Kinetics and Mechanism of Hydrolysis of Mono-S-Butyl Phosphorothioate via Conjugate Acid Species

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Investigation of hydrolytic bond cleavage of mono-S-butyl phosphorothioate was carried out at 98°C employing 5.0×10^{-4} mol dm^{-3} solution by using Allen's modified method of colorimetry.

INTRODUCTION

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

EXPERIMENTAL

Mono-S-butyl phosphorothioate was prepared by the method of POCl$_3$ by phosphorylation of butanethiol in the mixture of pyridine and benzene.[5, 6] The reactions were carried out at 98°C employing 5.0×10^{-4} mol dm^{-3} solution of monoester which were subsequently followed by the Allen's[6] modifiied 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 BDH quality.

RESULTS AND DISCUSSION

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

In order to determine whether or not there is effect of ionic strength or presence of acid catalysis, kinetic runs were made at three different ionic strengths (1.0, 2.0 and 3.0 μ) which were maintained by adequate mixture of NaCl and HCl. Hydrolysis of each ionic strength is denoted by a linear curve (not shown) that makes a positive slope with the acid axis, indicating the presence of acid catalysis. Since the slopes ($K_{H^+} = 2.20 \times 10^{-3}$, 2.33×10^{-3}, 2.46×10^{-3} min^{-1} mol^{-1} l) increase 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 show that maximum at 7.0 mol dm^{-3} HCl is due to salt effect.

From the study of the ionic strength effect, the total rates contributed by

conjugate acid and neutral forms can be calculated by the following 2nd emprical term of Debye-Hückel[7] equation:

$$K_e = K_{H^+} \cdot C_{H^+} + K_N \tag{i}$$

TABLE-2
RATE OF HYDROLYSIS OF MONO-S-BUTYL
PHOSPHOROTHIOATE (Ba-SALT) 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})	$10^3 K$ (Obs.) (min^{-1})	
0.1	0.205	2.492	2.697	2.187	
0.2	0.412	2.589	3.002	3.947	
0.5	3.051	2.904	6.855	4.254	
1.0	2.151	3.515	5.666	5.757	
2.0	4.533	5.152	9.685	9.557	
3.0	7.164	7.550	14.715	14.518	
4.0	10.064	11.066	21.130	20.158,	22.842[a] 25.131[b] 26.819[c] .
5.0	13.255	16.218	29.473	27.336	
6.0	16.761	23.768	40.529	36.295	
7.0	20.600	34.833	55.434	49.652	

a = 5% dioxane,   b = 10% dioxane,   c = 20% dioxane

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

The rate law may, therefore, be formulated as:

$K_e = 2.04 \times 10^3 \cdot C_{H^+} \exp (2.303 \times 0.0227) \cdot u + 2.39 \times 10^{-3} \exp (2.303 \times 0.166) \cdot u$

Arrhenius parameters[8] are determined for the hydrolysis at 4.0 mol dm^{-3} HCl (Table-2). That the magnitudes of Arrhenius parameters fall in the range of bi-molecular nature of reaction is further supported by Zücker-Hammett[10] (1.01), Hammett (0.35) and Bünnett (W = 4.28, W* = 0.27) plots (not shown).

TABLE-2
CALCULATED ARRHENIUS PARAMETERS

HCl mol dm^{-3}	Temp. (t°C)	$10^3 K_e$(obs) (min^{-1})	E (kcal/mol)	$A^3 \times 10$ (sec^{-1})	$-S^{\neq}$ (e.u.)
4.0	98	20.158	10.031	2.85	31.65
	90	15.430			
	80	10.000			
	70	6.743			

Bünnett-Olsen[11] parameter (O = 0.901 which is greater than 0.580) 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, be taken to indicate the formation of transition state in which charge is dispersed.

The effect of concentration of mono-ester on the rate of hydrolysis also confirms the order of reaction to be on with respect to the mono-ester by reducing either half ($K_e = 20.12 \times 10^{-3}$ min^{-1}) or double ($K_e = 20.101$ min^{-1}) the normal concentration ($K_e = 20.158$ min^{-1}) at 4.0 mol dm^{-3} HCl.

Comparative kinetic[12, 13] data (not shown) also support the bimolecular nature of hydrolysis involving P—S bond fission.

Thus, acid hydrolysis of mono-S-butylphosphorothioate involves bimolecular attack of water on phosphorus of conjugate acid species formed by fast pre-equilibrium proton transfer.
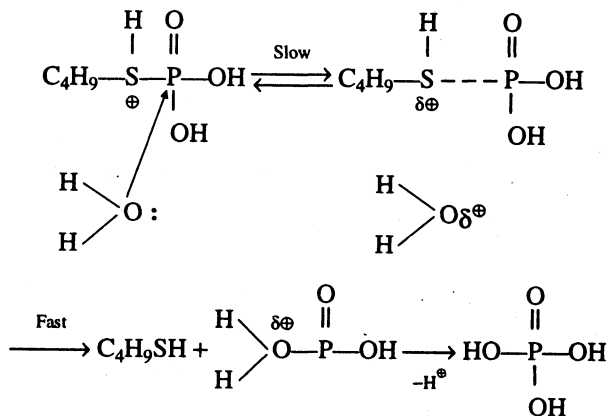
Mechanism

(a) Formation of conjugate acid species..

(b) By fast pre-equilibrium proton transfer from the undissociated mono-ester.
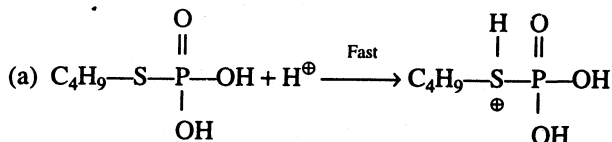
(I) Neutral form   (II) Conjugate acid form

(b) Bi-molecular heterolysis of P—S bond via heavily hydrated but unstable transition state, S_N^2 (P)

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