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

R. PATIL*, C.P. SHINDE and A. SAMADHIYA
School of Post-Graduate Studies in Chemistry
Jiwaji University, Gwalior-474011, India

Di-S-butyl phosphorothioate has been made in acid region (0.1 to 7.0 mol dm^{-3}) at 98°C in 10% dioxane-water mixture (v/v). 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, 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 phosphate diester involves P-S bond fission 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], 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 is important. Keeping this in view the hydrolytic bond cleavages of dis-S-butyl phosphorothioate has been investigated.

EXPERIMENTAL

Di-S-butyl phosphorothioate was prepared by treating butanethioate with H_3PO_4 in pyridine which is used as a solvent.

(Found: P = 12.00%, C = 36.28%, H = 6.791%, S = 24.34%)

The hydrolysis of di-S-butyl phosphorothioate (0.0005 mol dm^{-3}) was followed by colorimetric estimation of Allen[5]. The constant ionic strengths were maintained using mixtures of HCl and NaCl.

RESULTS AND DISCUSSION

The pseudo-first order rate coefficients were obtained (Table-1). Acid and pH log rate profile (figure not shown) showed that rates increased with decrease in pH up to 4.0 mol dm^{-3} HCl,[6, 7] then decreased with increase in acid molarity upto 7.0 mol dm^{-3}. The initial increase in the rate of hydrolysis is due to incursion of conjugate acid species. The cause of the bend at 4.0 mol dm^{-3} HCl may not be due to maximum protonation; because esters as a class are feebly basic substances, therefore, the cause of the bend has been attributed either to water activity or to the effect of ionic strength or may be due to both. To examine the above cause kinetic runs may be carried out at constant ionic strength[8] by using appropriate mixtures of NaCl and HCl at different ionic strengths (figure not shown). The acid catalysed rates are subjected to positive salt effect, as the slopes are progressing with the increase in ionic strength. The intercepts on the rate axis show the presence of a side reaction via neutral species. Since the intercepts on the rate axis increase in magnitude with the increase in ionic strength, neutral hydrolysis is subjected to positive ionic strength effect. Such results are obtained in case of hydrolysis of glycollides[9]. The reaction in the acid range can be represented by

$$K_e = K_{H^{\oplus}} C_{H^{\oplus}} + K_N \tag{1}$$

Using second empirical term of Debye-Hückel equation[10], Eq. (1), becomes Eq. (2).

$$K_e = K_{H_0^{\oplus}} \exp b_{H^{\oplus}}\mu + K_{N_0} \exp b_N \cdot \mu \tag{2}$$

where K_{H_0} and K_{N_0} are species conjugate acid and specific neutral rate coefficients at zero ionic strength respectively and b'_H + and b'_N are constants.

The rates estimated from equation (2) are in close agreement with the experimental observed rates, up to 4.0 mol dm^{-3} HCl (Table-1).

In the region of 0.1 mol dm^{-3} to 4.0 mol dm^{-3} the rate law is represented by Eq. (3).

$$\begin{aligned} K_e &= 79.432 \times 10^{-5}\, C_{H^{\oplus}} \exp (0.02173 \times 2.303)\mu \\ &\quad + 39.810 \times 10^{-5} C_{H^{\oplus}} \exp (0.1875 \times 2.303)\mu \end{aligned} \tag{3}$$

The rates above 4.0 mol dm^{-3} HCl, however, deviate probably due to decrease in the reactivity of the neutral form as a result of decrease in water activity. Therefore, the rates beyond 4.0 mol dm^{-3} HCl were calculated employing Bronsted-Bjerrum[11] [Eq. (4)].

$$K_e = K_{H_0} + C_{H^+} \exp b_{H^+} \cdot \mu(a_{H_20})_n + K_{N_0} \exp b_N(a_{H_20})^n \tag{4}$$

$$\begin{aligned} K_e &= 79.432 \times 10^{-5} C_{H^{\oplus}} \exp (0.01273 \times 2.303)\mu \cdot (a_{H_20})^n \\ &\quad + 39.810 \times 10^{-5} \exp (0.1875 \times 2.303) \cdot \mu(a_{H_20})^n \end{aligned}$$

where $(a_{H_20})^n$ is water activity term[12] and n is an integer, which increases with increase in activity. The revised estimated rates now agree well with the experimentally observed rates (Table-1). It is clear from the above results that di-S-butyl phosphorothioates in acid solution occur via both conjugate acid and neutral species and their rates are subjected to both ionic strength and water activity.

Solvent effect (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; this is in accordance with Chanley's observation[14].

TABLE-1

ESTIMATED AND EXPERIMENTAL PSEUDO-FIRST ORDER RATE COEFFICIENTS FOR THE HYDROLYSIS OF DI-S-BUTYL PHOSPHOROTHIOATE AT 98°C

HCl mol dm^{-3}	$K_H^+C_H^+ \times 10^5$ (min^{-1})	$K_N \times 10^5$ (min^{-1})	$K_e \times 10^5$ (min^{-1})	$-\log K_e \times H_2O$	$K_e \times 10^5$ (min^{-1}) (ested.)	$K_e \times 10^5$ (min^{-1}) (expt.)	5 + log K_e (estd.)	5 + log K_e (expt.)
0.1	7.903	41.567	40.470		49.470	40.470	1.694	1.698
0.2	15.763	43.402	50.164		58.664	59.164	1.772	1.768
0.5	38.737	49.402	88.139		88.139	88.139	1.945	1.953
1.0	75.556	61.305	136.861		136.861	139.981	2.136	2.146
2.0	143.747	94.406	238.149		238.149	240.905	2.376	2.381
3.0	205.026	145.378	350.404		350.404	355.018 152.054^c 91.622^d	2.544	2.550 2.182 1.962
4.0	260.075	223.872	483.947		483.947	481.810 725.870^a 817.221^b	2.684	2.682
5.0	309.243	344.746	653.989		475.689	449.689 184.926^c 110.153^d	2.677	2.677 2.267 2.042
6.0	352.874	530.884	883.758	$(0.211)^2$	234.229	232.598	2.369	2.366
7.0	391.642	814.523	1209.165	$(0.279)^3$	175.977	181.976	2.245	2.260

Note—a = 20% dioxane, b = 30%, dioxane, c = 80°C, d = 70°C

Thermodynamic parameters[12] for the reaction at 3.0 mol dm^{-3} HCl were found to be E = 12.446 kcal mol^{-1}, A = 8.038×10^3 sec^{-1}, $\Delta S^* = 47.682$ e.u. The corresponding values at 5.0 mol dm^{-3} HCl were E = 13.044 kcal mol^{-1}, A = 3.614×10^3 sec^{-1}, $\Delta S^* = 44.698$ e.u. These values are indicative of bimolecular nature of hydrolytic reaction. Bimolecular nature of reaction is further supported by slopes of the plots of Zücker and Hammett[15] (1.0), Hammett[16] (0.437) and Bünnett[17] (W = 7.0, W* = 2.857). Bünnett and Olsen[18] (O = 1.33 which is greater than 0.58) (plots not shown) suggested that water is involved as a proton transfer agent in the rate determining step.

Since the rate coefficients are fairly similar and are independent of initial concentration of (diester) the reaction may be taken to the kinetically of first order[19]. The hydrolysis of the diester occurring via the cleavage of P-S bond fission follows the isokinetic relationship[20–23] (figure not shown).

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