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Kinetics and Mechanism of Hydrolysis of Tri-2,4,6–Tribromothiophenyl Phosphate via Conjugate Acid species

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Hydrolysis of tri–2,4,6–tribromothiophenyl phophate has been made in acid region (0.1–7.0 mol dm^{-3} HCl) at 98°C in 30% aqueous dioxan (v/v) mixtures. Acid log rate profile has a rate maximum at 2.0 mol dm^{-3}. In general di- and tri-aryl phosphate have been found to give such maxima in the strong acid region. The lowering in rates after 2.0 mol dm^{-3} may be due to the negative effect of ionic strength and water activity *i.e.* reduction in concentration of water which brings about bi-molecular hydrolysis. 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 terms of Debye-Hückel equation, have been found in close agreement with the observed rates. Bi-molecular behaviour has been decided by the Arrhenius parameters and by the analysis of molecularity data. The triester involves P–S bond rupture which is strengthened by comparative kinetic data.

INTRODUCTION

Phosphates having C–S–P linkages are of great importance. They are used for antiviral activity[1], radioactive tracer techniques[2] for biological investigations, insecticidal activity[3] and textile commodities[4], due to these uses, the knowledge regarding their bond cleavages and their stabilities are important. Taking this in view the hydrolysis of tri-2,4,6-tribromothiophenyl phosphate has been investigated.

EXPERIMENTAL

Tri-2,4,6-tribromothiophenyl phosphate was prepared by treating 2,4,6-tribromothiopenol with $POCl_3$ by the method of Rudert[5].
(Found: C = 11.99%, H = 0.34%, S = 5.30%. P = 1.70%, Br = 79.77%
Calcd: C = 11.97%, H = 0.33%, S = 5.32%. P = 1.72%, Br = 79.76%).

The hydrolysis of tri-2,4,6-tribromothiophenyl phosphate (0.0005 mol dm^{-3}) was followed by colorimetric estimation of Allen[6] in 30% dioxane-water mixture.

The constant ionic strengths were maintained using appropriate mixtures of HCl and NaCl.

RESULTS AND DISCUSSION

The pseudo first order rate coefficients for the hydrolysis of the present tri-ester in the range of 0.1 to 7.0 mol dm^{-3} HCl are found to increase with the increase in acid molarity upto 2.0 mol dm^{-3} (Table-1). Further rise in acidity decreases the rate constants due to negative effect of ionic strength. Hydrolysis at each ionic strength (1,2 and 3 μ) is denoted by a linear curve, that makes a negative slope with the acid axis indicating the presence of acid catalysis. (Slopes K_{H^+} = 8.31, 5.31 and 3.32 for 1,2 and 3 μ respectively). These curves make intercept on the rate axis indicate that the hydrolysis of the tri-ester by neutral species has also been subjected to ionic retardation like acid catalysed rates. (Intercept K_N = 9.5, 8.8 and 8.1 for 1,2 and 3 μ respectively).

TABLE 1
RATE OF HYDROLYSIS OF TRI-2,4,6-TRIBROMOTHIOPHENYL PHOSPHATE AT 98°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})	$10^3 K_{Obsd.}$ (min^{-1})
0.1	1.259	8.974	10.23	10.22
0.2	2.399	8.933	11.33	11.30
0.5	5.236	8.820	14.05	14.06
1.0	8.313	8.630	16.94	16.92
2.0	10.50	8.260	18.76	18.77
3.0	9.933	7.907	17.84	17.85^a, 17.89^b 17.92^c
4.0	8.356	7.568	15.92	15.90
5.0	6.592	7.244	13.83	13.85^a, 13.98^b 14.03^c
6.0	4.991	6.934	11.92	11.94
7.0	3.674	6.637	10.31	10.32

a = 30% dioxane; b = 40% dioxane; c = 50% dioxane

From the study of ionic strength effect, the total rates contributed by conjugate acid, neutral forms can be calculated by the following second empirical term of Debye-Hückel equation[7].

$$Ke = K_{H^+} \cdot C_{H^+} + K_N \tag{1}$$

Here Ke = Observed rate constant

K_H^+ = Specific acid catalysed rate

K_{N^+} = Specific neutral rate

The sum of neutral and acid rates agree well with the experimentally observed rates (Table-1). The rate law may therefore be formulated as:

(1) In the region 0.1 mol dm^{-3} to 2.0 mol dm^{-3} HCl

$$Ke = K_{H_0^+} \cdot C_{H^+} \cdot \text{Exp}\, b'_{H^+} \cdot \mu + K_{N_0} \cdot \text{Exp}\, b'_N \cdot \mu$$

$$= 13.18 \times 10^{-3} \cdot C_{H^+} \cdot \text{Exp}\,(2.303X - 0.2)\mu$$

$$+ 9.016 \times 10^{-3} \cdot \text{Exp}\,(2.303X - 0.019)\mu$$

(2) In the region 2.0 mol dm^{-3} HCl.

$$Ke = K_{H_0^+} \cdot C_{H^+} \cdot \text{Exp}\, b'_{H^+} \cdot \mu + (a_{H_2O})^n + K_{N_0} \cdot \text{Exp}\, b'_N \cdot \mu(a_{H_2O})^n$$

$$= 13.18 \times 10^{-3} \cdot C_{H^+} \cdot \text{Exp}\,(2.303X - 0.2) \cdot \mu(a_{H_2O})^n$$

$$+ 9.016 \times 10^{-3} \cdot \text{Exp}\,(2.303X - 0.019) \cdot \mu \cdot (a_{H_2O})^n$$

[a_{H_2O} is water activity and n is an integer]

Arrhenius parameters[8] 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.

Bi-molecular nature of reaction is further supported by Zücker-Hammett[9] (0.807), Hammett[10] (0.216) and Bunnett[11] (w = 9.025, w* = 4.038) plots.

TABLE 2

CALCULATED ARRHENIUS PARAMETERS

HCl mol dm^{-3}	Temp. T°C	10^3K_e (Obsd) (min^{-1})	E KCal $mole^{-1}$	A × 10^3 Sec^{-1}	$-\Delta S^{\neq}$ e.u.
3.0	78	6.607			
3.0	88	10.47	13.07	14.91	23.56
3.0	98	17.78			
5.0	78	5.495			
5.0	88	8.511	12.67	6.688	25.16
5.0	98	13.80			

Bunnett-Olsen[12] parameter (φ = 1.66, 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. Solvent effect on the rate of hydrolytic reaction may therefore be taken in accord with chanley's[13] observation. It indicates the formation of a transition state in which charge is dispersed.

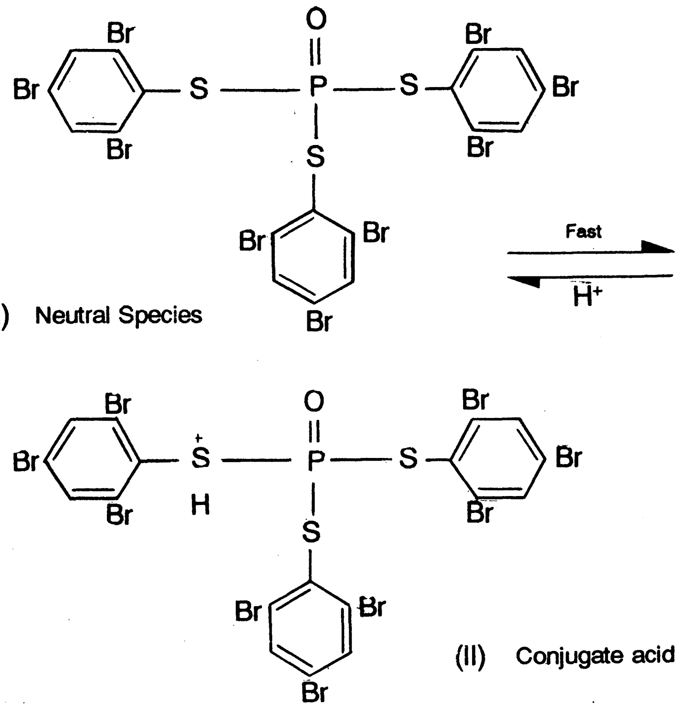
The concentration effect of triester on the rate of hydrolysis also confirms the order of reaction to be one with respect to the triester by reducing either half ($Ke = 15.82 \times 10^{-3}\ min^{-1}$) or double ($Ke = 15.95 \times 10^{-3}\ min^{-1}$) the normal concentration ($Ke = 15.90 \times 10^{-3}\ min^{-1}$) at 4.0 mol dm^{-3} hydrochloric acid.

Bimolecular nature of the hydrolysis of triester involving P–S bond fission is further supported by comparative kinetic data[14] for the hydrolysis of other esters and isokinetic relationship.

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

Machanism of Hydrolysis

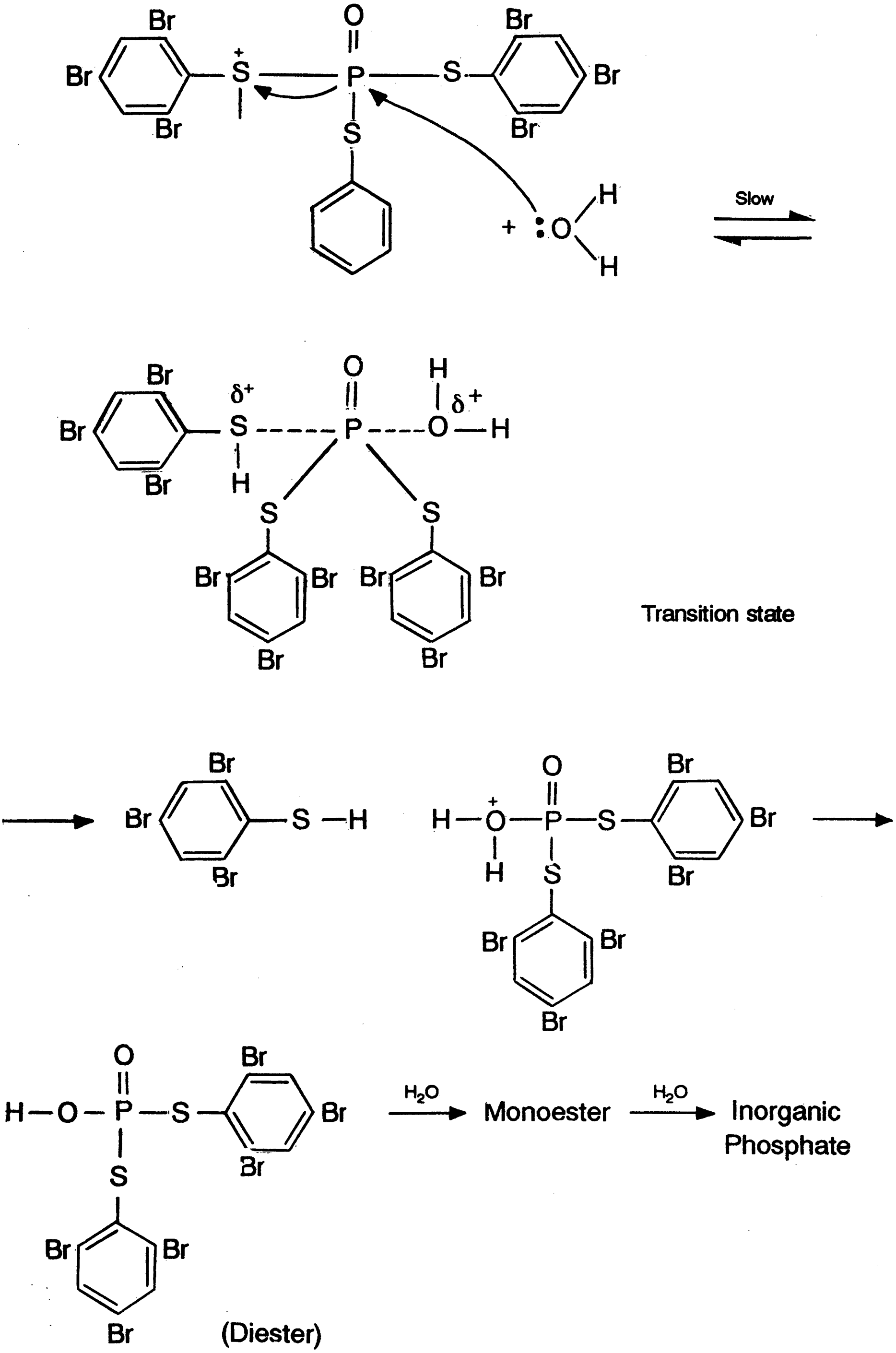
(a) Formation of conjugate acid species (II) of the triester (I) by the fast pre-equilibrium proton transfer.



(I) Neutral Species

(II) Conjugate acid species

(b) Bimolecular heterolysis of P–S bond of the conjugate acid species (II), S_N^2 (P).


Slow
Transition state
H₂O
Monoester
H₂O
Inorganic Phosphate
(Diester)

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