-1}) at 4.0 mol dm^{-3} HCl.

A comparative kinetic data[13,14] (not shown) also support the bi-molecular nature of the hydrolysis involving P–S bond fission.

Thus, acid hydrolysis of mono– 2,4,6– tribromothiophenyl phosphate involves bimolecular attack of water on phosphorus of conjugate acid species formed by fast pre-equilibrium proton transfer.

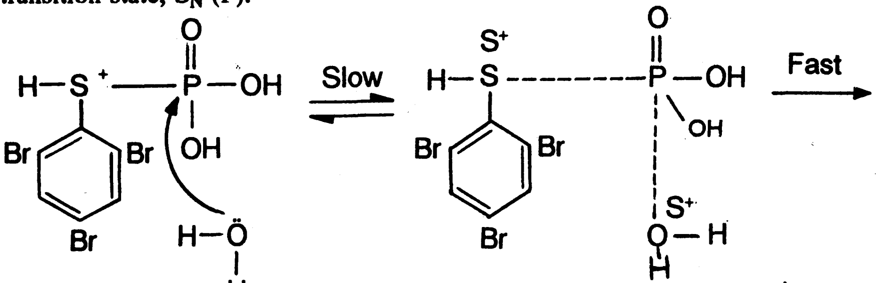
Mechanism

(a) Formation of conjugate acid species (II) by fast pre-equilibrium proton transfer from the undissociated mono-ester (I)

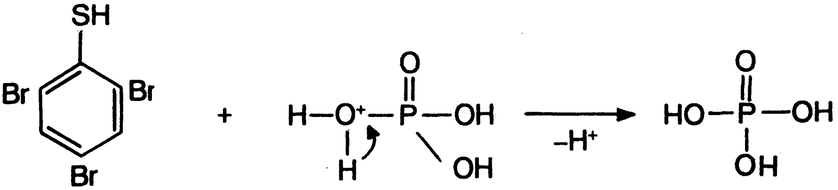


(I) Neutral form (II) Conjugate acid form

(b) Bi-molecular heterolysis of P–S bond via heavily hydrated but unstable transition state, $S_N2(P)$.



(Transition state)



REFERENCES

1. Synthesis and antiviral activity, *Chem. Abstr.*, **54**, 1303f, (1961).
2. A.H. Schlesinger, *Chem. Abstr.*, **49**, 5517c (1955).
3. G. Gardner and B.A. Kilby, *J. Chem. Soc.*, **3**, 1769 (1950).
4. H.N. Dayer, *Chem. Abstr.*, **53**, 1772g (1959).
5. Otto Poul, *Ber.*, **28**, 816 (1895).
6. P. Rudert, *Ber.*, **26**, 565 (1893).
7. R.J.L. Allen, *Biochem. J.*, **34**, 858 (1940).
8. J.E. Leffler and E. Gurnwald, The Rates and Equilibria of Organic Reactions, John Wiley and Sons, Inc., New York, pp. **177**, 286 (1889).
9. S.Z. Arrhenius, *Phys. Chem.*, **4**, 226 (1889).

10. R. Patil, C.P. Shinde and A.K. Bhadoria, *Asian J. Chem.*, **3**, 450 (1991).

11. L. Zücker and P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1932).

12. J.F. Bunnet and F.P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).

13. R.D. Gilliom, Introduction to Physical Organic Chemistry, Addison Wesley, pp. **167**, 169 (1970).

14. C.P. Shinde, R. Patil and A.R. Nikam, *Acta Cienc. Indica*, **15 C**, 97 (1989).

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