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Kinetics of Hydrolysis of S,S,S-Tri-isopropyl Phosphoro-Trithioate as Defoliating Agent

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Hydrolysis of S,S,S-tri-isopropyl phosphoro-trithioate has been studied in acid (0.1 to 6.0 M HCl) and buffer (1.20 to 7.80 pH) in 30% aqueous-dioxane mixture v/v. The rates of hydrolysis were lower in buffer solutions but with the rise in acidity the rates increased up to 6.0 M HCl. This is also reported that aryl diesters and triesters usually show maximum hydrolysis at 4.0 M acid. The rise in rate has been found to be due to acid catalysis which is of specific nature. The effects of ionic strength, substrate concentration and solvent effect were studied. Various thermodynamic parameters have also been calculated.

INTRODUCTION

Trisubstituted esters of orthophosphoric acid are studied to a lesser extent as compared to mono and diesters. The thiol esters resulting from thion-thiolo[1] rearrangement have practical importance, because of their susceptibility to hydrolysis and thereby increased physiological activity accompanied by an increased toxicity to mammals and insects. The study of tri-ethyl phosphorus-trithiolate and phosphate under acidic, neutral and alkaline conditions was done by Thain[2]. He pointed out that the hydrolysis of thiol ester proceeded with P–S bond supported by Hüdson and Keay *et al.*[3] In view of this a systematic study of thioates served an academic interest by the kinetic study of hydrolysis of organo-phosphates to a great extent which in turn may provide the substantial basis for understanding the reaction of complicated esters.

EXPERIMENTAL

S,S,S-tri-isopropyl phosphoro-trithioate was prepared by S,S,S-tri-isopropyl trithiophosphite oxidation[4] at 80°C for 26 hrs. After 80% conversion of phosphite into phosphate, it was contacted with 10 ml of boiling hydrogen peroxide (30%) for 1/2 hr to reach conversion up to 97%. Finally it was shaken with 4% sodium hydroxide solution to remove mono and diester, then washed and dried a liquid S,S,S-tri-isopropyl phosphoro-trithioate was obtained.

Kinetic study of the hydrolysis of thioate was made by Allens' modified method[5]. The progress of the reaction was followed by estimating the rate of appearance of inorganic phosphate colorimetrically. The concentration of the tri-thioate was maintained at 5×10^{-4} M throughout the study.

RESULTS AND DISCUSSION

Kinetic study of the hydrolysis of S,S,S-tri-isopropyl phosphoro-trithioate has been made in acid region 0.1 to 6.0 M hydrochloric acid. The rate rises less rapidly up to 1.0 M HCl and more rapidly in the region 1.0 to 4.0 M HCl. Somewhat less rise in rate is observed in 5.0 and 6.0 M HCl. The presence of the maximum rate at 4.0 M acid extends a support to the conclusion of Bunton *et al.* that simple aliphatic phosphates, although more basic than aryl phosphates, fail to show maximum in strong acid region (Table 1).

TABLE 1

OBSERVED AND CALCULATED RATES FOR HYDROLYSIS OF S,S,S-TRI-ISOPROPYL PHOSPHORO-TRITHIOATE AT 50°C.

S. No.	HCl M	10^3 K min^{-1} (estimated 10^{3+} K_{N_0} min^{-1})	10^3 $K_{H^+}C_{H^+}$ min^{-1} (by eq. II)	10^3 $K_{H^+}C_{H^+}$ min^{-1} (by eq. III)	10^3 K min^{-1} (observed and calculated rates)
1.	0.1	0.124	0.044	—	0.124 0.124 obsd.
2.	0.2	0.179	0.099	—	0.179 0.301 obsd.
3.	1.0	1.255	1.175	—	1.179 1.697 obsd.
4.	2.0	7.014	6.934	—	6.934 10.599 obsd.
5.	3.0	—	30.690	—	30.690 38.370 obsd.
6.	4.0	—	120.800	—	120.800 155.230 obsd.
7.	5.0	—	445.700	182.6	182.600 168.440 obsd.
8.	6.0	—	1549.000	221.8	221.800 211.840 obsd.

In order to determine ionic strength effect was examined by carrying out kinetic runs at constant ionic strength which were using appropriate mixtures of NaCl and HCl. We have plotted a graph between rate constants and acid molarity. Three linear curves for three different ionic strengths (μ) are obtained. The rate axis shows that small intercepts are made. These indicate the small contribution of the species other than conjugate acid species[1]. Rate coefficient increases with increase in ionic strength (μ); hence the effect of ionic strength is positive on the basis of these reactive species. The calculated rates are obtained by applying

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

On further applying the 2nd empirical term of Debye-Hückel equation[6], the relationship may be represented as

$$K_{H^+} = K_{H_0^+} \cdot b_{H^+} \cdot \mu \qquad (2)$$

or

$$\log K_{H^+} = \log K_{H_0^+} + b'_{H^+}\mu$$

Acid rates ($K_{H^+}C_{H^+}$) are obtained by multiplying the specific rates by acid molarity

$$K_{H^+} \cdot C_{H^+} = K_{H_0^+} \cdot C_{H^+} \cdot b_{H^+} \cdot \mu \qquad (3)$$

Results (Table 1) show that there is deviation in dilute acid (0.1 M to 0.2 M) and at molarities higher than 4.0 M. The difference in the lower acidities can be compensated by adding neutral rates to the theoretical acid catalysed rates, while in the region of 5 and 6.0 M HCl. The effect of water activity is involved. Agreement between theoretical and experimental rates has been sought by introducing water activity parameters.

$$K_{H^+}C_{H^+} = K_{H_0^+}C_{H^+}b_{H^+}\mu(aH_2O)^n \qquad (4)$$

where $(aH_2O)^n$ represents water activity term. The values of **n** at 5.0 and 6.0 M have been calculated as 2.5 and 4.0 respectively.

The concepts of Hammett[7] and Zücker et al.[8] lead to slopes 1.636 and 2.857. The relation between modified log rate constants and log acid molarity is linear with the slope of ~ unity for the hydrolysis, indicating the probability of bimolecular reaction path. Bunnett parameters (ω, 10 and ω^*, -16.232) emphasise that water acts as a nucleophile too. Some modified observations were also found by Bunnett.[9] The value of ϕ, 1.3, postulates that the rate depends on hydrogen ion concentration and water activity.

Thermodynamic parameters[10] indicate that the reaction is mainly governed by conjugate acid species. The slopes of the linear curves were used to determine the values of activation energy (E, 19.025). The intercepts on the log rate axis were used to calculate frequency factor (A, 1.355×10^9 sec^{-1}) and these two values were used to estimate the entropy of activation ($\Delta S^\ddagger$ – 18.83 e.u.). Comparative lower value of E together with $-\Delta S^\ddagger$ indicates that the reaction is bimolecular.

The effect of concentration on the substrate has been observed and it was found that the contribution of the conjugate acid species is far greater than that of the neutral species. Rate constants were determined by first order equation which shows that they are independent of the concentrationn of the ester.

According to the transition state theory there is an equilibrium between reactants and the transition state. Shifting of this equilibrium depends upon the comparative stabilization of the transition state. More the stabilization state, more will be the rate of reaction. The qualitative theory of Hüghes and Ingold[11] predicts a significant elevation in rate when a changeover is made from more to less polar solvent in the reaction, which has a transition state with charge dispersion. Present observation shows that there is a slight increase in the reaction rate by a change-over from 30 to 50% aqueous dioxane mixture. Specific acid catalysis, therefore, involves the transition state in which the charge is dispersed.

Acid catalysed hydrolysis may undergo a change of C–S or P–S bond fission considering the different in-bond energies of P–S and C–S bonds. The former should involve less amount of energy for its fission. Similar conclusion can also be reached considering isokinetic relationship[12] and comparative kinetic rate data showing similar behaviour and suggesting P–S bond fission for this trithioate (Table 2).

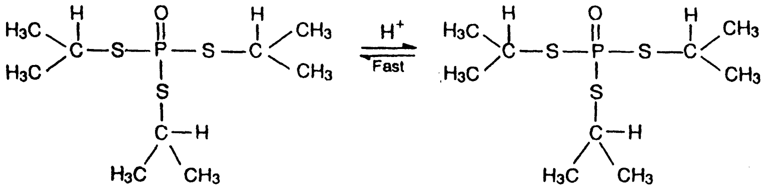
TABLE 2
COMPARATIVE KINETIC DATA FOR THE HYDROLYSIS OF SOME TRIESTERS VIA THEIR CONJUGATE ACID SPECIES.

S. No.	Triesters	Temperature °C	Medium M HCl	E K.Cal/mol^{-1}	$-\Delta S^{\ddagger}$ e.u	Fission
1.	*p*-Bromophenyl	98	1	13.73	47.70	P–O
2.	1-Bromo-2-naphthyl	98	3	14.45	42.18	P–O
3.	Benzyloxyphenyl	98	5	15.90	36.60	P–O
4.	2,4-Dichlorophenyl	98	1	17.50	32.20	P–O
5.	*o*-Ethoxyphenyl	90	1	17.70	26.90	P–O
6.	*p*-Chloro-m-methyl phenyl	—	4	22.80	21.50	P–O
7.	2,6-Dimethoxy phenyl	98	4	21.60	19.20	P–O
8.	S,S,S-Tri-isopropyl	40	2	19.02	18.83	P–S*

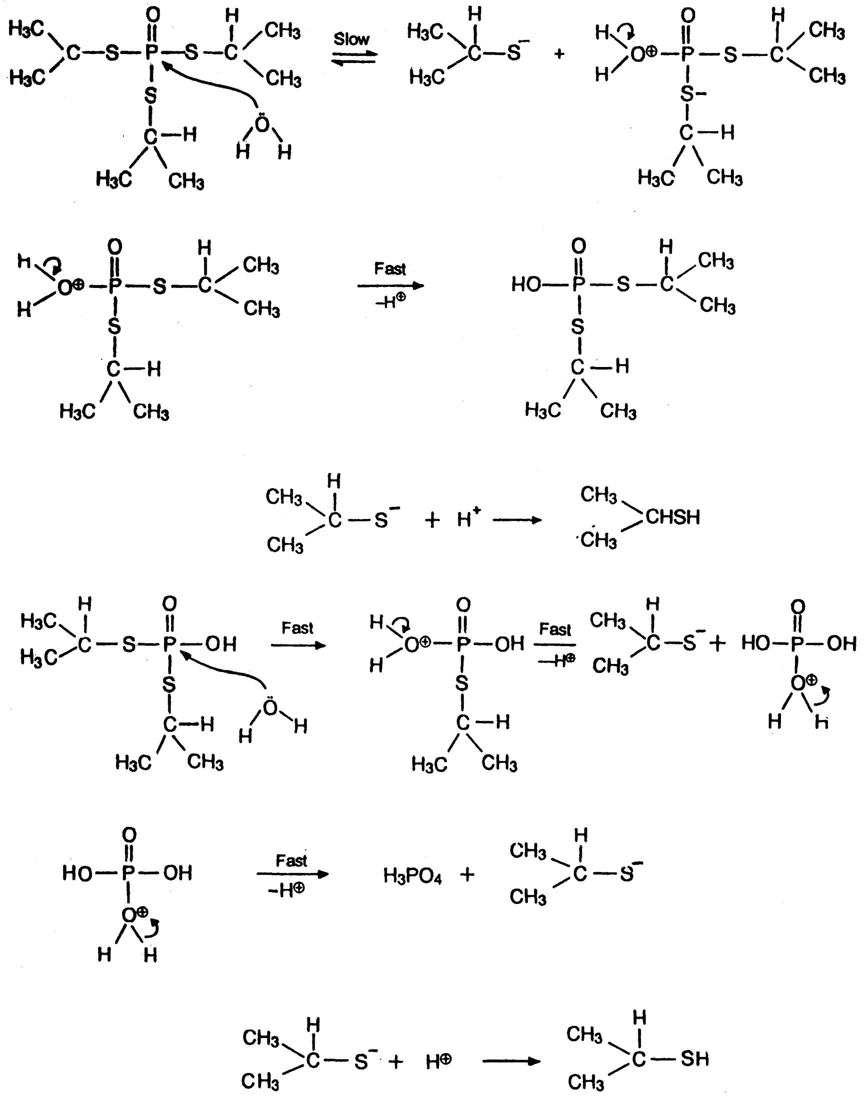
*Proposed fission.

All the above results and reasonings suggest an altogether different path-way. Bimolecularity of the acid catalysed hydrolysis of the phosphorotrithioate is more probable on the basis of Zücker Hammett hypothesis. Magnitude of Arrhenius parameters also supports this view. Pseudo first order reactions in the phosphorotrithioate are in accord with a specific nature of acid catalysed hydrolysis. Mechanism of acid catalysed hydrolysis of the phosphoro-trithioate may be formulated as follows:

(i) Protonation transfer of the esters by a fast pre-equilibrium proton transfer



(ii) Bimolecular attack of water on phosphorus



On the above observations the following conclusions may be drawn from the kinetic study of phosphoro-trithioate:

(a) The acid catalysis is of specific nature

(b) Molecularity of hydrolysis is bimolecular rather than unimolecular.

(c) In acid media hydrolysis is mainly via conjugate acid species.

(d) Kinetic laws are applicable to acid catalysis:

From 0.1 to 1.0 M HCl,

$$K_e = K_{N^+} + K_{H^+} \cdot C_{H^+}$$

From 1.0 to 4.0 M HCl

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

From 5.0 to 6.0 M HCl

$$K_e = K_{H^+} \cdot C_{H^+}(aH_2O)^n$$

In the buffer region (1.24 to 7.4) the rates first gradually fall in the range of pH 1.24 to 5.6 with the increase in the pH value. Further rise in pH shows elevation in rates. The first lower in rates has been found to be due to the decrease in more reactive conjugate acid species, while approximately constant rates in the region pH 3.2 to 5.2 are due to hydrolysis via neutral species alone. The rise of rate is observed and can be attributed to the incursion of more nucleophilic hydroxide ion. Kinetic law for various ranges may be shown as:

From pH 1.24 to 2.20,

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

From pH 3.2 to pH 5.2,

$$K_e = K_N$$

From pH 5.2 to 7.8,

$$K_e = K_N^{\circ} \cdot OH^-$$

It may, therefore, be concluded that phosphoro-trithioates undergo their hydrolysis via both neutral and conjugate acid species. The rate of hydrolysis of neutral species being comparatively very slow is overpowered by hydrolysis via more reactive conjugate acid species in moderately strong acid media.

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